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Electrical conductivity characterization and variation of carbon fiber reinforced cement composite

XIUFENG WANG*
Department of Ceramic Engineering, Northwest Institute of Light Industry, Xianyang, 712081, People's Republic of China
YONGLAN WANG, ZHIHAO JIN
School of Materials Science and Engineering, Xi'an Jiaotong University, Xi'an 710049, People's Republic of China

Electrical conductivity of carbon fiber reinforced cement composite (CFRCC) was measured. The conductivity of specimens increased by several orders of magnitude while the volume fraction of fibers reached a higher value than the critic concentration. The microstructure associated with electrical percolation phenomena was observed. The mechanism of conduction was interpreted as being due to fibers touching each other. The changes of electrical conductivity under three different loading levels were investigated. The percolation threshold value decreased with loading. The relative changes of electrical conductivity both under single loading and cyclic loading could sense the stress in non-elastic, elastic and fracture region with sensitive response. The influences of fiber volume fraction and fiber length on the sensitivity of electrical conductivity measurement were discussed. The results provide some new information for the fabrication of conductive and intrinsically smart carbon fiber reinforced cement composites.

1. Introduction
Conventional cement based-materials, such as cement, mortar and concrete, are poor electrical conductors under dry conditions [1, 2]. To modify the electrical conductivity by adding conductive particles, e.g. carbon fibers, in the materials will enlarge their industrial application in electricity, electronics, military etc., for example, in electromagnetic interface shielding, electrostatic discharge, self-regulated heater, conductive floor panels and rust protection of reinforcing steel in concrete structures [3–6]. Besides these, carbon fiber reinforced cement composites (CFRCC) have been considered as intrinsically stress/strain sensor for damage assessment [7, 8]. The use of CFRCC in non-structural or function-structural applications indicate that CFRCC will be subject to electrical conductivity convenient measurement, conductivity characterization with different fiber length and volume fraction, and variation of conductivity under loading.

As the filler concentration of fiber varies, the conductivity exhibits a well-known percolation phenomenon [6]. With different fiber length, the percolation threshold will be changed. Below or above the critic fiber content, the materials will perform sensitivity of conductivity to the loading level. This paper presents some experimental results of the electrical conductivity characterization and variation of CFRCC and discusses the relationship between electrical conductivity and microstructure.

2. Experimental result
The experiments are concerned with two series of carbon fiber reinforced mortar with varying fiber volume fraction and fiber length. The raw materials include 525R Portland cement (Xi'an Yanta Cement Factory), standard sand (fine aggregate, Pingtan, Fujian Province), carbon fiber and methycellulose (Great Britain). Carbon fiber is high strength polyacrylonitrile (PAN) based carbon fiber made in Jilin Carbon Factory. The properties are tensile strength 2928 MPa, modulus of elasticity 205 GPa, diameter 7.2 μm, specific gravity 1.76 $g \cdot cm^{-3}$, and volume resistivity $3.0 \times 10^{-3} \Omega \cdot cm$. Continuous filaments of carbon fibers were cut to different nominal length from 1 mm to 10 mm.

The CFRCC circular plates were fabricated by a hydrothermal hot-pressing method [9]. A conventional mixing procedure was adopted. First, short chopped carbon fibers were added to 0.4% methycellulose fiber dispersing solution and stirred about 2 min until homogeneously dispersed. Then cement and sand were slowly added on sequence by continuous stirring about 3 min. The cement/sand ratio was 2 and water/cement

* Author to whom all correspondence should be addressed.

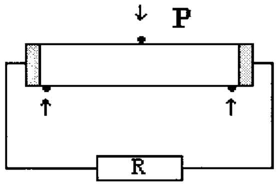

Figure 1 Schematic show of test set up.

ratio was 0.3. After that, the mortar was transferred into the hydrothermal hot-pressing autoclave for hydrothermal processing under 180 °C, 1 h. After a schedule run (6–8 h), the plate was taken out and cured in a curing container at 25 °C, RH 100% conditions for 28 days prior to testing.

The rectangular parallelepiped specimen was used for measurement with the size of 6 mm width × 8 mm thickness × 36 mm long by cutting the plate with a diamond saw. The ends of specimen were carefully polished and coated with silver conductive paste then wrapped with copper foil.

The experimental setup is schematically shown in Fig. 1. The electrical conductivity of the specimen was calculated using the following equation

$$\sigma = \frac{1}{\rho} = \frac{L}{S} \cdot \frac{1}{R} \tag{1}$$

where σ and ρ are the electrical conductivity and resistivity, L and S are the length and cross-sectional area of the specimen respectively, and R is the resistance measured.

The measurement of electrical conductivity under loading conditions was done by a three point bending method with a span 30 mm and 0.5 mm/min loading speed by using INSTRON-1195 electronic testing machine. In a test, the load vs. load-displacement and load vs. electrical resistance plots were recorded.

3. Results and discussion

3.1. Effect of fiber volume fraction on conductivity

The electrical conductivity values versus fiber volume fraction V_f with different fiber length are plotted in Fig. 2. It can be seen that the electrical conductivity of specimen increased by several orders magnitude at a specific volume fraction V_{fc} for a given carbon fiber length. This means that carbon fibers will form

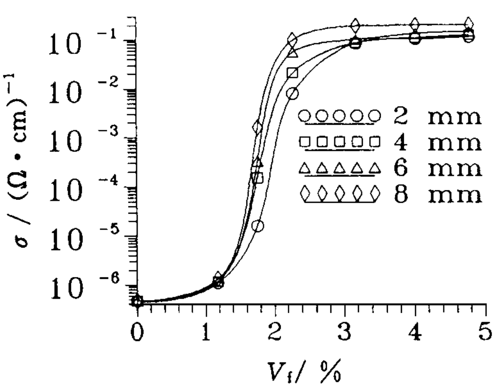

Figure 2 Electrical conductivity vs. fiber volume fraction with different fiber length.

a conducting network when $V_f > V_{fc}$. While there is a comparable difference between V_f and V_{fc}, the effect of fiber volume fraction on the conductivity of the composite is small. Therefore, the conductivity versus fiber volume fraction curves has a typical feature of percolation phenomena, which can be analyzed by the percolation particles.

In conductive fiber reinforced cement-based composites, the properties and microstructure of non-conductive components do not have much influence on composite conductivity and fiber content is the most important factor determining the conductivity of the system because of the magic difference of electrical conductivity between matrix and fiber [6].

Many models have been proposed to describe the conductivity of composite. A commonly used one is expressed as the following form [10]:

$$\sigma \propto (V - V_c)^t \tag{2}$$

Where σ is the conductivity of composites, V and V_c are the volume fraction of conductive phase and the percolation threshold respectively, t is a constant dependent on the structure and properties of the material, V_c and t may be calculated by fitting equation (2) with least-square method.

The microstructures of the materials around the percolation threshold were observed by HITACHI-2700 scanning electronic microscope (SEM). The micrograph of the fracture surface is shown in Fig. 3. It can be seen that carbon fibers are randomly distributed in the matrix when $V_f < V_{fc}$. The content was so insufficient that only limited scale clusters were formed and there was no percolation network (Fig. 3A). When $V_f < V_{fc}$, fibers connected and the network was formed (Fig. 3B). The fracture surfaces corroded 10 days in 20% phosphorus acid solution clearly show the state of fiber connection, see Fig. 3C and D.

3.2. Effect of fiber length on electrical conductivity

The effect of fiber length on electrical conductivity has been shown in Fig. 2. We found in the experiment that the electrical conduction network could not formed when a definite fiber volume fraction did not reached, even longer fibers were used. The fiber length has a negative relationship with the percolation threshold. As a result, the electrical conductivity is strongly dependent on fibers filler concentration whilst fiber length is at second position for influencing the conductivity.

Under standard percolation condition, i.e. the two mixing phases are assumed equal spheres; the percolation threshold is 0.16, which is called Scher-Zallen invariability. For non-sphere particles, such as fiber, cylinder or plate, the percolation threshold calculation should consider the excluded volume effect [11]. At this situation, V_{fc} can be calculated from the equation below

$$V_{fc} = 1 - \exp\left(-B_c \frac{V}{\langle V_{ex} \rangle}\right) \tag{3}$$

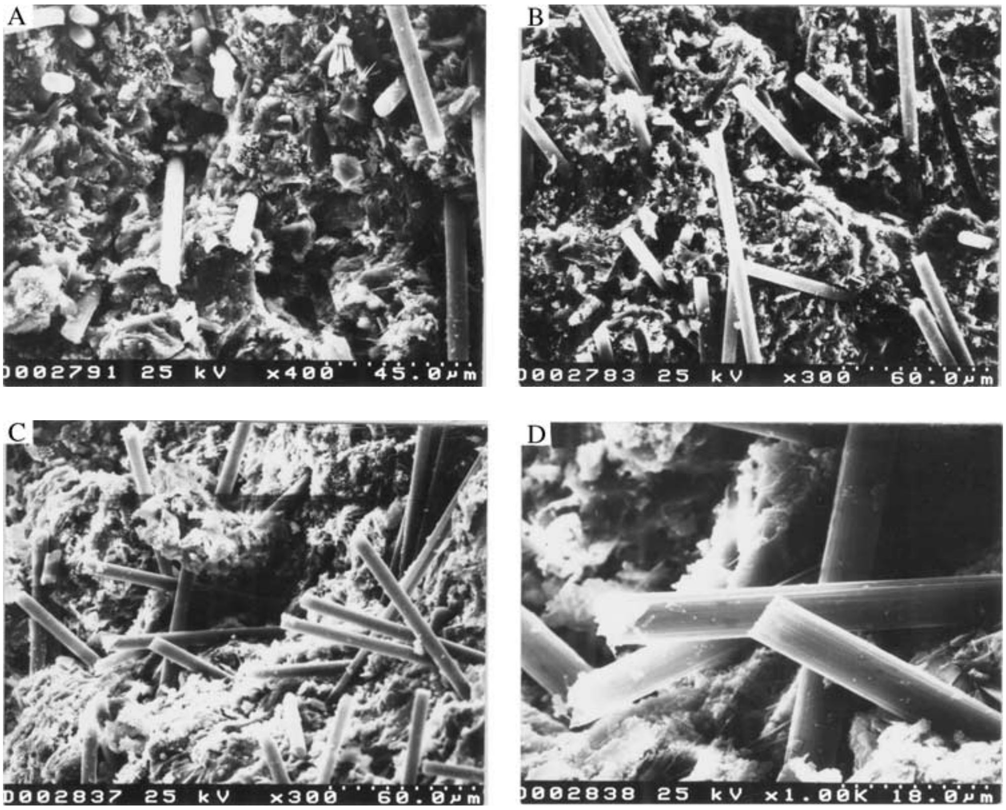

Figure 3 SEM photo micrographs illustrating the connection of fibers (A) $V_f = 1.16\%$, (B) $V_f = 2.21\%$, (C) $= 2.21\%$, corroded 10 days in 20% H_3PO_4 solution, (D) magnification micrograph of C.

where B_c is a constant, V and $\langle V_{ex}\rangle$ are the volume of one particle and the average excluded volume.

In our experiment, short chopped carbon fibers may be considered as very large aspect ratio sticks randomly array in the metrix. So it is a correlation percolation problem, the volume of a fiber is $V = \pi r^2 l$ and the average excluded is $V_{\langle ex\rangle} = \pi l^2 r$. We get $V_{fc} = B_c \frac{r}{l}$, $B_c = 1.4$ [11]. For large aspect ratio sticks, Equation 3 is simplified as

$$V_{fc} = 1.4\frac{r}{l} \quad (4)$$

We may conclude that the percolation threshold is depended on fiber length and diameter, and V_{fc} will lineally decrease with increasing fiber aspect ratio.

The results of V_{fc} with different fiber length were fitted and plotted in Fig. 4. It seems not to be in agreement with the theoretical prediction of Equation 4 and values are about 10 times greater than the theoretical values. The result in agreement with previous finding in such materials [6], is thought to be: (1) the reduction of fiber length during processing, more reduction ratio founded in longer nominal fiber length; (2) the length distribution of carbon fibers in matrix; (3) imperfect random distribution of the fibers; and (4) the interface effect between fiber and matrix.

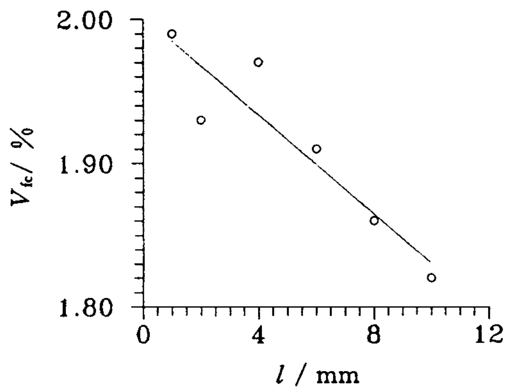

Figure 4 Percolation threshold vs. fiber length, $L = 6$ mm, 2.21% (V_f).

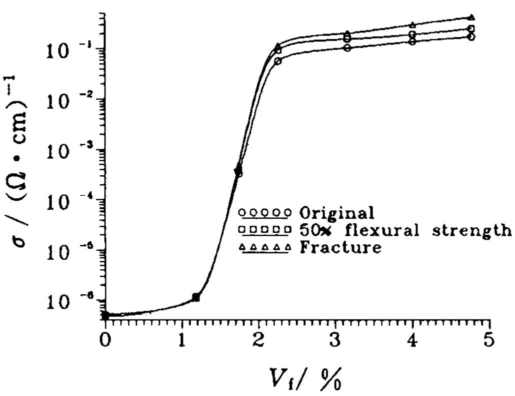

Figure 5 Electrical conductivity vs. fiber fraction under loading.

3.3. Effect of load on conductivity

Fig. 5 shows the relations of electrical conductivity vs. Fiber volume fraction under three loading conditions: unloading (original), 50% ultimate flexural strength, and ultimate flexural strength. Under loading, electrical percolation network still exits until fracture. Electrical conductivity gradually increased with flexural load. The increment in longer fiber specimens was relative lower. The electrical percolation threshold values of nominal

6 mm fiber specimens under different loading level were fitted to be: unloading, $V_{fc} = 1.91$; 50% ultimate flexural strength, $V_{fc} = 1.83$, and ultimate flexural strength $V_{fc} = 1.76$. Therefore, the electrical percolation threshold value is sensitive to stress.

The V_{fc} value is very important for us to determine the minimal fiber addition both in conductive cement-based composite and in smart materials structure. When percolation network forms, the composite is conductive and the relative change of electrical conductivity is comparatively easy to be measured because of high conductivity value. However, we should note that the fiber volume fraction should be limited in a reasonable level higher than V_{fc} for the functional and economical reason. The percolation threshold value may be considered as a parameter for functional structure component design even we still don't know the exact relation between the minimal fiber content $V_{f\min}$ associate with the rule of mixture and V_{fc}.

3.4. Relative changes of electrical conductivity under loading

In order to account the effect of load, we assume that the contact resistance is negligible, so the overall macroscopic resistivity is dominated by conduction through the fibers. As showed in Fig. 3, the conductivity is dependent on the network formed by conductive carbon fibers. The relation of load (P) and electrical conductivity (σ) versus crossbeam displacement (δ) under once loading is schematically shown in Fig. 6A. Under loading, there exited a complex stress field accompany fiber pullout and fracture, the electrical conductivity smoothly increased as load increasing, because some fibers on the network were pressed tightly. The electrical conductivity reached to the highest point at ultimate flexural strength then sharply turned down. As a result, the change of electrical conductivity versus cross beam displacement presents the load versus crossbeam displacement of the specimen Fig. 6C and E. By proper

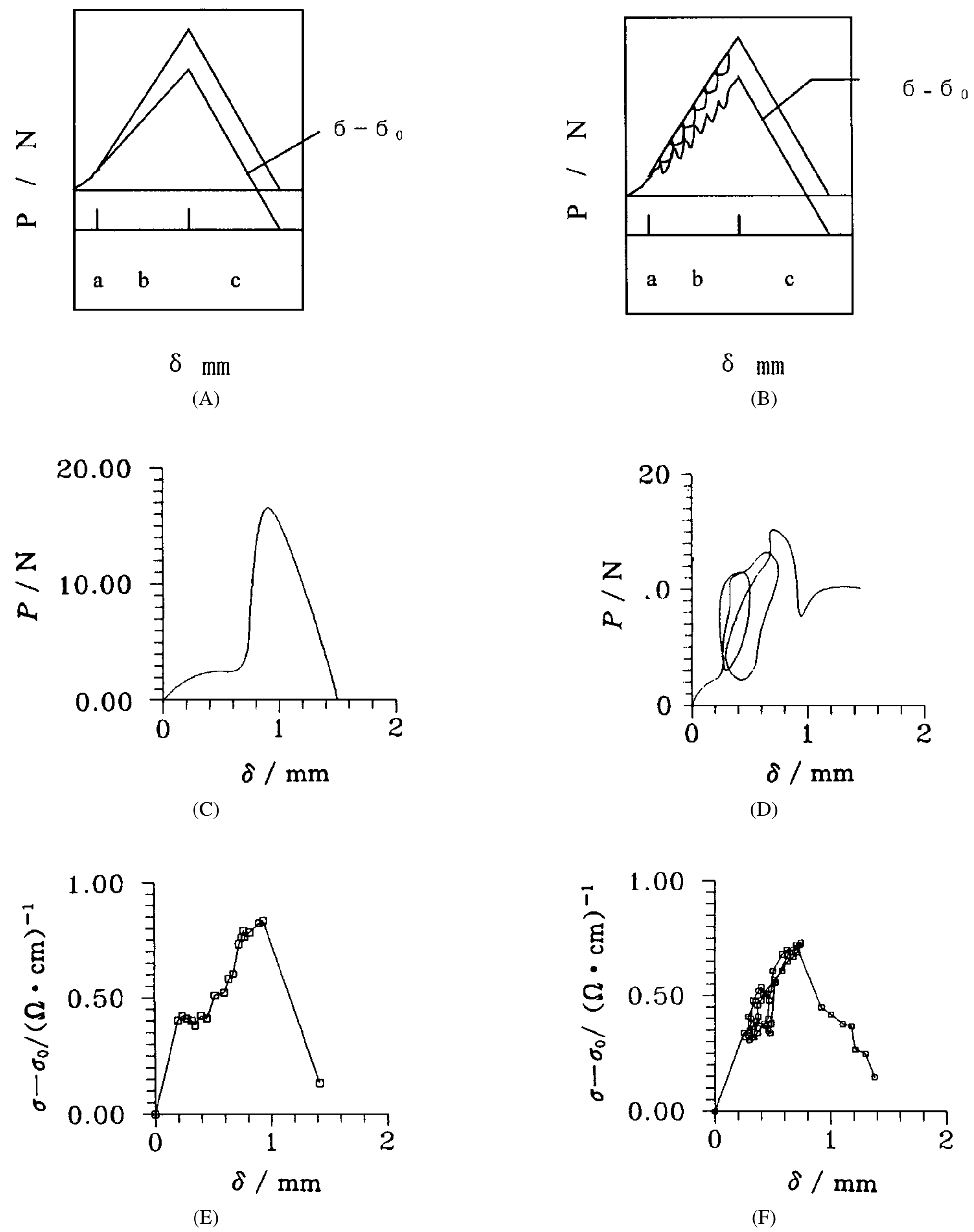

Figure 6 Load-relative changing of electrical conductivity-crossbeam displacement curves in three point bending.

controlling the content and length of fiber, carbon fiber reinforced cement composite may be a kind of intrinsically smart material as a stress/strain sensor using in non-elastic, elastic and fracture measurement.

The change of electrical conductivity under cyclic loading in elastic region may be considered as repeats of single loading. The reverse drop in conductivity was dependent on the stress dropping level. Nevertheless, there was a permanent damage during cyclic loading, which could be represented by the change of electrical conductivity (Fig. 6B, D and F).

3.5. Effect of fiber content and fiber length on the relative changes of electrical conductivity

Fig. 7 is a plot of relative changes of electrical conductivity between unloading and ultimate flexural strength. When $V_f < V_{fc}$, the conductivity was very low and the relative changes of conductivity was small. When $V_f > V_{fc}$, the change scope increased obviously, which means that the sensitivity increased. However, the relative change of electrical conductivity started nearly liner decrease when more fibers were added. The relative change of electrical conductivity against volume fraction curve exhibits a maxim value shape. Therefore, a proper volume fraction accessed V_{fc} should be chosen for a sensitive measuring.

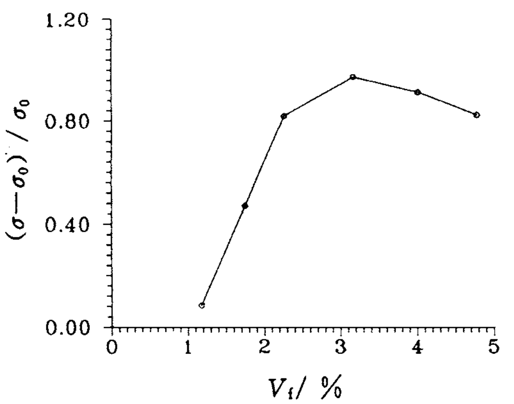

Figure 7 Relative changing of electrical conductivity with fiber volume fraction under loading.

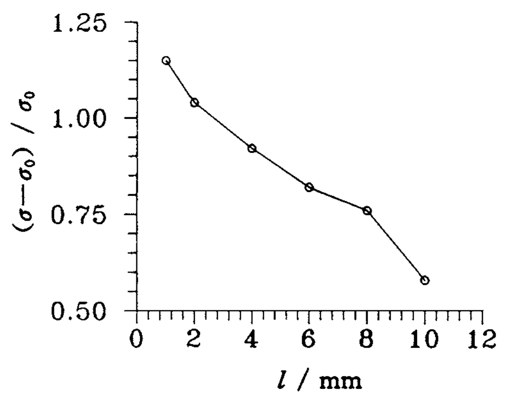

Figure 8 Relative changing of electrical conductivity with fiber length under loading.

Fig. 8 shows the effect of fiber length on the sensitivity. The fiber length had a negative linear relation with relative change of electrical conductivity when the percolation threshold was accessed. For a sensitive measuring shorter fiber is better than the longer ones. Nevertheless, shorter fiber will lead a higher V_{fc} value thus need a higher fiber addition.

4. Conclusions

This conclusion underlines the importance of fiber volume fraction and length on electrical conductive and smart purpose of carbon fiber reinforced cement composites. In CFRCC exits percolation phenomena and the percolation threshold is an important parameter in design of conductive and intrinsically smart cement-based composites. The unequal increment of electrical conductivity leads the percolation threshold have a tendency of decrease under loading since the fiber connection states differ from each other for different fiber volume fraction specimens. The magic increment of electrical conductivity under loading may be used to indicate the bonding stress increment of a specimen with fiber volume fraction just lower the percolation threshold.

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