PERGAMON

Carbon 39 (2001) 369–373

CARBON

Effect of carbon fiber grade on the electrical behavior of carbon fiber reinforced cement

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Received 15 February 2000; accepted 27 April 2000

Abstract

Electrical conduction in cement reinforced by short carbon fibers below the percolation threshold is governed by carrier hopping across the fiber–matrix interface. The activation energy is decreased by increasing the fiber crystallinity, but is increased by using intercalated fibers. The carbon fibers contribute to hole conduction, which is further enhanced by intercalation, thereby decreasing the absolute thermoelectric power and the resistivity.

Keywords: A. Carbon composites, Carbon fibers, Intercalation compounds; D. Electrical properties, Transport properties

1. Introduction

The electrical behavior of carbon fiber reinforced cement is relevant to the use of this material for strain sensing [1–7], which is important for smart structures, highway traffic monitoring, weighing of vehicles in motion, and structural vibration control. The addition of short carbon fibers to cement decreases the electrical resistivity, due to the high conductivity of the carbon fibers compared to cement. The decrease occurs even when the fibers are at a volume fraction below the percolation threshold [8,9], because the cement matrix is slightly conducting. Short fibers rather than continuous fibers are preferred for concretes because of the desire for low cost and feasibility of incorporation of the fibers in a concrete mix. A low volume fraction of fibers is preferred because of the importance of low cost, good workability and high compressive strength (low air void content).

The strain sensing ability of carbon fiber reinforced cement [1–7] is associated with piezoresistivity, i.e. the change of the electrical resistivity with strain. The origin of the piezoresistivity relates to the effect of strain on the fiber–matrix contact resistivity. The effect is reversible. The fractional change in resistance per unit strain (i.e. the gage factor) is as high as 700.

In addition to providing the strain sensing ability, carbon fiber addition to cement increases the tensile and flexural strengths, tensile ductility and flexural toughness, and decreases the drying shrinkage [10,11].

To help the dispersion of the short fibers in a concrete mix, silica fume (a particulate of particle size around 0.1 μm) is usually added to the mix [12]. The fine particulate nature of silica fume also causes the liquid permeability of the concrete to decrease, thereby improving the corrosion resistance of embedded steel reinforcing bars. Hence, in spite of the increased conductivity of the concrete due to the carbon fibers, the corrosion resistance is better than plain concrete [13].

Carbon fiber surface treatments (such as ozone and silane treatments [14,15]) and the use of admixtures (such as silica fume and latex [12]) have been previously used to enhance the properties of carbon fiber reinforced cement. However, the effect of carbon fiber grade, which affects the bulk properties of the fibers, has not been previously investigated. Due to the desire for low cost, previous work mostly involved amorphous carbon fibers, such as those made from isotropic pitch.

This work provides a comparative study of three grades of carbon fibers in their effects on the electrical behavior of cement paste. These grades are (i) amorphous pristine fibers, (ii) crystalline pristine fibers, and (iii) crystalline intercalated fibers. The amorphous fibers used were based on isotropic pitch. The crystalline fibers used were actually partly crystalline; they were based on mesophase pitch

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0008-6223/01/$ – see front matter
PII: S0008-6223(00)00127-5

(Thornel P-100, Amoco Performance Products, Inc., Ridgefield, CT). The intercalate used was bromine [16–18]. Comparison of grades (i) and (ii) gives the effect of fiber crystallinity, which governs the fiber resistivity. Comparison of grades (ii) and (iii) gives the effect of intercalation, which cannot be attained in amorphous fibers and which enhances the fiber resistivity through charge transfer between the intercalate and carbon. Bromine is an acceptor, thereby increasing the hole concentration in the carbon.

The electrical behavior of cement pastes containing short carbon fibers at volume fractions below the percolation threshold was studied in this work by measuring the resistivity and its variation with temperature, in addition to measuring the thermoelectric power.

2. Experimental methods

2.1. Materials

The amorphous carbon fibers were isotropic pitch based, unsized, and of length ~5 mm and density 1.6 g/cm^3, as obtained from Ashland Petroleum Co. (Ashland, KY). The fiber resistivity is 3.0×10^{-3} Ω cm.

The crystalline carbon fibers (Thornel P-100) were mesophase pitch based, unsized and of length ~5 mm and density 2.16 g/cm^3, as obtained from Amoco Performance Products, Inc. (Ridgefield, CT). The fiber resistivity is 2.2×10^{-4} Ω cm.

Intercalation of the crystalline carbon fibers was conducted by exposure of the fibers to bromine vapor in air at room temperature for 2 weeks to attain a stage 2 (saturated, $C_{16}Br_2$, with 83% weight uptake) intercalation compound. After this, the fibers were removed from the bromine vapor and allowed to undergo bromine desorption in air at room temperature for 2–3 months in order to attain a stable compound, with about 20% weight uptake (relative to the pristine material) and a density of 2.5 g/cm^3.

No aggregate (fine or coarse) was used. The cement used was portland cement (Type I) from Lafarge Corp. (Southfield, MI). The fibers used were in the amount of 0.5% by weight of cement (corresponding to less than 0.5 vol.%, which is below the percolation threshold [8]). The silica fume (Elkem Materials, Inc., Pittsburgh, PA, EMS 965) was used in the amount of 15% by weight of cement. The methylcellulose, used in the amount of 0.4% by weight of cement, was Dow Chemical Corp., Midland, MI, Methocel A15-LV. The defoamer (Colloids, Inc., Marietta, GA, 1010) used along with methylcellulose was in the amount of 0.13 vol.%.

2.2. Composite fabrication

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. The water–cement ratio was 0.35. The methylcellulose mixture, cement, water, silica fume and fibers 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.

Three types of carbon fiber silica fume cement pastes were prepared, as listed in Table 1.

2.3. Testing

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 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) which 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

Table 1
Resistivity, absolute thermoelectric power and activation energy for electrical conduction for three types of cement paste

	Fiber content		Resistivity (Ω cm)	Absolute thermoelectric power (μV/°C)[a]	Activation energy (eV)
	% by weight of cement	vol.%			
Amorphous, pristine	0.5	0.48	$(1.5\pm0.1)\times10^4$	0.89±0.09	0.36±0.05
Crystalline, pristine	0.5	0.36	$(1.3\pm0.1)\times10^4$	0.47±0.11	$(7.5\pm0.8)\times10^{-3}$
Crystalline, intercalated	0.5	0.31	$(6.7\pm0.5)\times10^3$	−11.5±1.13	0.30±0.03

[a] 1.96±0.05 μV/°C for plain cement paste (without fibers or silica fume) and 1.98±0.03 μV/°C for silica fume cement paste without fibers [22].

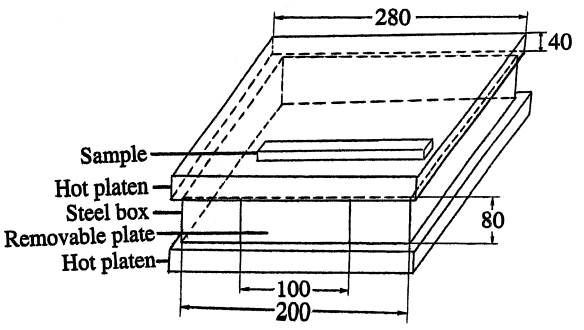

Fig. 1. Experimental set-up for measuring the temperature dependence of the electrical resistivity at and above room temperature. Dimensions are in millimeters.

the sample to come out. The temperature was raised continuously from 20 to 80°C at a constant rate of 0.011°C/s and then lowered to 20°C over a time of 3–4 h at a rate which decreased with time (cooling with the power of the platens turned off). Six samples of each of the three types of paste were tested.

Thermopower measurement was performed on rectangular samples of size 75×15×15 mm, such that heat (up to 65°C) was applied at one of the 15×15 mm ends of a sample by contacting this end with a resistance heated platen of size much larger than 15×15 mm. The other end of the sample was near room temperature. The thermal contact between the platen and the sample end was enhanced by using a copper foil covering the 15×15 mm end surface. Silver paint was applied between the foil and the sample surface covered by the foil to further enhance the thermal contact. Underneath the copper foil was a copper wire which had been wrapped around the perimeter of the sample for the purpose of voltage measurement. Silver paint was present between the copper wire and the sample surface under the wire. The other end of the rectangular sample was similarly wrapped with copper wire and then covered with copper foil. The copper wires from the two ends were fed to a Keithley 2001 multimeter for voltage measurement. A T-type thermocouple was attached to the copper foil at each of the two ends of the sample for measuring the temperatures of the two ends. Voltage and temperature measurements were done simultaneously using the multimeter. The voltage difference divided by the temperature difference yielded the Seebeck coefficient with copper as the reference, since the copper wires at the two ends of a sample were at different temperatures. This Seebeck coefficient plus the absolute thermoelectric power of copper (+2.34 μV/°C) [19] is the absolute thermoelectric power of the sample. Six samples of each of the three types of cement paste were tested. Each sample was heated at one end at a rate of 0.009°C/s and then cooled with the power of the platen turned off. The heating rate was constant, but the cooling rate was not.

3. Results and discussion

Table 1 shows the resistivity, absolute thermoelectric power (during cooling, due to possible moisture loss from the cement matrix during heating) and the activation energy (determined from the Arrhenius plot obtained from the temperature dependence of the resistivity) for various cement pastes. The resistivity is decreased slightly by using crystalline fibers rather than amorphous fibers and is further decreased by intercalating the crystalline fibers, in spite of the lower fiber volume fractions for the crystalline fiber cement pastes.

The absolute thermoelectric power is positive, indicating electron conduction, for the pastes without fibers (footnote of Table 1). It is decreased by the addition of amorphous pristine fibers, indicating contribution to hole conduction by the fibers, as previously reported [20–22]. The use of crystalline pristine fibers instead of amorphous pristine fibers further decreases the absolute thermoelectric power, due to the increased extent of hole conduction, as reflected by the decrease in resistivity. The use of crystalline intercalated fibers instead of crystalline pristine fibers further decreases the absolute thermoelectric power so much that it becomes negative, indicating predominant hole conduction in the composite. Fig. 2 shows the curves of Seebeck voltage (with copper as the reference) vs. temperature difference for cement pastes with the three grades of carbon fibers. The slope is the Seebeck coefficient with copper as the reference. The curves during heating and cooling essentially overlap, although the curves shown are for cooling.

The resistivity decreases with increasing temperature for all samples of each type of paste. This trend is due to the fiber–matrix interface being a barrier against carrier transport. This barrier is described by the activation energy,

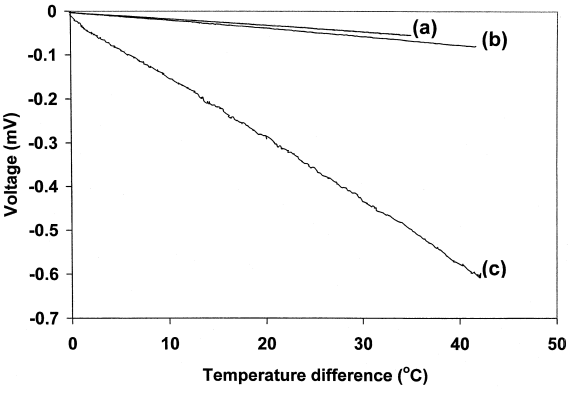

Fig. 2. Variation of the Seebeck voltage (with copper as the reference) vs. the temperature difference during heating and cooling for cement pastes with (a) amorphous pristine carbon fibers, (b) crystalline pristine carbon fibers, and (c) crystalline intercalated carbon fibers.

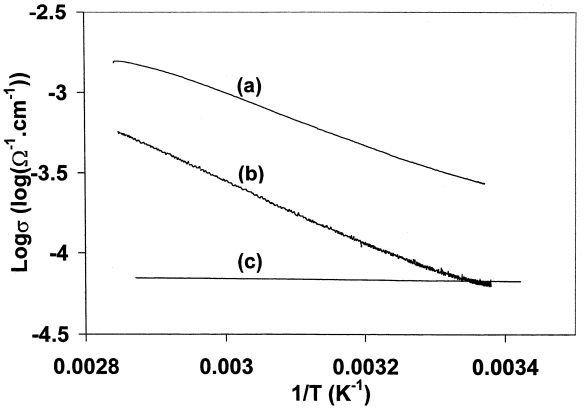

Fig. 3. Arrhenius plot of the logarithm of the electrical conductivity vs. the reciprocal of the absolute temperature for cement pastes with (a) amorphous pristine carbon fibers, (b) crystalline pristine carbon fibers, and (c) crystalline intercalated carbon fibers.

which is determined from the slope of the Arrhenius plot. Fig. 3 shows the Arrhenius plots for cement pastes with the three grades of carbon fibers during cooling.

Table 1 also shows that the activation energy is decreased greatly by the use of crystalline pristine fibers instead of amorphous pristine fibers. This is attributed to the crystallinity (and probably the radial cross-sectional morphology as well) of the crystalline pristine fibers facilitating the carrier hopping between the fiber and the matrix. This means that the fiber crystallinity greatly affects the electrical behavior, due to the easier carrier hopping rather than just the higher fiber conductivity.

Table 1 also shows that intercalation greatly increases the activation energy. This is probably due to the interaction between the bromine intercalate in the fiber and the moisture in the cement paste. The interaction may degrade the fiber–matrix interface, thereby increasing the activation energy. Due to the high hole concentration resulting from intercalation, as indicated by the thermoelectric power, the resistivity is decreased by intercalation, despite the large increase in activation energy.

4. Conclusion

The electrical conduction behavior of short carbon fiber cement-matrix composites below the percolation threshold is affected by the fiber grade, which affects the fiber–matrix interface as well as the fiber resistivity. The conduction is governed by carrier hopping across the fiber–matrix interface. The activation energy for the hopping is much decreased by increasing the fiber crystallinity, but is increased by intercalating the fibers. The carbon fibers, whether intercalated or not, contribute to hole conduction, thereby decreasing the absolute thermoelectric power and the resistivity. In particular, bromine intercalation greatly enhances hole conduction, thereby making the absolute thermoelectric power negative (−12 μV/°C).

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