CARBON FIBER REINFORCED CEMENT AS A MIXED ELECTRONIC IONIC CONDUCTOR

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Abstract

Cement reinforced with short carbon fiber is attractive for its electrical properties. The electrical conductivity rendered by the fiber allows piezoresistivity-based sensing of strain. This composite material, even below the percolation threshold, is a mixed electronic ionic conductor, due to the carbon fiber providing holes and the cement providing ions. The electrical conduction behavior is characterized by comparing the behavior for the case in which the electrical contacts used for passing current are an electronic conductor and the case in which these contacts are an ionic conductor. Electronic conduction dominates the conductivity, even below the percolation threshold. The electronic conduction exhibits an activation energy of 0.4 eV, due to the electron transfer across the fiber-cement interface. The relative dielectric constant is increased from 21 to 54 (10 kHz) by the fiber addition, due to the surface functional groups on the ozone-treated carbon fiber. The ozone treatment of the fiber surface helps the ionic conduction, as shown by comparing results with and without the treatment. It also promotes the hydrophylicity of the fiber. This paper reviews the electrical behavior of carbon fiber reinforced cement.

Introduction

Cement reinforced with short carbon fiber has received considerable recent attention due to its piezoresistivity (phenomenon in which the electrical resistivity changes with the strain), which allows it to be a sensor of its own strain or stress (Chen and Chung, 1993, 1996; Chung, 2002a, 2002b; Wen and Chung, 2005, 2006a). This behavior makes the cement-based structural material multifunctional. Due to the importance of this application, there is a need to understand more fully the electrical behavior of carbon fiber reinforced cement. Therefore, this work is a review on the electrical behavior of carbon fiber reinforced cement.

Percolation

The electrical resistivity of carbon fiber reinforced cement decreases with increasing fiber volume fraction, such that the resistivity decreases by orders of magnitude at the percolation threshold (Chen and Chung, 1995; Reza et al., 2001; Wang et al., 2002; Chen et al., 2004; Chiarello and Zinno. 2005). The percolation threshold is between 0.5% and 1.0% for carbon fiber reinforced cement without aggregates (Chen and Chung, 1995). The severity of the piezoresistive effect is described by the gage factor, which is defined as the fractional change in resistance per unit strain. The gage factor is increased only slightly when the percolation threshold is exceeded (Chen and Chung, 1996; Wen and Chung, 2005), so, for maintaining low cost, high workability and low air void content (which means high compressive strength), a fiber volume fraction below the percolation threshold is used. Therefore, this work focuses on the electrical behavior of carbon fiber reinforced cement below the percolation threshold.

Fiber dispersion

The electrical conductivity of carbon fiber reinforced cement below the percolation threshold increases with increasing degree of fiber dispersion (Chung, 2005). The degree of dispersion can be improved by the use of admixtures and fiber surface treatment. Silica fume, which is in the form of fine particles of size around 0.1 μm, is a particularly effective admixture for improving the degree of fiber dispersion, due to the fine particles helping to separate the fibers during mixing. The degree of fiber dispersion can also be improved by the use of fiber surface treatments (e.g., ozone treatment, which provides oxygen-containing functional groups on the surface of the fiber (Fu et al., 1998) that increase the degree of hydrophilicity of the carbon fiber. As carbon is hydrophobic in nature and water is in the mix, improved hydrophilicity is helpful for increasing the wettability of the fiber by water (Fu et al., 1998).

The interface between fiber and the cement matrix is also affected by admixtures and fiber surface treatment (Fu and Chung, 1995a, 1997). This interface affects the quality of the electrical contact between the fiber and the cement matrix, thereby affecting the electrical conduction. Polymeric admixtures such as latex (Zayat and Bavasi, 1996; Cao and Chung, 2001), as used for increasing the toughness and decreasing the water permeability, line the interface, thereby increasing the contact electrical resistivity between fiber and matrix. Ozone treatment of the carbon fiber results in functional groups on the surface of the fiber, thereby also increasing the contact resistivity (Fu et al., 1998).

Electronic vs. ionic conduction

In this paper, the term "electronic conduction" refers to conduction by electrons and/or holes. Cement itself is well-known for its ionic conductivity, which is particularly high when the cement contains a substantial amount of free water. However, carbon fiber is an electronic conductor (with the charge carriers being electrons and/or holes (Kelly, 1981; Sun et al., 1998) rather than an ionic conductor. The dominance of ionic conduction in carbon fiber reinforced cement tends to be assumed by cement scientists, because cement, which is mainly an ionic conductor, is the matrix. However, the thermoelectric behavior of carbon fiber reinforced cement indicates holes as the main carrier (Sun et al., 1998; Guerrero et al., 2002; Cao and Chung, 2005). Furthermore, the p-type character increases upon using bromine intercalated (p-type) carbon fiber in the cement (Wen and Chung, 2000).

Whether carbon fiber is present or not in cement, a decrease in the free water content (for example, by drying) increases the electrical resistivity. However, it has negligible effect on the thermoelectric power (Cao and Chung, 2005). This means that the carrier that moves in response to a temperature gradient is electrons/holes rather than ions, though the movement of ions in response to a voltage gradient contributes to the electrical conductivity. Thus, the movement of electrons/holes in response to a voltage gradient should not be neglected.

The method of electrical conductivity measurement conventionally used in the cement field involves the use of current contacts (i.e., electrical contacts for the passing of current) in the form of an ionic conductor, e.g., water or an aqueous solution, which is applied with a liquid absorbing material such as a sponge or paper towel (Peled et al. 2001). Embedded in the absorbing material is a metal, such as stainless steel, which allows connection of the electrical contact to the external circuit. Electrical contacts in the form of an ionic conductor do not allow electrons to flow from the metal wire associated with the external electrical circuit to the specimen. As ions cannot flow in a metal, ions cannot flow all the way around the circuit. Hence, ions flow in the specimen while only electrons flow in the external circuit.

The method of electrical conductivity measurement conventionally used in electrical engineering involves the use of all electrical contacts (both current and voltage contacts) in the form of an electronic conductor (not an ionic conductor), such as a metal or a conductive paste. This configuration provides an electron circuit, so that electrons can go all the way around the circuit, which includes the specimen and the external metal wire. Ions can still move inside the specimen in response to the voltage gradient, but the ionic movement is more sluggish and more limited than the electron movement.

Because the two methods mentioned above give information on different aspects of electrical conduction, comparison of results obtained by the two methods is valuable for distinguishing between electronic conduction and ionic conduction. Such a comparison is an avenue (known as the blocking electrode method in the field of mixed ionic electronic conductors (Porat et al., 1997)) for revealing the mechanism of conduction. Carbon fiber reinforced cement, even below the percolation threshold, is a mixed electronic ionic conductor, due to the carbon fiber providing holes and the cement providing ions (Wen and Chung, 2006b).

The electronic conduction is much more significant than ionic conduction in the dry state for carbon fiber reinforced cement below the percolation threshold (Wen and Chung, 2006b). This implies that electronic conduction is even more significant above the percolation threshold. This is consistent with the report that the relative dielectric constant is decreased as the carbon fiber volume fraction in cement is increased from a value below the percolation threshold to one above the percolation threshold (Wen and Chung, 2001a). That electronic conduction dominates above the percolation threshold is because the electrical continuity provided by the fibers above the threshold makes the fibers dominate the conduction and the fibers are an electronic conductor. Therefore, the use of electrical contacts in the form of electronic conductors in practical applications (e.g., strain sensing) that utilize the electrical conductivity of carbon fiber reinforced cement is valid, whether the fiber volume fraction is below or above the percolation threshold.

Effect of carbon fiber

The carbon fiber affects both the electronic conduction and the ionic conduction (Wen and Chung, 2006b). That it affects the ionic conduction is consistent with the report that carbon fiber addition to cement increases the relative dielectric constant (from 21 to 54 at 10 kHz, due to the surface functional groups on the ozone-treated carbon fiber) (Wen and Chung, 2001a) and hastens electric depolarization (Cao and Chung, 2004). This effect of the fibers is probably because of the functional groups on the fiber surface (Fu et al., 1998). The electric dipoles associated with the functional groups may interact with the ions that contribute to ionic conduction. In contrast, the addition of steel fiber to cement decreases the relative dielectric constant (Wen and Chung, 2001a). Although carbon fiber and steel fiber are both electronic conductors, their surface chemistry is very different.

Effects of fiber surface treatment and admixtures

Ozone treatment of carbon fiber promotes the hydrophylicity of the fiber, thereby improving the fiber-cement interface and the degree of fiber dispersion (Fu et al., 1998). The ratio of wet ionic conductivity to dry ionic conductivity is much higher for treated fiber than untreated fiber, whether silica fume or latex is present (Wen and Chung, 2006b). This means that the fiber treatment helps ionic conduction, probably because of the interaction of the moving ions with the electric dipoles associated with the surface functional groups imparted by the ozone treatment.

Latex as an admixture helps provide a relatively high ionic conductivity; silica fume as an admixture helps provide a relatively high electronic conductivity (Wen and Chung, 2006b). When silica fume is present with the fiber, the fractional electronic contribution in the dry state is 0.99 (Wen and Chung, 2006b). When latex is present with the fiber, the corresponding value is 0.72-0.78 (Wen and Chung, 2006b). That silica fume enhances the fractional electronic conduction contribution is attributed to the good fiber dispersion, which is known to be helped by the presence of silica fume (Chung, 2005). It is also known that latex results in poorer fiber dispersion than silica fume (Chen et al., 1997). The good fiber dispersion rendered by silica fume makes the fiber more influential in affecting the conductivity, thereby causing the electronic contribution to be more significant to the overall conductivity.

The ratio of wet ionic conductivity to dry ionic conductivity is higher for latex than silica fume, whether the fiber is treated or not (Wen and Chung, 2006b). This effect of latex is consistent with the report that latex addition (20% by mass of cement, as in this work) to cement increases the relative dielectric constant (Wen and Chung, 2001a). In contrast, silica fume addition (15% by mass of cement, as in this work) to cement decreases the relative dielectric constant (Wen and Chung, 2001a). The difference between latex and silica fume is particularly large when the fiber is treated (Wen and Chung, 2006b). This is consistent with the notion that the fiber treatment helps ionic conduction.

Effect of moisture

The wet ionic conductivity is large compared to the dry ionic conductivity (Wen and Chung, 2006b). This is consistent with the report that the AC conductivity of cement (without fiber) decreases with the hydration time (Dotelli and Mari, 2001). The ratio of the wet ionic conductivity to the dry ionic conductivity is higher when latex rather than silica fume is used (Wen and Chung, 2006b). The wet ionic conductivity is much higher than the dry overall conductivity when latex is present, but is lower than or comparable to the dry overall conductivity when silica fume is present; the wet ionic conductivity is lower than the dry overall conductivity when the fiber is not treated and silica fume is present.

In the dry state (the state of practical importance attained by room temperature drying), electronic conduction is more significant than ionic conduction. In the wet state (water saturated state), ionic conduction dominates (Wen and Chung, 2006b). That electronic conduction is much more significant than ionic conduction in the dry state is consistent with the report that holes dominate the Seebeck effect of carbon fiber reinforced cement (dry state) (Sun et al., 1998; Guerrero et al., 2002). Moreover, it is consistent with the fact that the DC electrical resistivity increases with increasing curing age less significantly for carbon fiber reinforced cement (dry state) than for plain cement (dry state) (Fu and Chung, 1995b). It is also consistent with the report that electric polarization is small in carbon fiber reinforced cement (dry state) compared to plain cement (dry state) (Wen and Chung, 2001b).

Effect of temperature

The electrical resistivity of carbon fiber reinforced cement (as measured using electrical contacts in the form of an electronic conductor) diminishes with increasing temperature (Wen and Chung, 1999; McCarter et al., 2007). The trend is the same whether the specimen is dry or wet. The effect is much more pronounced when the cement contains silica fume rather than latex (Wen and Chung, 1999). This trend is due to the energy needed for electrons to jump across the fiber-cement interface. The activation energy is 0.4 eV when the cement contains silica fume (Wen and Chung, 1999), but is less when silica fume is absent (McCarter et al., 2007). The small effect of temperature in case of latex is because of the presence of latex at the fiber-cement interface and the electrically insulating character of latex.

Effect of frequency

The electrical resistivity of carbon fiber reinforced cement (wet state, without silica fume, as measured using electrical contacts in the form of an electronic conductor) diminishes with increasing frequency from 1 to 100 kHz, in contrast to the absence of frequency effect on the resistivity for plain cement that has no fiber (McCarter et al., 2007). The activation energy increases with increasing frequency in this range, in contrast to the absence of frequency effect on the activation energy for plain cement that has no fiber (McCarter et al., 2007). These frequency effects of carbon fiber reinforced cement are probably due to the effect of frequency on the interaction of the carbon fiber surface functional groups with the ions.

Conclusion

Carbon fiber reinforced cement is a mixed electronic ionic conductor, even below the percolation threshold. The relative importance of electronic conduction and ionic conduction depends on the admixture, the fiber surface treatment and the moisture content (wet or dry). Silica fume, which helps the fiber dispersion, promotes electronic conduction and enables a substantial decrease of the resistivity with increasing temperature. Latex as an admixture promotes ionic conduction. Fiber surface treatment using ozone promotes ionic conduction. Moisture also promotes ionic conduction.

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