J Mater Sci (2007) 42:2200–2203
DOI 10.1007/s10853-007-1517-x

LETTER

Activation energy and conduction in carbon fibre reinforced cement matrices

**W. J. McCarter · G. Starrs · T. M. Chrisp ·
P. F. G. Banfill**

Received: 19 December 2006 / Accepted: 12 January 2007 / Published online: 15 February 2007

Introduction

Cement-based materials form an important group of structural materials; however, the ability of such materials to serve both structural and non-structural functions could further enhance their range of application. The capacity to simultaneously provide both structural and non-structural applications is defined as *multifunctional* and the addition of fibres to cement matrices is one such area which could give cement-based materials multifunctional capabilities. On the structural side, it is known that fibre additions offer a convenient and practical means of achieving improvements in many of the mechanical properties of plain concrete such as enhanced toughness, fatigue resistance, impact resistance, tensile strength, flexural strength, reduced creep and shrinkage and improvements in the post-cracking behaviour. However, the addition of small amounts of electrically conductive fibres to cement, such as carbon fibre, will make the material electrically conductive which could open up a wide range of non-structural applications; for example, in electrical grounding and static charge dissipation, electromagnetic interference shielding, self-sensing (with respect to deformation and damage), piezoresistivity, electric current rectification (using a cement-based pn-junction), radio wave reflection, electrical-resistance heating and overlays for cathodic protection [see, for example, 1–13].

Whilst a considerable amount of work has now been published in all of these areas, there is a dearth of information on the influence of temperature on electrical properties of carbon fibre reinforced cement mortars. This forms the focus of this letter.

In the experimental program, mortar specimens were made with CEM I (42.5N) Portland cement (ASTM Type I) and a siliceous sand of maximum particle size 2 mm. Water reducing plasticizer (Fosroc Conplast P515) was used in all mixes at a dosage of 0.6% (by weight of cement). The carbon fibre used throughout the experimental programme was Sigrafil C®. The fibre had a diameter of 7.5 μm and a density of 1,800 kg/m^3; its electrical conductivity was 62,500 S/m and contained glycerine as a water soluble size (at approximately 4% by mass of fibre). Two fibre lengths were used, 3 mm and 6 mm, both at a dosage of 0.5% (by volume). A mortar with a sand/cement ratio of 0.5 and water/cement ratio of 0.5 (by mass) was used in all tests. Materials were mixed using a 10 dm^3 Hobart planetary motion mixer. Specimens were cast in plexiglas moulds and had overall dimensions 4 × 4 × 16 cm (long); three specimens were cast for each mixture. To ensure intimate contact with the sample, two, stainless-steel mesh-electrodes were embedded within the samples at the time of casting and placed 15 cm apart. The specimens were demoulded after 24-h and cured under saturated conditions at 20 °C until required for testing, which was, approximately, 12 months. Regarding the latter, this ensured that the influences of cement hydration on electrical properties were negligible.

Electrical measurements were taken using an Agilent 6423 LCR meter at three spot frequencies covering two decades: 1, 10 and 100 kHz. Specimens were equilibrated in a water-bath at the appropriate tem-

W. J. McCarter (✉) · G. Starrs · T. M. Chrisp ·
P. F. G. Banfill
School of the Built Environment, Heriot-Watt University,
Edinburgh EH14 4AS, Scotland, UK
e-mail: w.j.mccarter@hw.ac.uk

perature prior to measurement, which covered the range 10–60 °C. Thermal equilibrium was checked by monitoring the internal temperature of a sample which had a thermistor embedded within it at the time of casting.

Figure 1 presents the variation in resistivity (ρ, ohm-cm) with increasing temperature (°C) for the plain mortar samples (Fig. 1(a)) and samples containing 3 mm (Fig. 1(b)) and 6 mm (Fig. 1(c)) carbon fibres. It is evident for all mixtures that resistivity exhibits an inverse temperature relationship with resistivity decreasing with increasing temperature although specimens containing carbon fibres are not as sensitive to changes in temperature as the plain mortar specimens. It is also evident from Fig. 1 that the addition of a small amount of carbon fibres to the mortar matrix (0.5% by volume) results in a marked decrease in resistivity, with 6 mm fibres producing a lower resistivity than specimens with the same volume of 3 mm fibres. This is attributed to the fact that the longer fibres can more easily form a continuous fibre network through the matrix and discussion of this feature is well documented [1, 5, 9, 12]. Figure 1 also highlights a marked frequency dependence of the resistivity of carbon fibre mortars which is not present in the plain mortar samples, and is discussed below.

The conductivity (σ, S/cm) versus temperature relationships for the carbon fibre specimens and the reference mortar without fibres are plotted in Arrhenius format in Fig. 2, viz.

$$\sigma = \mathrm{A}e^{-\left[\frac{\mathrm{E_a}}{\mathrm{kT}}\right]} \qquad (1)$$

where, in the above equation, A is a pre-exponential constant; k is the Boltzmann constant (8.6174×10^{-5} eVK^{-1}); T is the absolute temperature (K) and $\mathrm{E_a}$ the activation energy for the conduction process (eV). This Figure also displays the response at each test frequency. Table 1 presents the activation energy obtained from the Arrhenius plots in Fig. 2. The value obtained for the plain mortar at 1 kHz (0.2 eV) is in good agreement with previously published studies [14, 15] where the activation energy for plain Portland cement mortars, with water/cement ratios in the range 0.45–0.55 and a sand/cement ratio of 3:1 (by mass) undergoing an increasing temperature regime (10–50 °C), has been quoted as lying in the range 0.20–0.22 eV.

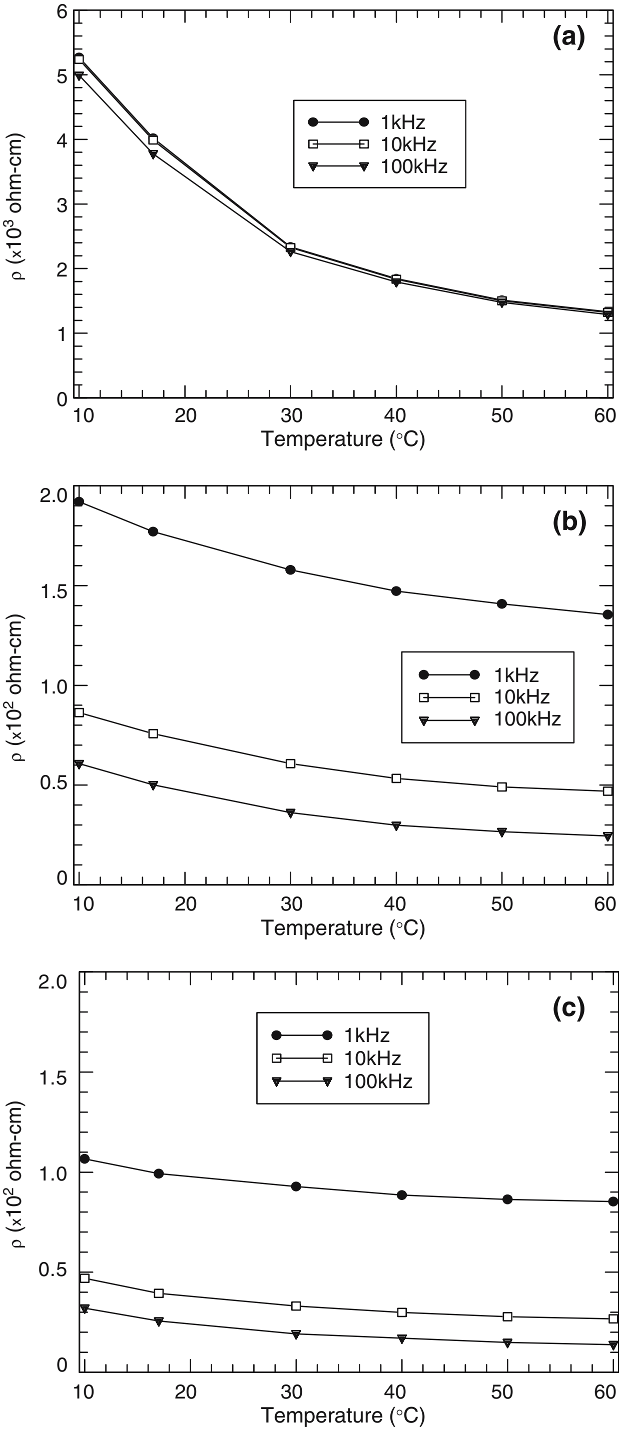

Fig. 1 Variation in resistivity, ρ, with temperature at 1, 10 and 100 kHz for (**a**) plain cement mortar; (**b**) mortar containing 3 mm carbon fibres, and (**c**) mortar containing 6 mm carbon fibres

Figure 2 and Table 1, however, highlight several new features of carbon fibre cement-composites. The activation energy of the carbon fibre specimens is considerably lower than that of the plain mortar with the activation energy decreasing with increasing fibre length and increasing with increasing frequency. The activation energy of the plain mortar specimens, on the other hand, remains relatively constant over the frequency range under investigation. From Fig. 2 it is apparent that at any particular temperature, the

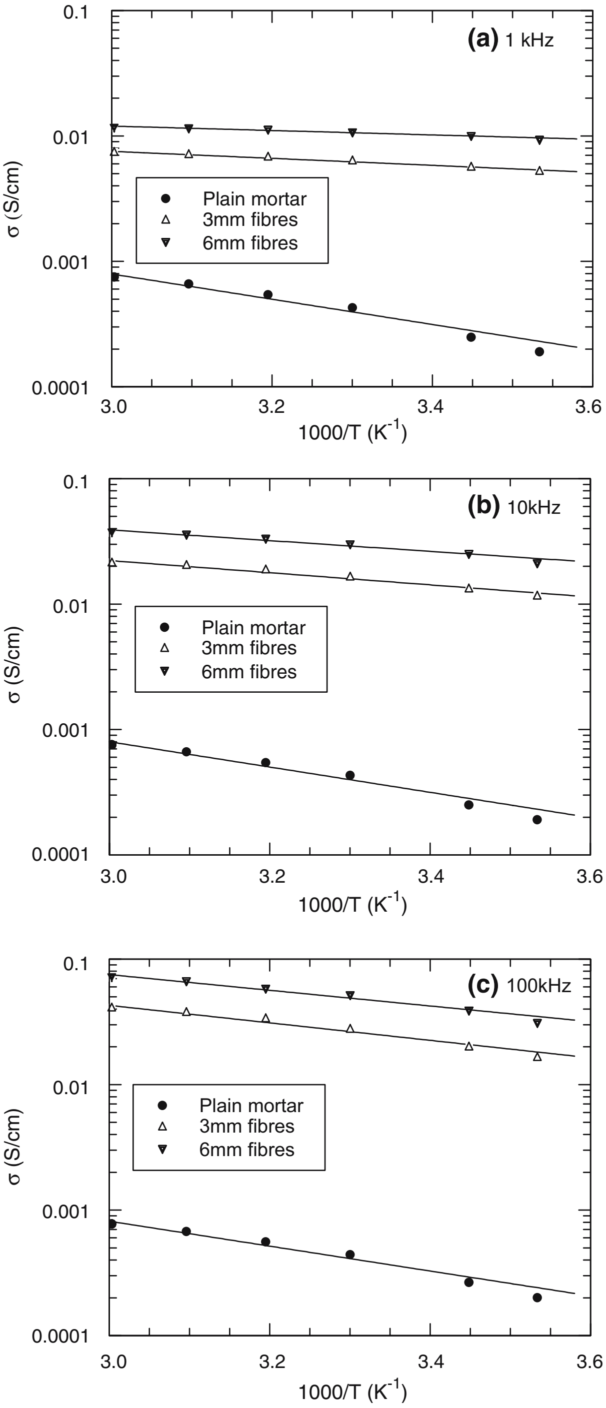

Fig. 2 Arrhenius plots for conductivity (σ) vs. reciprocal absolute temperature for plain Portland cement mortar and mortar containing 3 mm and 6 mm carbon fibres at three test frequencies (**a**) 1 kHz; (**b**) 10 kHz, and (**c**) 100 kHz

Table 1 Activation energy for conduction in plain mortar and carbon-fibre mortar samples

Frequency (kHz)	Plain mortar (eV)	3 mm fibres (eV)	6 mm fibres (eV)
1	0.20	0.055	0.035
10	0.20	0.096	0.085
100	0.20	0.14	0.12

conductivity of the carbon fibre specimens increases with increasing frequency whereas that of the plain mortar remains virtually unchanged. This implies that the fibres are introducing significant dispersion in conductivity. It is also interesting to note that for the carbon fibre specimens, the degree of dispersion in conductivity increases within increasing temperature. For example, consider the 3 mm fibres: at 1 kHz the conductivity at 10 °C is 0.0052 S/cm (denoted σ_l) whereas at 100 kHz is 0.016 S/cm (denoted σ_h) and represents a frequency dispersive increase of 208% (i.e. $100 \times (\sigma_h - \sigma_l)/\sigma_l$); at 60 °C the values at 1 and 100 kHz are, respectively, 0.0074 S/cm and 0.041 S/cm and represents a dispersive increase of 454%.

In plain cement mortar the main conduction process will be through the motion of free ions (e.g. Ca^{2+}, Na^+, K^+, OH^-, SO_4^{2-}) in the interstitial aqueous phase contained within the continuous capillary pore network. Since aqueous ionic conductors display a negative temperature coefficient of resistivity, it is understandable that conduction through plain cement mortar also displays such a dependency (see Fig. 1). Figure 3 presents the Arrhenius plot for a simulated pore-solution at a frequency of 10 kHz. The activation energy obtained from these data is 0.16 eV whereas the activation energy of the plain mortar is 0.20 eV (Table 1). This difference must indicate that the conductive properties of the pore fluid within the confines of the

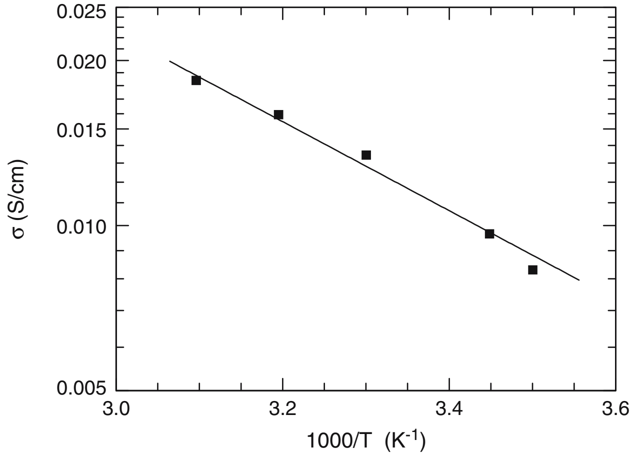

Fig. 3 Arrhenius plot for simulated pore solution (activation energy, E_a = 0.16 eV)

filamentary capillary pore system are different from that of the free electrolyte.

The introduction of fibres into the plain cement mortar results in three possible conduction pathways:

(i) conduction via the capillary pore water within the cement paste;
(ii) conduction through the fibres in contact thus forming a continuous pathway; and,
(iii) conduction through the carbon fibres and cement paste in series.

The volume of fibres used within the experimental programme (0.5%) lies within the percolation zone where a continuous fibre network can form [16, 17]. So, whilst path (i) would be the principal path through the plain cement mortar, for carbon fibre composites paths (ii) and (iii) must exert a significant influence on conduction which is borne out by the overall increase in bulk conductivity and reduction in activation energy in comparison to the plain mortar. Path (ii) would result in ohmic contacting conduction through the motion of free electrons. In path (iii), cement paste ''interrupts'' the formation of a continuous path and conduction could result from electrons ''tunneling'' from fibre to fibre (hence, an electron tunneling conduction mechanism). Thus, within the percolation zone, these two conductive processes would dominate in carbon fibre composites, although the distribution between these processes would be dependent upon the carbon fibre content.

The work has highlighted that over the temperature range 10–60 °C carbon fibre cement matrices have a lower activation energy than plain Portland cement, although the activation energy for carbon fibre systems increases markedly with increasing frequency. Possible conduction mechanisms for these materials have been presented. In addition, carbon fibres introduce significant dispersion to the bulk conductivity, which is not present in the plain mortar samples. It has also been shown that dispersive effects increase with increasing temperature.

Acknowledgements The Authors wish to thank the Engineering and Physical Sciences Research Council, United Kingdom, for financial support (Research Grant GR/S49193).

References

1. Chiou J-M, Zheng Q, Chung DDL (1989) Composites 20(4):379
2. Chen P-W, Chung DDL (1993) Smart Mater Struct 2:22
3. Xie P, Gu P, Beaudoin JJ (1996) J Mater Sci 31:4093
4. Peled A, Torrents JM, Mason TO, Shah SP, Garboczi EJ (2001) Am Concr Inst Mater J 98(4):313
5. Wen S, Chung DDL (2001) Cem Concr Res 31:665
6. Chung DDL (2002) J Mater Eng Performance 11(2):194
7. Idem, Marcel Dekker Inc., New York, (2003) (ISBN 0–8247-4610-4) 296pp
8. Idem (2004) J Mater Sci 39(8):2645
9. Idem (2004) Smart Mater Struct 13:562
10. Reza F, Batson GB, Yamamuro JA (2004) Cem Concr Comp 26(7):873
11. Chung DDL (2004) Adv Cem Res 16(4):167
12. Wang S, Wen S, Chung DDL (2004) Ibid 16(4):161
13. Wen S, Chung DDL (1999) Cem Concr Res 29:961
14. McCarter WJ (1995) J Am Ceramic Soc 78(2):411
15. McCarter WJ, Starrs G, Chrisp TM (2000) Cem Concr Res 30:1395
16. Chen B, Wu K, Yao W (2004) Cem Concr Comp 26(4):291
17. Chiarello M, Zinno R (2005) Ibid 27(4):463