CONTRASTING FUNCTIONAL ADVANTAGES OF PITCH-BASED AND PAN-BASED CARON FIBERS IN CEMENT-MATRIX COMPOSITES

David G. Meehan, Sivaraja Muthusamy and D.D.L. Chung

Composite Materials Research Laboratory
University at Buffalo
State University of New York
Buffalo, NY 14260-4400, U.S.A.

Introduction

Pitch and polyacrylonitrile (PAN) are the two most common precursors of carbon fibers. Isotropic-pitch-based carbon fiber tends to be less expensive than PAN-based carbon fiber. However, due to the wider use of PAN-based carbon fiber than pitch-based carbon fiber in polymer-matrix structural composites, PAN-based carbon fiber is more widely available than pitch-based carbon fiber. The electrical conductivity of a carbon fiber increases with increasing degree of graphitization. PAN-based carbon fiber is less graphitizable than pitch-based carbon fiber, but graphitized pitch-based carbon fiber is expensive and is thus not cost effective anyway. The pitch-based carbon fiber used in prior work [1-3] has not been graphitized. Furthermore, PAN-based carbon fiber tends to be smaller in diameter than pitch-based carbon fiber. For example, the diameter of PAN-based carbon fiber is typically 7 μm [4], in contrast to the diameter of 15 μm for the pitch-based carbon fiber of prior work [1-3].

Prior work addressed the flexural strength [3,5-9] and electrical resistivity [1-3,10] of cement containing pitch-based and PAN-based carbon fibers, which are both effective for enhancing these properties. The fiber efficiency factor is defined as the ratio of the composite strength to the fiber strength, divided by the fiber volume fraction. Comparison of PAN-based and pitch-based fibers in relation to the flexural strength of their cement-matrix composites showed that PAN-based fiber (diameter 7 μm and ductility 1.4%) is lower in the efficiency factor than the pitch-based fiber (diameter 18 μm and ductility 2%) [5]. The relatively low ductility of the PAN-based fiber contributes to causing a low efficiency factor.

Carbon fiber reinforced cement is attractive not only for its mechanical properties, but also for its functional properties, such as electromagnetic interference (EMI) shielding and self-sensing (i.e., the sensing of its own strain and damage) [11]. Comparison of pitch-based and PAN-based carbon fibers in terms of their effectiveness for providing functional properties to the cement is the focus of this paper.

Experimental methods

Isotropic-pitch-based unsized fibers (diameter 15 μm, length 5 mm, aspect ratio 300, electrical resistivity 3×10^{-3} Ω.cm, Ashland Petroleum Co., production discontinued) and PAN-based unsized fiber (diameter 7 μm, length 8 mm, aspect ratio 1000, electrical resistivity 2×10^{-3} Ω.cm, Grade PANEX33CF0250-01, Zoltek) were subjected to ozone surface treatment, which involved exposure to ozone gas (0.6 vol.%, in oxygen) at 160°C for 10 min for improving the wettability of fibers by water [12].

Fibers in the amount of 0.50% by mass of cement (corresponding to 0.24 vol.% of the mortar) were used. In case of the pitch-based fibers (15 μm diameter) in cement paste, the percolation threshold is between 0.5 and 1.0 vol.% [13]. In case of pitch-based fibers (7 μm diameter), the percolation threshold is between 0.4 and 0.8 vol.%, both in cement paste and in mortar with sand/cement ratio 1.0 [14].

The cement was Portland cement (Type I). The sand, was natural sand (100% passing 2.36 mm sieve, 99.9% SiO_2), with sand/cement ratio 1.0. The water/cement ratio was 0.35. No coarse aggregate was used. Silica fume (Elkem Materials Inc., microsilica, EMS 965) was used in the amount of 15% by mass of cement to help the fiber dispersion. Methylcellulose (Dow Chemical Corp., Methocel A15-LV) was used in the amount of 0.4% by mass of cement. The defoamer (Colloids Inc., 1010) was used in the amount of 0.13 vol.%.

A rotary mixer with a flat beater was used for mixing. Methylcellulose was dissolved in water and then the defoamer and fibers were added and stirred by hand for about 2 min. Then, the methylcellulose mixture, cement, water and silica fume were mixed for 5 min. The specimens were demolded after 1 day and then allowed to cure at room temperature in air (relative humidity = 100%) for 28 days.

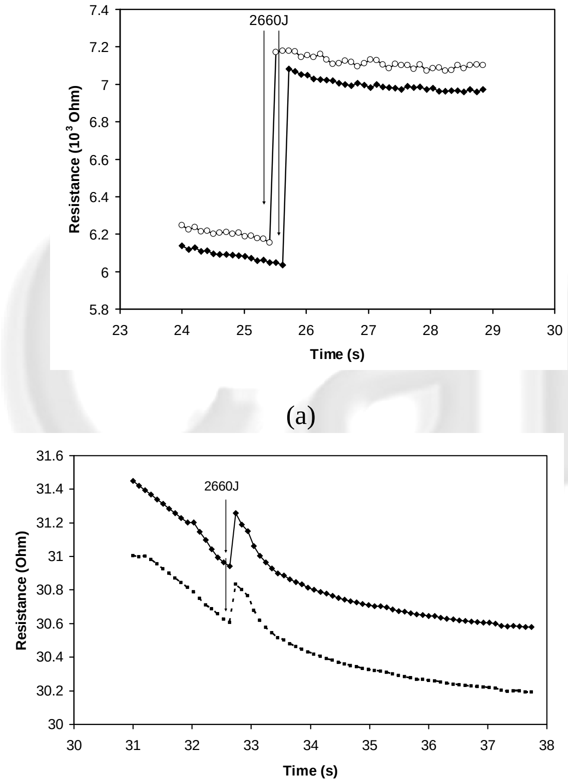
The self-sensing of damage was tested by measuring the DC surface resistance of a specimen upon impact of its surface. Before, during and after impact using a steel hemisphere (19 mm diameter), which was dropped from a controlled height, resistance measurement was made. The impact energy was calculated from the mass of the hemisphere assembly (0.740 kg) and the initial height of the hemisphere. The resistance was measured by using the four-probe method, with four electrical contacts (each being a line) in the form of silver paint and copper wires on the surface receiving the impact, such that the electrical contacts were symmetrically positioned on the two sides of the point of impact. The point of impact was centered between the voltage contacts.

The volume resistivity was measured using the four-probe method, with four electrical contacts applied by silver paint around the whole perimeter at four planes perpendicular to the length of the specimen. The four planes were symmetrical around the mid-point along the length of the specimen.

For EMI shielding testing, the attenuations upon transmission was measured using the coaxial cable method (the transmission line method). The set-up consisted of an Elgal (Israel) SET 19A shielding effectiveness tester with its input and output connected to a Hewlett-Packard (HP) 8510A network analyzer. The frequency was 1.0 GHz. The specimen placed in the center plane of the tester (with the input and output of the tester on the two sides of the specimen) was in the form of an annular ring of outer diameter 97 mm (3.8 in.) and inner diameter 29 mm (1.1 in.). Silver paint was applied at both inner and outer edges of each specimen and at the vicinity of the edges in order to make electrical contact with the inner and outer conductors of the tester. The sample thickness was 4.3 mm.

Results and discussion

Fig. 1 shows the resistance upon impact at 2,660 J. The resistance increases abruptly and irreversibly upon impact. The fractional change in resistance upon impact is much higher for pitch-based fiber mortar (Fig. 1(a)) than PAN-based fiber mortar. Hence, the sensing ability is superior for the pitch-based fiber cement. This superiority relates to the much lower resistance of PAN-based fiber cement, as shown in Fig. 1. Indeed, the volume resistivity, as separately measured, was 1.6×10^5 and 5.3×10^3 Ω.cm for pitch-based and PAN-base fiber mortars respectively. The large difference in resistivity is attributed to the lower aspect ratio of the pitch-based fiber and the consequent lower percolation threshold. It cannot be merely due to the difference in fiber resistivity.



(a)

(b)

Fig. 1 Surface resistance of cement mortar upon impact at 2,660 J. The two curves in each graph are for two specimens. (a) Pitch-based fiber. (b) PAN-based fiber.

The shielding effectiveness at 1 GHz was 26.9 ± 2.5 dB without sand and 25.9 ± 3.4 dB with sand. In contrast, pitch-based carbon fiber gave shielding effectiveness 9 dB at 1 GHz (0.5% by mass of cement in cement paste, corresponding to 0.5 vol.%) [1]. Hence, PAN-based fiber is more effective than the pitch-based fiber for providing shielding. The shielding superiority of the PAN-based fiber is partly due to the smaller diameter of the PAN-based fiber compared to the pitch-based fiber. This explanation is supported by prior work which shows that a smaller diameter gives a lower percolation threshold [13,14]. Fiber of a smaller diameter provides a larger fiber-cement interface area per unit volume of the composite. Due to the skin effect (the phenomenon in which the electromagnetic radiation only penetrates the near surface region of a conductor) and the reflection mechanism of shielding, a larger interface area promotes shielding.

Conclusions

Pitch-based carbon fiber reinforced mortar is more effective than PAN-based fiber mortar for self-sensing, but the PAN-based fiber mortar gives much lower electrical resistivity and much higher EMI shielding effectiveness. This difference is attributed to the higher aspect ratio of the PAN-based fiber and the consequent lower resistivity of the PAN-based fiber mortar. A lower resistivity helps the shielding, but self-sensing requires conductivity such that the resistivity is not too low.

References

[1] Wen S, Chung DDL. Partial replacement of carbon fiber by carbon black in multifunctional cement-matrix composites. Carbon 2007;45(3): 505-513.

[2] Chiou J, Zheng Q, Chung DDL. Electromagnetic interference shielding by carbon fiber reinforced cement. Composites 1989;20(4): 379-381.

[3] Chen P, Chung DDL. Concrete reinforced with up to 0.2 vol.% of short carbon fibers. Composites 1993;24(1):33-52.

[4] Wang C, Li K, Li H, Guo L, Jiao G. Influence of CVI treatment of carbon fibers on the electromagnetic interference of CFRC composites. Cement & Concrete Composites 2008;30:478-485.

[5] Katz A. Effect of fiber modulus of elasticity on the long term properties of micro-fiber reinforced cementitious composites. Cement and Concrete Composites 1996;18:389-399.

[6] Katz A, Bentur A. Effect of matrix composition on the aging of CFRC. Cement and Concrete Composites 1995;17:87-97.

[7] Katz A, Bentur A. Mechanical properties and pore structure of carbon fiber reinforced cementitious composites. Cement and Concrete Research 1994;24(2):214-220.

[8] Toutanji HA, El-Korchi T, Katz, RN. Strength and reliability of carbon-fiber-reinforced cement composites. Cement and Concrete Composites 1994;16:15-21.

[9] Kojima A, Ohte T, Ohtani S. Strengthening of cement composites with surface modification carbon fiber by cold plasma. Journal of Photopolymer Science and Technology 1993;6(3):351-352.

[10] Reza F, Batson, GB, Yamamuro, JA, Lee JS. Volume electrical resistivity of carbon fiber cement composites. ACI Materials Journal 2001; 98(1):25-35.

[11] Chung DDL. Electrically conductive cement-based materials. Adv. Cem. Res. 2004;16(4):167-176.

[12] Wen, S, Chung DDL. Strain sensing characteristics of carbon fiber reinforced cement. ACI Material Journal 2005; 102(4):244-248.

[13] Chen P, Chung DDL. Improving the electrical conductivity of composites comprised of short conducting fibers in a non-conducting matrix: the addition of a non-conducting particulate filler. Journal of Electronic Materials 1995;24(1):47-51.

[14] Chen B, Wu K, Yao W. Conductivity of carbon fiber reinforced cement-based composites. Cement and Concrete Composites 2004;26(4):291-297.