Cement and Concrete Composites 77 (2017) 49–59

Contents lists available at ScienceDirect

Cement and Concrete Composites

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

Experiments and micromechanical modeling of electrical conductivity of carbon nanotube/cement composites with moisture

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ARTICLE INFO

Article history:
Received 7 November 2015
Received in revised form
20 September 2016
Accepted 7 December 2016
Available online 19 December 2016

Keywords:
Electrical conductivity
Cement paste
Multi-walled carbon nanotubes
Moisture
Micromechanical model

ABSTRACT

Carbon nanotube (CNT)/cement composites have been proposed as a multifunctional material for self-sensing and traffic monitoring due to their unique electric conductivity which changes with the application of mechanical load. However, material constituent and environmental factors may significantly affect the potential application of these materials. Therefore, it is necessary to understand an influence of material constituent such as porosity and dispersion of CNT and environmental factor such as moisture on the electrical conductivity of CNT/cement composite. This paper investigates the effect of moisture on the effective electrical conductivity of CNT/cement composites. To prepare the specimens, multi-walled carbon nanotubes (MWCNTs) are well dispersed in cement paste, which is then molded and cured into cubic test specimens. By drying the specimens from the fully saturated state to the fully dry state, the effective electrical conductivity is measured at different moisture contents. As the water in the specimen is replaced by air voids, the electrical conductivity significantly decreases. Different ratios of MWCNTs to cement have been used in this study. Micromechanical models have been used to predict the effective electrical conductivities. A comprehensive model is proposed to take into account the effects of individual material phases on the effective electrical conductivity of CNT/cement composites with moisture effect.

1. Introduction

Multifunctional cementitious-based composites using carbon nanotubes (CNTs) have attracted significant interest because of the improvement of their overall mechanical [1–4], electrical [5,6], and thermal properties [7,8]. Particularly, many researchers have conducted an electro-mechanical characterization of composites for sensing applications [9]. Azhari and Banthia [10] developed conductive cement-based composites using carbon fibers and carbon nanotubes, for application as a self-sensing material. Han et al. [11] investigated the piezoresistivity of multi-walled carbon nanotubes (MWCNTs)/cement composites as a function of the concentration of MWCNTs and the water-cement ratio for traffic monitoring applications.

The strain sensor using CNT dispersed composites is operated by a change in electrical resistance when it is subjected to mechanical loading such as compression or tension [12,13]. The sensor resistance depends on the electrical conductivity and geometry of the composites in sensor fabrication. Therefore, knowing the electrical conductivity of the composite is important for sensor design. In general, there are three main factors that affect the electrical conductivity of cementitious-based composites containing MWCNTs. First, cement hydrate, as the matrix material, plays a role on the effective electrical conductivity of the composite although its electrical conductivity is quite low. Second, the voids in the matrix are filled with a combination of moisture and air, the voids will modify the effective electrical conductivity, which is very sensitive to ambient relative humidity, as the conductivity of liquid phase is much higher than that of air or cement hydrates in the composites [14,15]. Third, MWCNTs also change the electrical conductivity of the composites due to their excellent electrical conductivity and the formation of a network of MWCNTs.

Since cementitious-based composites are typical heterogenous materials with a significant amount of micro-voids and the dispersion of MWCNTs in these materials is random, a micromechanics-based approach is a useful tool to predict the

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http://dx.doi.org/10.1016/j.cemconcomp.2016.12.003
0958-9465/

effective material properties of the composite. For example, Princigallo et al. [16] studied the effect of the aggregate on the electrical conductivity of high-performance concretes. They investigated the properties of the interfacial zones by analyzing the electrical conductivity using several modeling approaches such as hard core soft shell model, differential effective medium theory, and the Lu-Torquato model. Schwarz et al. [17] employed a parallel model to predict the effective electrical conductivity as a function of the properties of the pore solution, the porosity, and also a pore connectivity factor. Liu et al. [18] proposed an analytical model which is a combination of effective medium and percolation theory to predict the relative resistivity of cement paste and C-S-H. While some experiments have demonstrated the effect of moisture or MWCNTs in cementitious-based composites [19,20], it is still a challenging task to predict and model the effect of moisture and MWCNTs on the effective electrical conductivity of carbon nanotube/cement composites.

Mathematically, the effective electrical conductivity of a composite is a quantity exactly analogous to the effective dielectric permittivity, water permeability, and thermal conductivities, in a linear static state, so the modeling work can be conducted in the same fashion. Effective electrical properties of random composites have been widely studied by analytical, numerical, and experimental methods [21]. Maxwell-Garnett's model was one of the first to describe the effective permeability of composites containing randomly dispersed spherical particles [22,23]. Because this model considers neither higher multipole moments nor interactions between particles, it generally underestimates the effective electrical conductivity when the particle permeability is higher than the matrix permeability, and vice versa, especially for composites with high volume fraction of particles [24]. Bruggeman extended Maxwell-Garnett's model by an iterative procedure and provided good agreement with experimental results. However, the effect of the microstructure has not been directly considered [25]. Yin and his colleagues have attempted to investigate the effective conductivity for particulate composites with some idealized microstructures [26,27].

However, because CNT/cement composites exhibit such complex microstructures, which contain randomly dispersed and irregularly shaped voids that are filled by water or air and also curved MWCNTs, shown in Fig. 1, none of micromechanic-based models can surely predict their effective electrical conductivities. Similarly to our previous work on viscoelastic behavior for asphalt mastics [28,29], this paper will review existing micromechanics-based models, investigate the applicability of each model to the present composite through comparison with experiments, and thus establish an accurate formulation to predict the effective electrical properties of CNT/cement composites.

Three steps are considered to formulate the effective electrical conductivity of the composites based on the microstructure and size scales. In what follows, Section 2 will introduce the micromechanics-based models, which are generally developed for two-phase composites, and discuss the assumptions and applicability for each model. Section 3 will introduce an experimental procedure to measure the electrical conductivity of MWCNT/cement composites containing moisture. Section 4 will validate the formulation with experimental data, compare the models for the best performance, and thus establish a reliable model for the electrical conductivity of the CNT/cement composites. Some conclusive remarks will be provided in Section 5.

2. Micromechanics-based models for effective electrical conductivity of cement paste

The micromechanics-based model was developed to estimate the overall material properties of composites. Various models are used to predict the effective electrical conductivity of CNT/cement composites, which is a quantity exactly analogous to effective dielectric permittivity, magnetic permeability, and thermal conductivity, in a linear static state [30]. For a multiphase composite containing discrete elements embedded in a continuous matrix, electrical conduction through the solid may depend on the properties of the individual material phases and its microstructure. The effective electrical conductivity can be obtained from the average of the local field in each material phase.

Consider a two-phase composite containing dispersions in a continuous matrix. To evaluate the effective electrical conductivity, the average electric field **E** and average current density **I** can be calculated from the volume averages of the two material phases as

$$\langle E_i \rangle_D = \phi \langle E_i \rangle_\Omega + (1-\phi)\langle E_i \rangle_M \tag{1}$$

$$\langle I_i \rangle_D = \phi \langle I_i \rangle_\Omega + (1-\phi)\langle I_i \rangle_M \tag{2}$$

where the subscripts D, Ω, and M represent the composite, dispersed phase, and matrix phase, respectively; φ is the volume fraction of the dispersed phase; and each material phase is assumed to be isotropic satisfying

$$\langle I_i \rangle_\Omega = \sigma_\Omega \langle E_i \rangle_\Omega \text{ and } \langle I_i \rangle_M = \sigma_M \langle E_i \rangle_M \tag{3}$$

in which σ_D and σ_M are the electrical conductivities of the two phases, respectively. The effective electrical conductivity can be calculated as

$$\sigma_{eff} = \frac{|\langle I_i \rangle_D|}{|\langle E_i \rangle_D|} = \frac{\phi \langle I_i \rangle_\Omega + (1-\phi)\langle I_i \rangle_M}{\phi \langle I_i \rangle_\Omega / \sigma_\Omega + (1-\phi)\langle I_i \rangle_M / \sigma_M} \tag{4}$$

The parallel and series models provide the absolute upper and lower limits on the effective electrical conductivity of the composites. However, in general, the electrical conduction behavior of composites containing dispersed phases is far more complex than the above cases. Similarly to elastic modeling, in micromechanics to obtain the effective electric conductivity [27,28], a uniform electric current density can be applied on the boundary of a composite and the local electrical fields will be disturbed by the material inhomogeneities. If the average electrical current on the dispersed phase can be obtained, from the above relation between the averaged electric field and the applied loading, the effective conductivity can be derived. The calculation is typically based on the solution for one particle, which may have more than one surface layer, embedded in a continuous matrix [31].

As in simple cases, one can assume the electric field or electric current density in both material phases are the same, which can mimic a laminate composite with the plane direction oriented parallel or perpendicular to the electric current direction, so that one can obtain the parallel and series models, respectively, as follows

$$\sigma_{eff}^{parallel} = \phi \sigma_\Omega + (1-\phi)\sigma_M \tag{5}$$

$$\sigma_{eff}^{series} = \frac{\sigma_\Omega \sigma_M}{\phi \sigma_M + (1-\phi)\sigma_\Omega} \tag{6}$$

Consider a single spherical particle Ω embedded in a large continuous matrix phase M under a uniform electrical current density I^0 in the far field. Due to the mismatch between the particle and the matrix, the local electric current density in the neighborhood of the particle will not be uniform any more. However, the electric current density on the particle is still uniform as [30].