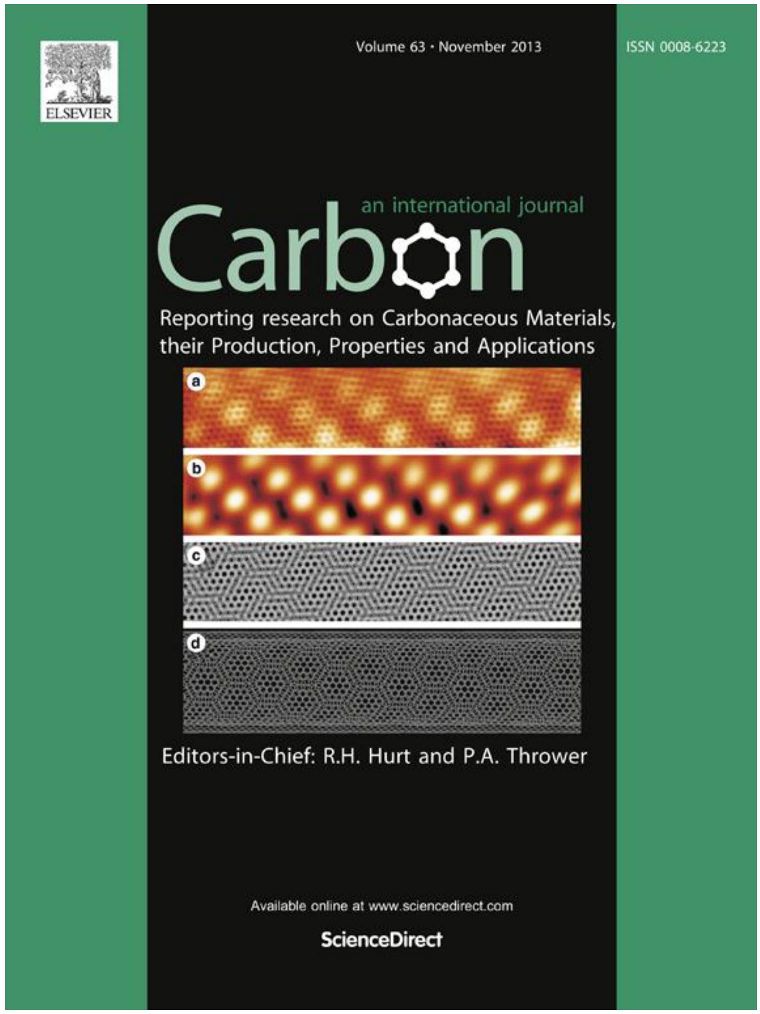
Volume 63 • November 2013
ISSN 0008-6223
ELSEVIER
an international journal
Carbon
Reporting research on Carbonaceous Materials, their Production, Properties and Applications
a
b
c
d
Editors-in-Chief: R.H. Hurt and P.A. Thrower
Available online at www.sciencedirect.com
ScienceDirect

CARBON 63 (2013) 446–453

Available at www.sciencedirect.com

SciVerse ScienceDirect

journal homepage: www.elsevier.com/locate/carbon

Comparative evaluation of cement-matrix composites with distributed versus networked exfoliated graphite

Po-Hsiu Chen, D.D.L. Chung *

Composite Material Research Laboratory, University at Buffalo, State University of New York Buffalo, NY 14260-4400, USA

ARTICLE INFO

Article history:
Received 28 March 2013
Accepted 27 June 2013
Available online 8 July 2013

ABSTRACT

Cement with distributed exfoliated graphite (isotropic) is made by incorporating exfoliated graphite in the wet cement mix; cement with networked exfoliated graphite (anisotropic) is made by compressing a dry mixture of exfoliated graphite and cement particles, followed by curing with water. The graphite layers in the latter are preferentially oriented in the plane perpendicular to the compression direction; the in-plane electrical resistivity is much lower than the out-of-plane resistivity and the loss tangent, storage modulus and loss modulus are much higher for out-of-plane flexure than in-plane flexure. The latter gives higher density, lower electrical resistivity, higher compressive strength and superior vibration damping than the former. Compared to plain cement, it gives higher density and higher compressive strength. In contrast, cement with distributed exfoliated graphite gives lower density and lower compressive strength than plain cement, though it gives lower resistivity and superior damping. Distributed exfoliated graphite is detrimental when silica fume is present. The high damping of cement with networked exfoliated graphite is attributed to the effective sandwiching of the network ligaments by the cement matrix (constrained-layer damping); the high density and compressive strength are attributed to the low porosity caused by the compression of the exfoliated graphite during composite fabrication.

1. Introduction

Cement-matrix composites containing graphite particles as an admixture have been previously investigated due to their low electrical resistivity [1–3], high thermoelectric power [1] and high thermal conductivity [4] compared to the case without the graphite particles and the relevance of their properties to electromagnetic interference (EMI) shielding [3], electricity generation [1], thermal storage [4] and fuel cell bipolar plates [2]. The graphite particles are small graphite flakes, which differ from exfoliated graphite. Little attention has been previously given to the incorporation of exfoliated graphite in cement [5,6].

In contrast to graphite flakes, exfoliated graphite has a cellular structure (an accordion-like structure) [7,8], due to the vaporization of the intercalate or the emission of gasses resulting from the decomposition of the intercalate during heating and the consequent ballooning of each intercalate island during exfoliation [9–11]. Exfoliation involves expansion in the direction perpendicular to the graphite layers by up to hundreds of times. An exfoliated graphite flake is known as a worm, due to its shape. The stretching of the balloon wall

* *Corresponding author:* Fax: +1 716 645 2883.
E-mail address: ddlchung@buffalo.edu (D.D.L. Chung).
URL: http://alum.mit.edu/www/ddlchung.
0008-6223/$ - see front matter
http://dx.doi.org/10.1016/j.carbon.2013.06.097

during the ballooning is enabled by the sliding of the graphite layers in the balloon wall relative to one another. Thus, exfoliated graphite consists of cell walls (balloon walls) and voids. The cell wall is a nanoscale multilayer that consists of graphite layers. The feasibility of exfoliation relates to the easy sliding of the graphite layers relative to one another. The ease of sliding and the large area of the interfaces between the layers in the multilayer enable the cell wall to exhibit a high degree of viscous character [12].

Upon compression in the absence of a binder, exfoliated graphite forms a flexible sheet that is known as flexible graphite [13,14]. The sheet formation is due to the mechanical interlocking between the adjacent worms. The sheet exhibits preferred orientation of the graphite layers in the plane of the sheet, as indicated by the much lower in-plane electrical resistivity compared to the out-of-plane resistivity [15]. This preferred orientation and the cellular structure result in resiliency in the direction of the compression during sheet formation. The resiliency enables the applications of this material as fluid and EMI gaskets [14,15].

A method of incorporating exfoliated graphite in cement involves the dry mixing of exfoliated graphite and cement particles, followed by compression and subsequent curing [5]. The compression step enables mechanical interlocking between the adjacent worms, as in the process of making flexible graphite. The interlocking results in a graphite network, which persists after the curing of the cement. This method results in cement with networked rather than uniformly distributed exfoliated graphite. The networking is supported by the low resistivity (0.04 Ω cm perpendicular to the compression direction and 0.5 Ω cm in the compression direction) [5]. In contrast, the resistivity is 480 Ω cm for cement containing 37 vol.% graphite powder [1]. The cement with networked exfoliated graphite exhibits unprecedented vibration damping, with high values of loss modulus (7.5 GPa) and loss tangent (0.81), as measured under flexure [5].

An intuitively obvious method of incorporating exfoliated graphite in cement involves the addition of the exfoliated graphite to the wet cement mix and subsequent mixing and curing. This method is expected to result in the exfoliated graphite being distributed (ideally randomly and uniformly) in the resulting cement-based material. Moreover, due to the absence of compression in the processing, the exfoliated graphite is expected to retain its fluffiness to a substantial degree. However, this simple method has not been previously reported. Due to its applicability to the making of large structural components by conventional cement mixing and pouring, this method is more practical than the method mentioned above for making cement with networked exfoliated graphite.

Aggregates and other admixtures may be incorporated in cement along with exfoliated graphite. For example, silica fume (submicron silica particles) is an admixture that is effective for enhancing the damping (due to the large interface area between the fine silica particles and the cement matrix) [16], increasing the abrasion resistance, decreasing the liquid permeability, enhancing the bond strength to steel, and improving the fiber dispersion (in case that fibers are also used as an admixture) [17]. The incorporation of the exfoliated graphite to cement by direct addition to the wet cement mix is a method that allows convenient incorporation of aggregates and additional admixtures to the same mix. However, the method involving mixing the worms with cement powder and subsequent compression to form a graphite network does not allow incorporation of an additional solid admixture, because the presence of an additional solid admixture tends to hinder the mechanical interlocking of the exfoliated graphite. As a result, in case that the networked exfoliated graphite is used along with other solid admixtures or with aggregates, the cement with networked exfoliated graphite needs to be used as an admixture rather than a monolith. After formation in a slightly cured state, this cementitious admixture may be introduced to a cement mix along with other admixtures and/or aggregates and allowed to cure along with the additional cement present in the mix [18].

Comparison between cement with distributed exfoliated graphite and cement with networked exfoliated graphite is valuable for studying the effect of the exfoliated graphite structure on the behavior of the cement-matrix composite. Networking is important for electrical conduction, due to the high electrical conductivity of graphite. However, the sliding of the graphite layers relative to one another in the cell wall of exfoliated graphite does not require the graphite to form a network.

Due to the absence of prior work on cement with distributed exfoliated graphite and the presence of prior work on cement with networked exfoliated graphite [5,6], this paper is directed at evaluating the value of adding distributed exfoliated graphite to cement. Specifically, this paper is aimed at (i) investigating the mechanical, damping and electrical properties of cement with distributed exfoliated graphite, (ii) comparing the properties of cement with distributed exfoliated graphite with those of cement with networked exfoliated graphite, (iii) comparing the properties of cement with distributed exfoliated graphite with those of plain cement, and (iv) comparing the properties of cement with distributed exfoliated graphite and silica fume with those of cement with silica fume.

The approach of this work involves the preparation of cement paste with distributed exfoliated graphite and cement paste with networked exfoliated graphite, such that the exfoliated graphite is at the same mass proportion and then testing them in terms of (i) the compressive strength, (ii) the loss tangent, storage modulus and loss modulus (by dynamic flexure under forced resonance), and (iii) the electrical resistivity. Cement pastes with and without silica fume are included in the comparative study.

2. Experimental methods

2.1. *Materials*

Portland cement (Type I, ASTM C150) was used. Silica fume (Elkem Materials Inc., Pittsburgh, PA, microsilica, EMS 965, USA), if used, was at 15% by mass of cement, as in prior work [17]; it had particle size ranging from 0.03 to 0.5 μm, with average size 0.2 μm; it contained >93 wt.% SiO_2, <0.7 wt.% Al_2O_3, <0.7 wt.% CaO, <0.7 wt.% MgO, <0.5 wt.% Fe_2O_3, <0.4 wt.% Na_2O, <0.9 wt.% K_2O, and <6 wt.% loss on ignition.

For preparing cement with networked exfoliated graphite, the particle size of the cement was reduced by ball milling for 24 h, using ceramic cylinders as the grinding medium contained in a ceramic container. The milling reduced the typical cement particle size from 50 to 30 μm. This size reduction was performed because a smaller cement particle size would facilitate the adjacent worms to touch one another. However, for preparing cement with distributed exfoliated graphite, no milling of the cement was conducted.

Exfoliated graphite (worms) were obtained by rapid heating of expandable graphite flakes (graphite flakes intercalated with sulfuric acid and nitric acid in the presence of catalysts, with a flake size of 300 μm, as supplied by Asbury Graphite Mills, Asbury, NJ, USA, under the designation No. 3772) at 900 °C for 2 min with flowing nitrogen. The ratio of the volume of the worms to that of the corresponding flakes prior to exfoliation is 600, as obtained by measuring the bulk volume of the worms that resulted from the exfoliation of 5000 g of expandable graphite flakes. The worms were of length 2–4 mm. During exfoliation, the vast majority of the intercalate desorbed, so that the intercalate that remains after exfoliation is low in concentration and is strongly held to the graphite [9,19].

For cement with distributed or networked exfoliated graphite, no aggregate was used and the exfoliated graphite was used at 2.2% by mass of cement. With the density of the exfoliated graphite taken as 0.82 g/cm^3, this corresponds to the volume ratio of cement to exfoliated graphite of 12:1 [5].

For preparing cement with distributed exfoliated graphite, the water/cement ratio was 0.40. A high-range water reducing agent (Glenium 3000NS, BASF Construction Chemicals) was used at 1.0% by mass of cement. The defoamer (Colloids Inc., Marietta, GA, 1010, USA) was used at 0.13% (% of specimen volume). All the ingredients were mixed in a rotary mixer with a flat beater. In case of specimens for dynamic mechanical testing under flexure, the mix was poured into a 150 × 25 × 4 mm mold to form a beam-shaped flexural specimen. In case of specimens for static mechanical testing under uniaxial compression, the specimens were of size 51 × 51 × 51 mm, as provided by using mold cavities of these dimensions. In case of specimens for in-plane (horizontal plane during curing) electrical resistivity measurement, the specimens were of size 60 × 12 × 12 mm, with the 60 × 12 mm plane being in the horizontal plane during curing, as obtained by using mold cavities of this size. In case of specimens for out-of-plane (vertical plane during curing) electrical resistivity measurement, the specimens were of size 50 × 10 × 10 mm, with the 50 × 10 mm plane in the vertical plane during curing, as obtained by cutting a 51 × 51 × 51 mm cubic specimen. For all specimens, after filling the mold, an external vibrator was used to facilitate compaction and diminish the air bubbles. The specimens were demolded after 24 h and then cured at a relative humidity of nearly 100% for 28 days.

For the sake of comparison, cement pastes without exfoliated graphite were also prepared. The water/cement ratio was 0.35 in the absence of silica fume and was 0.40 in the presence of silica fume. The water reducing agent and defoamer were used as stated above in relation to cement with distributed exfoliated graphite.

For preparing cement with networked exfoliated graphite, the exfoliated graphite was mixed with the milled cement particles in the dry state for 24 h using a ball mill without any grinding medium. The masses of the exfoliated graphite and cement in the mixture were controlled. The compression of the mixture was conducted in the dry state in a cylindrical mold of length 45 cm and inner diameter 31.8 mm by applying a uniaxial pressure of 5.6 MPa via a matching piston. The entire thickness of a composite specimen was obtained in one 5.6 MPa compression stroke. Each specimen was in the form of a disc of diameter 31.8 mm. After this, the disc was exposed to water for curing the cement. The water exposure involved exposure to moisture for 2 days, followed by immersion in water for 26 days. The thickness was measured after the water exposure. Specimens for out-of-plane deflection had thickness ranging from 2.8 to 3.0 mm; specimens for in-plane deflection had thickness ranging from 7.7 to 8.2 mm. The graphite network amounted to 8 vol.% and the cement matrix amounted to 92 vol.%. For dynamic mechanical testing, the specimen was a beam of size 25 × 8 × 3 mm, as obtained by cutting the disc.

The silica fume had been subjected to silane treatment in order to improve its dispersion in the cement mix [20,21]. The silane coupling agent was a 1:1 (by mass) mixture of Z-6020 ($H_2NCH_2CH_2NHCH_2CH_2CH_2Si(OCH_3)_3$) and Z-6040 ($OCH_2CHCH_2OCH_2CH_2CH_2Si(OCH_3)_3$) from Dow Corning Corp. (Midland, MI) [20,21]. The amine group in Z-6020 served as a catalyst for the curing of the epoxy and consequently allowed the Z-6020 molecule to attach to the epoxy end of the Z-6040 molecule. The trimethylsiloxy ends of the Z-6020 and Z-6040 molecules then connected to the –OH functional group on the surface of the silica fume. The silane was dissolved in ethylacetate to form a solution with 2.0 wt.% silane. Surface treatment of the silica fume was performed by immersion in the silane solution, heating to 75 °C while stirring, and then holding at 75 °C for 1.0 h, followed by filtration and drying. After this, the silica fume was heated at 110 °C for 12 h.

2.2. *Testing methods*

For compressive strength measurement, the specimens were 51 × 51 × 51 mm in size. A hydraulic mechanical testing system was used. The displacement rate was 0.5 mm/min. Six specimens of each type were tested.

Dynamic flexural testing (ASTM D 4065-94, forced resonance method) at a controlled frequency of 0.2 Hz was conducted at room temperature under three-point bending using a dynamic mechanical analyzer (DMA7, Perkin Elmer Corp., Norwalk, CT, USA). The frequency of 0.2 Hz was chosen due to the relevance of low frequencies to large structures and the monotonic decrease of the loss tangent with increasing frequency from 0.2 to 2.0 Hz [16]. The loads used were large enough that the amplitude of the specimen deflection ranged from 5 to 7 μm (which was over the minimum value of 5 μm required by the equipment for accurate results). For the cement with networked exfoliated graphite, flexural testing was conducted for out-of-plane flexure and in-plane flexure, as illustrated in Fig. 1, using specimens that were obtained by cutting the specimen disc mentioned above. All specimens were 150 × 25 × 4 mm in size (span = 115 mm),

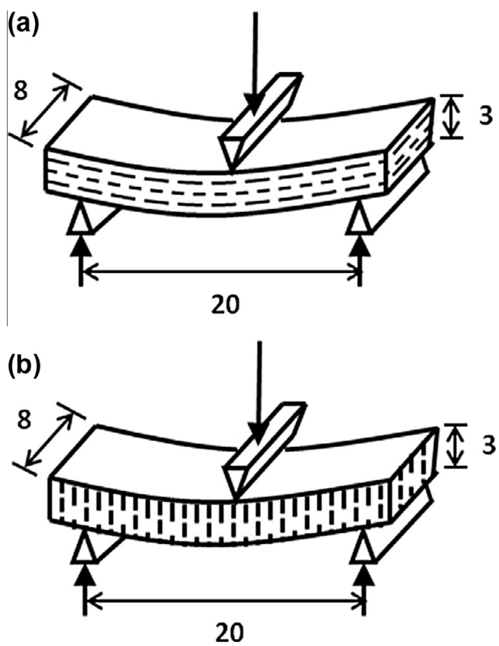

Fig. 1 – Specimen configuration for testing cement with networked exfoliated graphite under dynamic flexure (three-point bending). (a) Out-of-plane flexure. (b) In-plane flexure. The dashed lines represent the preferred orientation of the graphite layers. All dimensions are in mm.

except for the specimens of cement with networked exfoliated graphite, for which the size was $25 \times 8 \times 3$ mm (span = 20 mm). Four specimens of each type were tested.

The four-probe method was used for electrical resistivity measurement of cement with distributed exfoliated graphite. The outer two contacts (current contacts) were at the entirety of two end surfaces, as made by using silver paint in conjunction with aluminum foil. The inner two contacts (voltage contacts) were all the way around the perimeter in two planes (symmetrically positioned relative to the mid-point of the length of the specimen in the resistance measurement direction) perpendicular to the direction of resistance measurement, as made by using silver paint in conjunction with copper wire. For in-plane (horizontal plane during curing) resistivity measurement, the specimens were $60 \times 12 \times 12$ mm in size, with the inner contacts being 40 mm apart, and six specimens of each type were tested. For out-of-plane (vertical plane during curing) resistivity measurement, the specimens were $50 \times 10 \times 10$ mm in size, with the inner contacts being 40 mm apart, and four specimens of each type were tested.

The density was measured using either the cubic or beam-shaped specimens made for compressive or flexural testing. It was calculated from the measured weight and volume.

3. Results and discussion

Table 1 shows that the cement with networked exfoliated graphite exhibits higher density, much higher compressive strength and much lower electrical resistivity than the cement with distributed exfoliated graphite. The density of the cement with distributed exfoliated graphite is even lower than that of plain cement, because of the inherent porosity in each worm. Similarly, the density of the cement with distributed exfoliated graphite and silica fume is lower than that of cement with silica fume. Silica fume decreases the density, whether distributed exfoliated graphite is present or not. The density of cement with distributed exfoliated graphite and silica fume is close to that of cement with silica fume but without exfoliated graphite. The density of the cement with networked exfoliated graphite is even higher than that of plain cement, due to the compression step that consolidates each worm during the fabrication of this composite and the conformability of the compressed worms to the topography of the cement particles.

The very high compressive strength of cement with networked exfoliated graphite is because of the fact that this material deforms greatly without cracking [5]. The large deformation is apparently enabled by the sliding that is possible between the graphite layers in the cell wall of exfoliated graphite. In contrast, the compressive strength of the cement with distributed exfoliated graphite is even lower than that of plain cement, indicating that the distributed exfoliated graphite weakens the cement-based material. Similarly, the compressive strength of the cement with distributed exfoliated graphite and silica fume is lower than that of cement with silica fume. The weakening is consistent with the porosity in the distributed exfoliated graphite. On the other hand, silica fume enhances the compressive strength, whether distributed exfoliated graphite is present or not, partly due to the small particle size and the consequent refinement of the pore structure in cement [17]. However, the compressive strength of cement with distributed exfoliated graphite and silica fume is lower than that of plain cement (Table 1). Comparison between cement with silica fume and cement with distributed exfoliated graphite and silica fume shows that the addition of distributed exfoliated graphite to cement with silica fume decreases the compressive strength.

As shown in Table 1, the resistivity is anisotropic for the cement with networked exfoliated graphite, with the in-plane resistivity much lower than the out-of-plane resistivity, as expected due to the compression during the composite fabrication. However, the resistivity is isotropic for the cement with distributed exfoliated graphite, with the in-plane and out-of-plane resistivities essentially equal, as expected since the composite fabrication does not involve compression of the worms.

Although the resistivity is anisotropic for the cement with networked exfoliated graphite, the resistivity is low in both in-plane and out-of-plane directions. In particular, the in-plane resistivity is lower than that of plain cement by 7 orders of magnitude. The large difference in electrical resistivity between the cement with distributed exfoliated graphite and that with networked exfoliated graphite is consistent with the notion that the distributed exfoliated graphite in the former is not networked. Networking means percolation. Nevertheless, the resistivity of the cement with distributed exfoliated graphite is lower than that of plain cement by 2 orders of magnitude, indicating that the distributed exfoliated

Table 1 – Density, compressive strength and electrical resistivity.

Material	Density (g/cm^3)	Compressive strength (MPa)	Electrical resistivity (Ω cm)
Cement with networked exfoliated graphite	2.20 ± 0.03	278 ± 12 [b] [5]	$(36 \pm 9) \times 10^{-3}$ [a] [5] $(480 \pm 10) \times 10^{-3}$ [b] [5]
Cement with distributed exfoliated graphite	1.84 ± 0.06	41.2 ± 3.5	$(9.22 \pm 0.73) \times 10^{3}$ [a] $(10.02 \pm 1.31) \times 10^{3}$ [b]
Cement with distributed exfoliated graphite and silica fume[c]	1.68 ± 0.05	48.9 ± 2.8	$(9.87 \pm 0.60) \times 10^{3}$
Plain cement	2.01 ± 0.02 [18]	54.2 ± 2.1	$(4.9 \pm 0.4) \times 10^{5}$[1]
Cement with silica fume[c]	1.73 ± 0.02 [18]	67.1 ± 2.5	/

[a] In-plane.
[b] Out-of-plane.
[c] Silane treated.

graphite contributes to electrical conduction in spite of the essential absence of percolation.

Table 2 shows that the loss tangent, which describes the degree of viscous character, is much higher for the cement with networked exfoliated graphite than that with distributed exfoliated graphite. The loss tangent of the cement with networked exfoliated graphite is higher for out-of-plane flexure than in-plane flexure. (Prior work only reported for the case of out-of-plane flexure [5]). Since the graphite layers are preferentially oriented in the plane, out-of-plane flexure results in more shear between the graphite layers than in-plane flexure. Hence, the higher loss tangent for out-of-plane flexure than in-plane flexure supports the notion that the viscous deformation involves shear between the graphite layers. The loss tangent is marginally higher for the cement with distributed exfoliated graphite than plain cement, indicating that the distributed exfoliated graphite is not effective for enhancing the viscous character. Thus, the mechanism of viscous deformation involving the sliding of the graphite layers relative to one another [12] is strongly enhanced by using networked exfoliated graphite rather than distributed exfoliated graphite. The loss tangent is higher for cement with silica fume than plain cement, due to the slippage at the interface between silica and cement, as previously reported [16,17]. Similarly, the loss tangent is higher for cement with distributed exfoliated graphite and silica fume than cement with silica fume. The addition of distributed exfoliated graphite to cement with silica fume decreases the loss tangent. This means that the distributed exfoliated graphite is detrimental to the viscous behavior in the presence of silica fume and essentially does not affect the viscous behavior in the absence of silica fume. The loss tangent of the cement with networked exfoliated graphite is much higher than that of cement with silica fume. This is consistent with the large interfacial area for slippage between the graphite layers in exfoliated graphite compared to the interfacial area between the silica particles and the cement matrix. The cell wall of the exfoliated graphite of this work consists of a stack of about 60 graphite layers, as shown by the specific surface area of 45 ± 4 m^2/g (measured in this work by nitrogen adsorption using a Micromeritics ASAP 2010 instrument).

Table 2 shows that the storage modulus, which describes the elastic stiffness (the real part of the complex modulus), is much higher for the cement with networked exfoliated graphite than the cement with distributed exfoliated graphite. The storage modulus of the cement with networked exfoliated graphite is higher for out-of-plane flexure than in-plane flexure, as expected from the preferred orientation of the graphite layers in the plane. Out-of-plane flexure involves bending of the graphite layers, whereas in-plane flexure involves change in the distance between the graphite layers. The storage modulus of the cement with networked exfoliated graphite is comparable to that of cement with silica fume. This means that the networked exfoliated graphite is as effective as silica fume in providing stiffening. The storage modulus of the cement with distributed exfoliated graphite is comparable to that of plain cement, indicating that the distributed exfoliated graphite does not affect the stiffness in the absence of silica fume. The storage modulus of the cement with distributed exfoliated graphite and silica fume is lower than that of cement with silica fume, indicating that distributed exfoliated graphite is detrimental to the stiffness in the presence of silica fume.

Table 2 – Dynamic flexural properties.

Material	Storage modulus (GPa)	Loss tangent	Loss modulus (GPa)
Cement with networked exfoliated graphite	7.74 ± 0.28 [a] 9.73 ± 0.18 [b]	0.30 ± 0.04 [a] 0.76 ± 0.06 [b]	2.31 ± 0.08 [a] 7.35 ± 0.11 [b]
Cement with distributed exfoliated graphite	1.97 ± 0.33	0.042 ± 0.007	0.082 ± 0.009
Cement with distributed exfoliated graphite and silica fume[c]	3.13 ± 0.22	0.048 ± 0.005	0.150 ± 0.007
Plain cement	1.81 ± 0.12	0.030 ± 0.009	0.054 ± 0.001
Cement with silica fume[c]	7.13 ± 0.54	0.061 ± 0.008	0.435 ± 0.004

[a] In-plane deflection, with the plane of the beam containing the out-of-plane direction.
[b] Out-of-plane deflection, with the plane of the beam perpendicular to the out-of-plane direction.
[c] Silane treated.

Table 2 also shows that the loss modulus, which is the viscous modulus (the imaginary part of the complex modulus and equal to the product of the storage modulus and the loss tangent) and relates to the mechanical energy dissipation, is much higher for the cement with networked exfoliated graphite than the cement with distributed exfoliated graphite and the cement with silica fume. The loss modulus of the cement with networked exfoliated graphite is higher for out-of-plane flexure than in-plane flexure, as expected from the higher stiffness and the stronger viscous character for out-of-plane flexure. The loss modulus is higher for cement with distributed exfoliated graphite than plain cement, but is lower for cement with distributed exfoliated graphite and silica fume than cement with silica fume. This means that distributed exfoliated graphite increases the loss modulus in the absence of silica fume, but decreases the loss modulus in the presence of silica fume.

The addition of silica fume to cement with distributed exfoliated graphite increases the storage modulus, loss tangent and loss modulus (Table 2), but the values remain much lower than those of cement with networked exfoliated graphite. Similarly, the addition of silica fume to plain cement increases all three quantities. However, the addition of distributed exfoliated graphite to cement with silica fume decreases all three quantities. This means that cement with distributed exfoliated graphite and silica fume is inferior to cement with silica fume in terms of the damping behavior.

The networked exfoliated graphite is highly effective for improving the mechanical, damping and electrical properties of cement-based materials. An electrical connection, as needed for percolation, can be made by touching, without a mechanical connection, so a mechanical connection is more difficult to achieve than an electrical connection. Although the mechanical connection involving mechanical interlocking between the worms in the network is not strong, as indicated by the low tensile strength of flexible graphite [22], the connection is sufficiently strong for the network to act as a microscale net-like stretchable mechanical constrainer, thereby making cracking of the cement-based material difficult and greatly increasing the compressive strength.

The anisotropy in the cement with networked exfoliated graphite (Table 1) contributes to causing the relatively strong viscous character of the cement with networked exfoliated graphite, because the preferred orientation of the graphite layers in the plane of the beam subjected to bending facilitates shear of the layers relative to one another. However, the contribution of the anisotropy to enhancing the viscous character is not large, as shown by the fact that the loss tangent under in-plane flexure and that under out-of-plane flexure are different by only a factor of 2 (Table 2). This notion is also consistent with the fact that the loss tangent under uniaxial compression of an exfoliated graphite compact (without cement) is close for out-of-plane compression (0.229) and in-plane compression (0.269) respectively [7], even though in-plane compression facilitates shear between the graphite layers more than out-of-plane compression. Therefore, the very strong viscous behavior of cement with networked exfoliated graphite compared to cement with distributed exfoliated graphite is mainly attributed to the difference in structure rather than the difference in preferred orientation of the exfoliated graphite.

The synergy between networked exfoliated graphite and cement is noteworthy, as indicated by the low loss tangent but relatively high storage modulus of plain cement, the low storage modulus but high loss tangent of an exfoliated graphite compact (in the absence of cement) [12] and the high loss tangent and high storage modulus of cement with networked exfoliated graphite. The networked exfoliated graphite effectively provides a form of constrained-layer damping, which typically involves sandwiching a viscoelastic material between two sheets of stiff materials that are by themselves inadequate for damping [23]. Effectiveness in constrained-layer damping requires good bonding between the viscoelastic material and the sandwiching sheets. Since the bonding is never perfect, the thickness of the sandwiched viscoelastic material is preferably small. Distributed exfoliated graphite is inadequate for providing constrained-layer damping, because the distributed exfoliated graphite is fluffy and porous (as shown by the relatively low density of the cement with distributed exfoliated graphite, Table 1) and is consequently not as well sandwiched by cement as the networked exfoliated graphite. Furthermore, the distributed exfoliated graphite is macroscopic in size, compared to the microscopic size of the ligaments in the networked exfoliated graphite. The ligaments are formed during the compression step of the composite fabrication and have been observed by microscopy [5].

Constrained-layer damping utilizing exfoliated graphite also occurs in continuous carbon fiber polymer-matrix composite with exfoliated graphite at the interlaminar interfaces in the composite [24]. However, the degree of enhancement of the viscous behavior is not large, due to the inadequate sandwiching of the exfoliated graphite by the carbon fiber laminae. During the polymer-matrix composite fabrication, the worms are compressed between the laminae. In contrast, in the fabrication of cement with networked exfoliated graphite, the configuration in the mixture of the worms and cement particles enables compression of parts of each worm between cement particles, thereby resulting in a relatively fine-scale morphology of the sandwiched exfoliated graphite.

Compression of the cement mix containing distributed exfoliated graphite was tried but failed, because the mix flowed like a liquid. Thus, exfoliated graphite in a wet cement mix could not be deformed by compression, in contrast to the large deformation of the exfoliated graphite when it is with cement powder in the form of a dry mixture (the procedure used for making cement with networked exfoliated graphite).

As shown for an exfoliated graphite compact (in the absence of cement), the loss tangent decreases with increasing degree of compaction of the exfoliated graphite, due to the increasing difficulty of sliding between the graphite layers, such that the loss tangent is high only when the solid volume fraction in the compact is less than 4% [12]. This means that the degree of compaction of the exfoliated graphite in a cement matrix should not be excessive.

4. Conclusions

The composite with networked exfoliated graphite is made by uniaxial compression of a dry mixture of exfoliated graphite and cement particles, followed by exposure to water to cause curing of the cement. The compression step is responsible for the deformation of the exfoliated graphite, the formation of the graphite network [5] and the anisotropy in this network. In contrast, the composite with distributed exfoliated graphite is formed by wet mixing of exfoliated graphite, cement particles and water, so the exfoliated graphite is essentially not deformed and not networked and is essentially randomly (and hence uniformly) distributed. As a consequence, the composite with the distributed exfoliated graphite is isotropic.

Cement with networked exfoliated graphite is much superior to that with distributed exfoliated graphite, as shown by lower electrical resistivity, higher compressive strength and superior vibration damping performance. It is superior to plain cement in relation to the lower resistivity, higher compressive strength and superior damping performance. Furthermore, cement with networked exfoliated graphite exhibits higher density than cement with distributed exfoliated graphite and plain cement. The compressive strength and damping performance of the cement with networked exfoliated graphite are also higher than those of the cement with silica fume and those of the cement with distributed exfoliated graphite and silica fume.

Cement with distributed exfoliated graphite is inferior to plain cement in relation to the compressive strength, but is superior to plain cement in relation to the resistivity (lower) and damping performance. Furthermore, cement with distributed exfoliated graphite and silica fume is inferior to cement with silica fume in relation to the compressive strength and damping performance. Thus, distributed exfoliated graphite is not an attractive admixture, particularly when silica fume is used.

The high damping performance of cement with networked exfoliated graphite is attributed to the sliding between the graphite layers in the cell wall of exfoliated graphite and the effective sandwiching of the microscale network ligaments by the cement matrix, as needed for constrained-layer damping. The high density and high compressive strength of this material are attributed to the low porosity that is caused by the compression of the worms, which are conformable, during composite fabrication. In contrast, distributed exfoliated graphite remains porous and macroscopic in size, due to the absence of compression in the making of cement with distributed exfoliated graphite. Therefore, distributed exfoliated graphite is inadequate for providing appreciable constrained-layer damping.

Cement with networked exfoliated graphite is anisotropic, whereas cement with distributed exfoliated graphite is isotropic. For cement with networked exfoliated graphite, the preferred orientation of the graphite layers is in the plane perpendicular to the direction of compression during composite fabrication. As a result, the in-plane electrical resistivity is much lower than the out-of-plane resistivity and the loss tangent, storage modulus and loss modulus under dynamic flexure are much higher for out-of-plane flexure than in-plane flexure.

Acknowledgement

The authors thank Mr. Andi Wang of University at Buffalo, State University of New York, for technical assistance.

REFERENCES

[1] Wen S, Chung DDL. Thermoelectric behavior of carbon-cement composites. Carbon 2002;40(13):2495–7.
[2] Shen C, Pan M, Hua Z, Yuan R. Aluminate cement/graphite conductive composite bipolar plate for proton exchange membrane fuel cells. J Power Sources 2007;166(2):419–23.
[3] Bhattacharya S, Sachdev VK, Chatterjee R, Tandon RP. Decisive properties of graphite-filled cement composites for device application. Appl Phys A Mater Sci Process 2008;92(2):417–20.
[4] Yuan H, Lu C, Xu Z, Ni Y, Lan X. Mechanical and thermal properties of cement composite graphite for solar thermal storage materials. Sol Energy 2012;86(11):3227–33.
[5] Muthusamy S, Wang S, Chung DDL. Unprecedented vibration damping with high values of loss modulus and loss tangent, exhibited by cement-matrix graphite network composite. Carbon 2000;48(5):1457–64.
[6] Chung, D.D.L.; Muthusamy S., Cement-graphite composite materials for vibration damping. U.S. Patent 8,211,227 (2012).
[7] Chen P, Chung DDL. Dynamic mechanical properties of flexible graphite made from exfoliated graphite. Carbon 2012;50:283–9.
[8] Celzard A, Mareche JF, Furdin G. Modelling of exfoliated graphite. Prog Mater Sci 2005;50(1):93–179.
[9] Anderson SH, Chung DDL. Exfoliation of intercalated graphite. Carbon 1984;22(3):253–63.
[10] Chung DDL. Exfoliation of graphite. J Mater Sci 1987;22(12):4190–8.
[11] Inagaki M, Kang F, Toyoda M. Exfoliation of graphite via intercalation compounds. Chem Phys Carbon 2004;29:1–69.
[12] Chen P, Chung DDL. Viscoelastic behavior of the cell wall of exfoliated graphite. Carbon 2013;61:305–12.
[13] Ionov SG, Avdeev VV, Kuvshinnikov SV, Pavlova EP. Physical and chemical properties of flexible graphite foils. Mol Cryst Liquid Cryst Sci Technol A 2000;340:349–54.
[14] Chung DDL. Flexible graphite for gasketing, adsorption, electromagnetic interference shielding, vibration damping, electrochemical applications, and stress sensing. J Mater Eng Perf 2000;9(2):161–3.
[15] Luo X, Chung DDL. Electromagnetic interference shielding reaching 130 dB using flexible graphite. Carbon 1996;34(10):1293–4.
[16] Fu X, Chung DDL. Vibration damping admixtures for cement. Cem Concr Res 1996;26(1):69–75.
[17] Chung DDL. Improving cement-based materials by using silica fume. J Mater Sci 2002;37(4):673–82.
[18] Chen P, Chung DDL. Mechanical energy dissipation using cement-based materials with admixtures. ACI Mater J 2013;110(3):279–90.
[19] Chung DDL. Intercalate vaporization during the exfoliation of graphite intercalated with bromine. Carbon 1987;25(3):361–5.
[20] Xu Y, Chung DDL. Improving silica fume cement by using silane. Cem Concr Res 2000;30(8):1305–11.
[21] Xu Y, Chung DDL. Cement-based materials improved by surface treated admixtures. ACI Mater J 2000;97(3):333–42.

[22] Reynolds iii RA, Greinke RA. Influence of expansion volume of intercalated graphite on tensile properties of flexible graphite. Carbon 2001;39(3):479–81.

[23] Manoj NR, Barman S, Chandrasekhar L, Chakraborty BC, Ramesh R, Vishnubhatla RMR. Constrained-layer dampers for attenuation of structural vibration. Defence Sci J 2005;55(1):5–11.

[24] Han S, Chung DDL. Mechanical energy dissipation using carbon fiber polymer-matrix structural composites with filler incorporation. J Mater Sci 2012;47:2434–53.