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Conductivity of carbon fiber reinforced cement-based composites

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Abstract

The conductive behavior of carbon fiber cement-based composites is presented. The influence of carbon fiber volume, size, cement-based matrix, relative humidity and curing age on the characteristic of system were studied. The relationship between conductivity and volume fraction of carbon fiber indicated that the statistical percolation theory is suitable and applicable for the change rule of conductivity of system with the volume of carbon fiber. Based on the classic percolation theory, the percolation threshold of carbon fiber cement-based composites was determined as $\phi = \phi_{c2}$ and the conductive mechanism changes from electron tunneling conduction to ohmic contacting conduction. The studies have offered basic theory for smart cement-based composites.

Keywords: Carbon fiber; Cement-based composites; Percolation theory; Conductive properties

1. Introduction

Concrete, consisting primarily of Portland cement, fine and coarse aggregate, has been used as a primary building material for many years owing to its excellent engineering properties and durability. Normal concrete, however, is a poor electrical conductor, especially under dry conditions. The poor electrical conductivity limits its application as a functional material which may be required of in modern buildings, for example electromagnetic interference shielding, electrostatic discharge and others [1–3]. Therefore, the conductive behaviour of cement-based composites is now receiving considerable attention.

Normally, in order to produce conductive concrete, conductive phases, either conductive particles or conductive fibers, are introduced into the cement matrix. Concrete containing conductive fibers have superior flexural strength and toughness due to the effect of fiber reinforcement [4–6]. As an example, concrete containing 1% carbon fiber in volume shows a two-fold improvement in tensile and flexural strength, as well as a 30-fold increase in specific fracture energy over the unreinforced matrix. Although efforts have been made at investigating the mechanical properties of carbon fiber reinforced concrete, there is insufficient and conflicting information regarding its electrical conductivity. A carbon fiber reinforced cement-based composites is a complex multiphase system, and many factors influence the electrical conductivity of the system; for example, the microstructure of the matrix, carbon fiber volume fraction, and relative humidity of the specimen. In this paper, some scientific principles for the conductivity of such a system are reported. Theses include the effect of content and length of carbon fiber, water/cement ratio and sand/cement ratio on the electrical conductivity of cement-based composite systems. Tests are also conducted to determine the effect of relative humidity and specimen age on the electrical properties of CFRC (carbon fiber reinforced cement-based composite). Based on the classic percolation theory, how to determine the percolation threshold of carbon fiber cement-based composite are analyzed and discussed.

2. Experimental details

2.1. Materials and specimens

The carbon fibers were isotropic pitch-based and unsized. The fiber properties are shown in Table 1 and the length is variable according to the experiment requirement. Type III Portland cement was used throughout.

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Table 1
Properties of carbon fiber

Diameter (μm)	Density (g/cm^3)	Tensile strength (GPa)	Young's modulus (GPa)	Elongation at break (%)	Carbon content (w_c%)	Electrical resistivity (Ωcm)
7 ± 0.2	1.78	>3.0	220–240	1.25–1.60	>95	10^{-2}–10^{-3}

The silica fume (Elkem Materials) was used in the amount of 15% by mass of cement. The sand used met ISO standard. Water/cement (w/c) ratios were 0.25, 0.35, 0.45 and 0.50 (by mass). Sand/cement (s/c) ratios were 0, 1.0 and 2.0 (by mass).

The mortar mixtures were prepared in a laboratory mortar mixer. A Hobart mixer with a flat beater was used for mixing. The mixture, sand cement, water and carbon fibers were mixed in the mixer for 5 min. Rectangular specimens, 40 mm × 40 mm × 160 mm were cast in plexiglass molds. Two copper electrodes, 40 mm × 45 mm × 0.2 mm, were embedded in the fresh mix (see Fig. 1). After 24 h, the specimens were removed from the molds and transferred to a moist-curing room.

2.2. Electrical conductivity measurement

Generally, there are two basic types of electrical conduction in moist specimens: electronic and electrolytic [7]. The former is through the motion of free electrons in the conductive phases, e.g. carbon fibers, and the latter is through the motion of ions in the pore solution. In this investigation, the principal contribution to the electrical conduction is expected to be electronic. The electrical resistivity measurement, therefore, requires the elimination of the effect of electrolytic conduction.

In order to avoid the problems of polarization, alternating currents are often used for determining the resistivity of electrolytes and hence of cements and concretes. It has been suggested that the polarization effects during the passage of an alternating current are not eliminated but rather manifested in a different form. The polarization is in the form of introducing a capacitor in series or in parallel with the resistance. In any case, for a alternating current, there exists:

$$Z = \frac{V}{A} \tag{1}$$

where, Z is the system impedance in Ohms, V is the measured voltage, and A is the measured current. The impedance, Z, may be related in to the resistance, R, and the capacitance, C, in a parallel C–R arrangement as follows:

$$Z = \frac{R}{\sqrt{(1 + w^2C^2R^2)}} \tag{2}$$

where, $w = 2\pi f$, f being the applied frequency in Hertz (Hz); C = capacitance in farads.

As the frequency of the applied current is increased, the effect of the capacitance is reduced. Thus at high frequencies, Z approaches R. Typical patterns for a plain mortar specimen and CFRC specimens containing 0.2% and 0.6% by volume of fibers are shown in Fig. 2. All the resistance values were normalized with respect to their initial values, that is, the reading at 0.01 Hz. It appears that the resistance is approaching a constant value at a frequency higher than 100 kHz. So, a frequency of 100 kHz was adopted in this paper, where the calculated impedance was assumed equal to the resistance of system.

For the reason cited above, AC measurements were deemed appropriate for the present investigation. In this paper, AC measurement were performed by a potentiostat/galvanostat M273A connected with lock-in

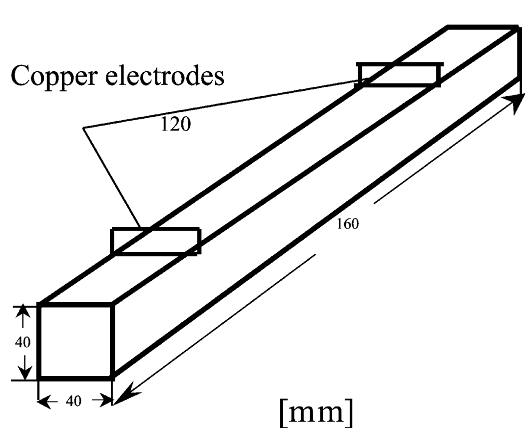

Fig. 1. Specimen for resistivity measurements.

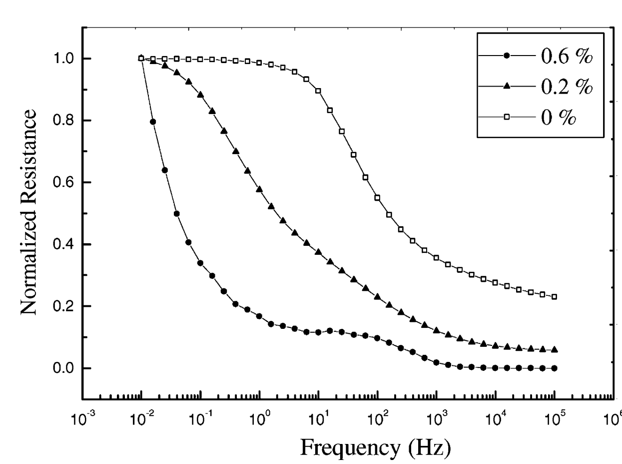

Fig. 2. Change in resistance with increasing frequency of AC test signal.

amplifier M5210 manufactured by EG&G PARC (Princeton Applied Research Co., USA). Measurement and data processing were supported by software M398 afforded by the same manufacturer. Amplitude of the sinusoidal voltage was chosen to be 10 mV. The technique of fast Fourier transform was applied in the frequency range 0.01–100 kHz.

According to the definition of electrical conductivity of a specimen, σ can be calculated using the following equation:

$$\sigma = \frac{1}{\rho} = \frac{L}{S}\frac{1}{R} \quad (3)$$

where σ and ρ are the electrical conductivity and resistivity, respectively; R is the resistance measured; L, S are the length and cross-sectional area of the specimen (see Fig. 1).

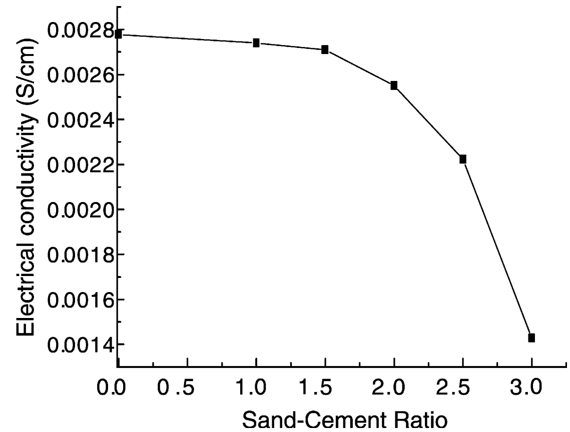

Fig. 4. Effect of sand–cement ratio on electrical conductivity of the system, $w/c = 0.45$, and carbon fiber content is 0.40%.

3. Experimental results

3.1. Effect of fiber volume content

The conductivity values versus volumetric fraction of carbon fiber for systems with different water/cement or sand/cement ratios at 28 day hydration are plotted in Fig. 3. It can be seen that the electrical conductivity values of the composites increase with increasing carbon fiber volume fraction. During the process of electrical conductivity increasing, there exists a narrow zone, where the conductivity increases with fiber content increasing sharply. Here, the narrow zone was defined as percolation transition zone ϕ_{c1}–ϕ_{c2} (ϕ_{c1}, the least fiber content for entering the percolation transition zone; ϕ_{c2}, the largest fiber content of percolation transition zone). However, the conductivity increases marginally with increasing content of fiber as $\phi < \phi_{c1}$ or $\phi > \phi_{c2}$. It is apparent that the value of ϕ_{c1} and ϕ_{c2} and the width of percolation transition zone are approximately independent of water/cement and sand/cement ratio. Whereas the conductivity decreases with increasing sand/cement ratio for a given carbon fiber volume fraction, especially for very low fiber concentration, see Fig. 4, where carbon fiber content is hold at 0.4%.

3.2. Effect of fiber length

The effect of carbon fiber length on the conductivity of the system is depicted in Fig. 5. The results indicate that fiber length has some effect on the value of ϕ_{c1} and ϕ_{c2} and the width of percolation transition zone. From Table 2, the value of ϕ_{c1} is low in the case of 15 mm, while ϕ_{c1} is high as the fiber length is 1 mm. The longer fibers may be more effective at proving a continuous conductive path because there is a greater probability of fiber to fiber contact along the length of the specimen.

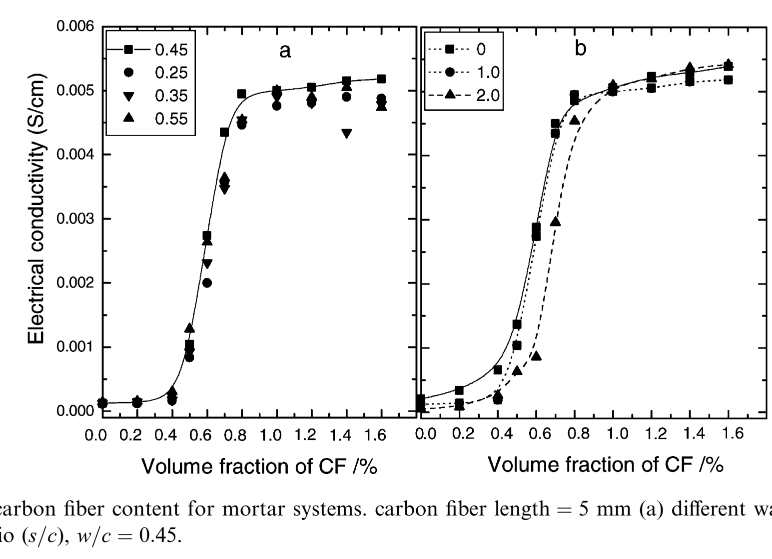

Fig. 3. Conductivity versus carbon fiber content for mortar systems. carbon fiber length = 5 mm (a) different water–cement ratio (w/c), $s/c = 1$; (b) different sand–cement ratio (s/c), $w/c = 0.45$.

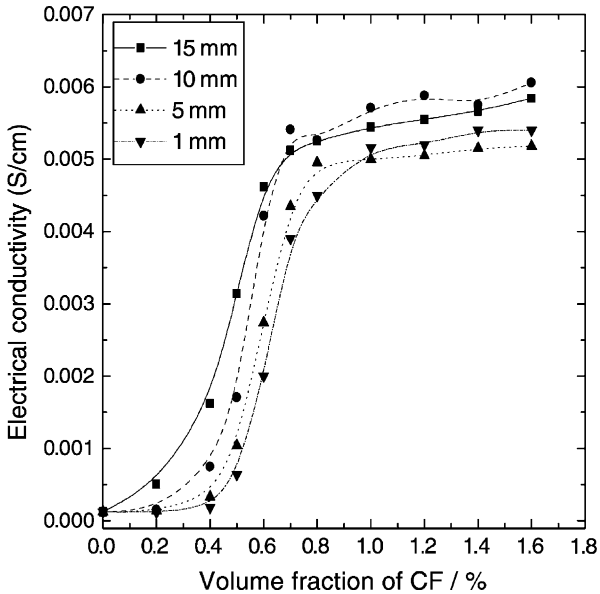

Fig. 5. Effect of carbon fiber length on the electrical conductivity of the system, $w/c = 0.45$, $s/c = 1$.

Table 2
Percolation transition region for the system with different fiber lengths

Carbon fiber length/mm	1	5	10	15
ϕ_{c1}/%	0.50	0.40	0.30	0.20
ϕ_{c2}/%	0.80	0.60	0.50	0.50

3.3. Effect of hydration time and relative humidity

Unlike other materials, cement hydration is continuous as long as moisture is made available. The microstructure of the system thus changes with curing time and relative humidity. Therefore, it might be expected that hydration time and relative humidity will influence the electrical conductivity of system. In Fig. 6, the relation between conductivity and ages of specimen in the case of sand/cement = 1 and fiber length being 5 mm. It is apparent that the percolation threshold value of carbon fiber concentration does not change with hydration time (in Fig. 6(a)), although the conductivity values show some change. In Fig. 6(a), three typical fiber contents were chosen, as illustrated in Fig. 6(b). They represent different connectivity stages of the carbon fiber network in the cement matrix, which plays important role in the electrical conductivity of carbon fiber composites. Point 3 ($\phi > \phi_{2c}$) represents the system in which the fiber network is well developed, point 2 ($\phi_{1c} \leqslant \phi \leqslant \phi_{2c}$) a system at the threshold point of incipient network formation, and point 1 ($\phi < \phi_{1c}$) fiber distributed homogeneously in the cement matrix without connection. It is apparent that the changes for system 1 is largest, and only marginal for systems 2 and 3.

Unfortunately, without the availability of an environmental chamber there was no means of maintaining a constant relative humidity at a target level. So, only two conditions were adopted for testing. One is that the specimen is taken from moist-curing room for testing directly, the other is that the specimen is dried at 80 °C

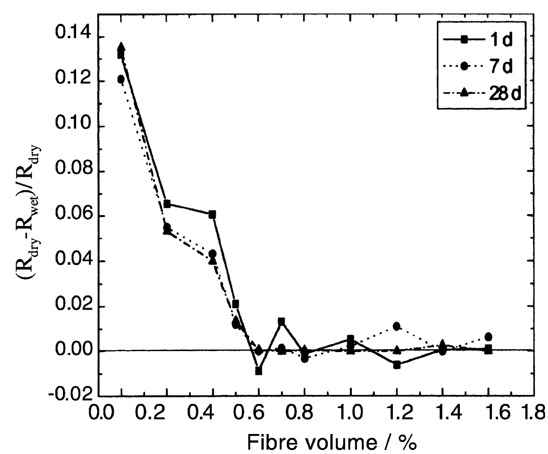

Fig. 7. Effect of humidity on the electrical resistivity of the system, $w/c = 0.45$, $s/c = 1$ and carbon fiber length = 5 mm.

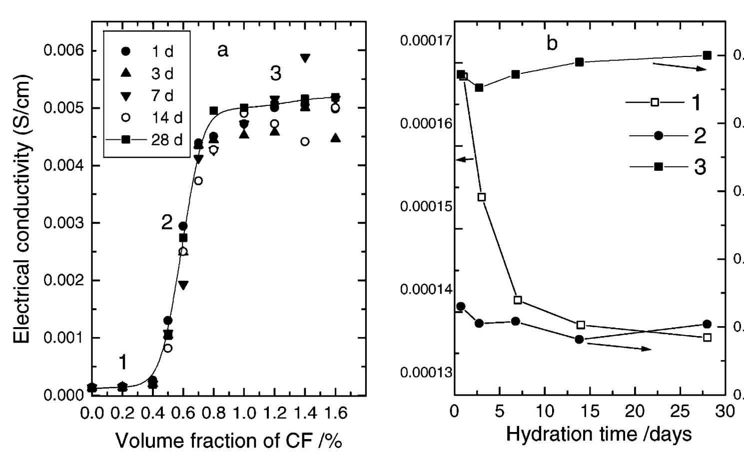

Fig. 6. Effect of hydration time on electrical conductivity of the system (a) on percolation threshold content; (b) on composite conductivity.

for 24 h before measurement. The test results are shown in Fig. 7. From the figure, it can be seen the relative humidity has an influence on the conductivity in the case of the composite containing low fiber contents and that this influence becomes less with increasing fiber content.

4. Analysis and discussion

From the experimental results as shown, it appears that conductivity versus fiber volume fraction curves for carbon fiber reinforced cement-based composites have typical features of percolation phenomena. Thus, the conductivity of system can, according to the percolation theory, be expressed by the following equation [8]:

$$\sigma_f = \sigma_0(\phi - \phi_c)^t \tag{4}$$

where σ_f is the conductivity of composite (S/cm), σ_0 is the conductivity of conductive phase (S/cm), ϕ is the volume fraction of conductive phase, ϕ_c is the critical fiber content for percolation threshold, and t is a constant that is independent of the microstructure of the material.

It can be seen that the value of ϕ_c and t is most important for determining the conductivity of the system. According to the definition of ϕ_c based on classic percolation theory, ϕ_c is a point where the conductive fiber clusters begin to be in contact with each other and hence form a continuous network through the entire matrix. However, the way to determine the value of ϕ_c is ambiguous and conflicting among the research. Brouers [9] proposed that the point ϕ_{c1} for a sudden transition in the system from an insulator to a conductor is the threshold, while Balberg [10] thought the point ϕ_{c2} is the correct threshold value. Carmona [11] proposed that the threshold should be the point where the rate of change of conductivity is greatest between $\phi_{c1} \sim \phi_{c2}$, i.e. $\phi_c = \phi|_{(d\sigma/d\phi)_{max}}$. Some researchers suggest that the value of ϕ_c and t can be obtained by fitting experimental data to Eq. (4).

As the research has shown, the value of t is very sensitive to the threshold ϕ_c. In our experiment, when the value of ϕ_c was adopted as $\phi_{c1} \leqslant \phi \leqslant \phi_{c2}$ for the system, the value of t can be obtained as $1.05 \leqslant t \leqslant 8.2$, see Fig. 8. The reason why the value of t varies is uncertainty in the value of ϕ_c. In percolation theory, it is suggested that there exists a critical threshold where the conductivity changes are sudden. In fact, there exists a narrow transition zone where the conductivity changes sharply, for example the percolation transition zone of ϕ_{c1}–ϕ_{c2} in our experiment. It is difficult to determine which point is the right value for ϕ_c.

Based on the experimental results from the study on the conductive behavior of high density polyethylene, Song [12] proposed the following formula for the relation between t and ϕ_c:

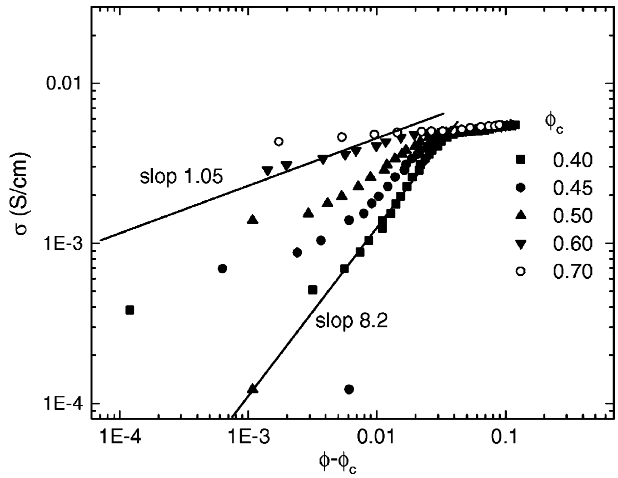

Fig. 8. Conductivity as a function of $(\phi - \phi_c)$ for CFRC, $w/c = 0.45$, $s/c = 1.0$, carbon fiber length = 5 mm.

$$t = t_{un}(\phi_c/\phi_{c2})^{-\chi} \tag{5}$$

At the same time the experimental data were fitted to Eq. (5) and obtained $t_{un} = 2.1 \pm 0.1$ and $\chi = 2.7 \pm 0.2$. Therefore, the value of t for the system in the case of different carbon fiber lengths is plotted as a function of ϕ_c $(\phi_{c1} < \phi_c < \phi_{c2})$ in Fig. 9. By fitting, $t_{un} = 2.0 \pm 0.1$ and $\chi = 3.0 \pm 0.1$ were obtained, which is similar to the result of Song. From Eq. (5), it is apparent that the value of t becomes variable as ϕ_c deviate from ϕ_{c2} and toward ϕ_{c1}. It is suggested that the conductive mechanism and the microstructure of percolation network for the system depends on the fiber content. In fact, as the fiber content reaches ϕ_{c1}, a small increase in fiber content will result in significant changes in the fiber network and cause a rapid increase in conductivity. So, according to the relationship between conductivity and fiber content, a model of fiber distributed and interconnected in the cement matrix is proposed and illustrated in Fig. 10 for different fiber volume fraction. From Fig. 11, the SEM micrographs for carbon fiber distributed in the

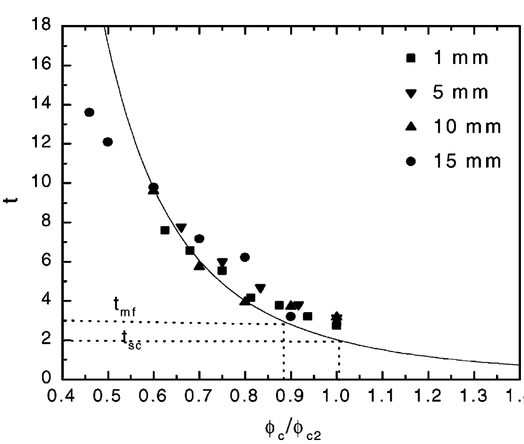

Fig. 9. Dependence of conductivity critical exponent t on ϕ_c/ϕ_{c2}.

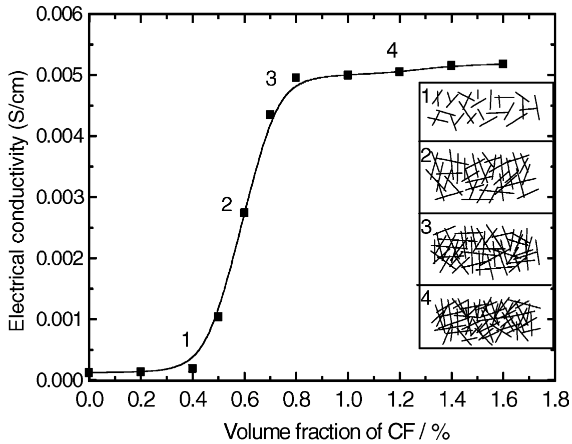

Fig. 10. Relationship between electrical conductivity and connectivity of carbon fibers.

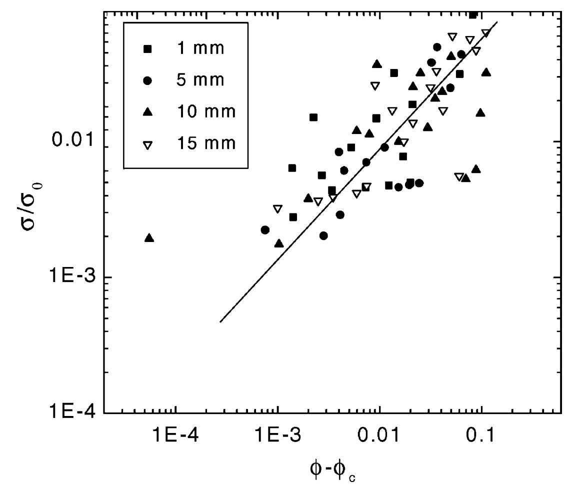

Fig. 12. Normalized conductivity (σ_c/σ_0) versus ($\phi - \phi_c$) for system, $w/c = 0.45$, $s/c = 1$.

cement matrix, in the region of very low fiber content the carbon fiber is distributed homogeneously in the volume of the non-conductive matrix. There are no contacts between adjacent fibers. As the concentration of carbon fiber increases, fibers begin to contact each other within an individual cluster, although the clusters are separate. This is the case, until the fiber content reaches ϕ_{c2}. Therefore, ϕ_{c2} is adopted as the threshold and σ_c/σ_0 versus $\phi - \phi_c$ is presented in Fig. 12 for the system with different fiber lengths. It is found that all experimental data lies near the line of $t = 2.5 \pm 0.1$, which suggests that the conductive behavior of CFRC is universal and independent of matrix, fiber parameter and other factors.

For the analysis cited above, it is proposed that in the percolation transition zone ϕ_{c1}–ϕ_{c2}, electron tunneling conduction is dominant during the process of conduction, while ohmic contacting conduction is dominant for the conduction of the system in the case of $\phi > \phi_{c2}$. So ϕ_{c2} is the critical point for whether the conductive behavior of carbon fiber reinforced cement-based composite is universal or non-universal.

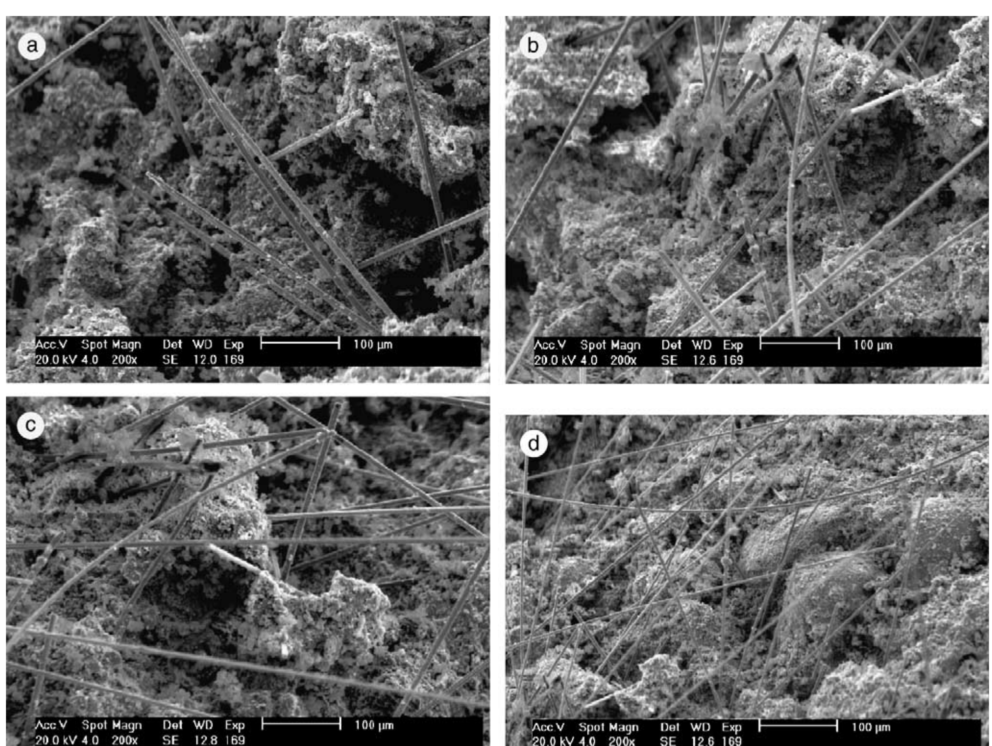

Fig. 11. SEM fractographs of system with different carbon fibre volume. (a) $V_f = 0.20\%$ (b) $V_f = 0.40\%$; (c) $V_f = 0.55\%$; (d) $V_f = 0.80\%$.

5. Conclusion

The relationship between conductivity and volume fraction of carbon fiber has shown that the statistical percolation theory is suitable and applicable for the change rule of conductivity of system with the volume of carbon fiber. Based on the classic percolation theory, the percolation threshold of carbon fiber cement-based composites was determined as $\phi = \phi_{c2}$ decisively. It was proposed that in the percolation transition zone ϕ_{c1}–ϕ_{c2}, electron tunneling conduction is dominant during the process of conduction, while ohmic contacting conduction is dominant for the conduction of the system in the case of $\phi > \phi_{c2}$.

Acknowledgement

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