Electrical Conduction and Percolation Behavior of Carbon Nanotubes/UPR Nanocomposites

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Abstract

The carbon nanotubes(CNT)/Unsaturated polyester resin (UPR) nanocomposites are fabricated, and their electrical conduction and percolation behavior are investigated experimentally and theoretically. The carbon nanotubes used in this study are those by the chemical vapor deposition (CVD) method; vapour grown carbon fiber (VGCF) has an average diameter of 150 nm and vapour grown nanofiber (VGNF) has about 80 nm in diameter. The electrical conductivity of the nanocomposites is measured as a function of carbon nanotube volume fraction to understand the percolation behavior. The nanocomposites show the electrical conductivity with low percolation threshold between 2 and 3 vol.%. Moreover, the percolation threshold is examined as a function of fiber aspect rate based on simulation calculations. The critical carbon nanotube volumes fraction is in good agreement between the theoretical prediction and the experiment results.

Keywords: Carbon nanotubes; Nanocomposite; Electrical properties; Percolation

1. Introduction

Polymeric composites are traditionally used as electrically insulating materials and generally known to have many structural applications, but their use in electronics has been relatively limited. In order to make the polymeric materials have electrical conduction, continuous pathways by electrical fillers must be established. Recently, carbon nanotubes (CNTs) have attracted great attentions because of their excellent properties, such as high stiffness and strength, remarkable thermal and electrical conductions [1-3]. Hence, carbon nanotube composites have been widely considered to be ideal candidates for advanced composite materials due to their possible technological applications. Coleman et al. [4-5] have reported that the poly (p-phenlyenevinylene-co-2, 5-dioctixy-m- phenlyenevinylene) (PMPV) can increase the conductivity dramatically by ten orders of magnitude when nanotubes are added to form a wholly organic composite. In a general way, the electrical properties of polymeric composites are determined by the dimension and distribution of electrical fillers in matrix. For carbon natnotube nanocomposites, the fiber orientation and length distributions of carbon nanotubes strongly affect the electrical conduction due to the connection of crossbar networks. The carbon nanotubes of vapor grown carbon fiber (VGCF) is known to exhibit good electrical conductivity different distinctively from other types of carbon

fibers. Since they have very small diameter, the VGCF tends to have a larger aspect ratio and surface area than general other short carbon fibers. Therefore, nanotube networks of VGCFs are mass-produced and reproducible in low-cost and high-efficiency, and they make the nanocomposites be ideal for applications. For example, they can be used for static-dissipative, semiconductive and electromagnetic interference (EMI) shielding materials applied in computer and cellular-phone housings.

The electrical conduction of nanocomposites with carbon nanotubes depends largely on the volume fractions of carbon nanotubes, and will be characterized well by a percolation transport process. As fiber content increases, they come into contact with each other to form the conduction pathways through matrix composites. A large number of conduction paths will result in low resistivity. In the present work, carbon nanotube/ unsaturated polyester resin nanocomposites are fabricated to study the formation of conducting channels based on the percolation theory [6-12]. The electrical resistivity of carbon nanotube composites with two types of CNTs is investigated as a function of fiber content to understand the percolation behavior. The effect of the aspect ratio and orientation of two carbon nanotubes on the critical concentration in percolating system is analyzed and discussed using the excluded area (or volume) approach [6-8] and Monte Carlo simulation [12].

2. The percolation approach

There are several methods capable of predicting the critical concentration in percolating systems. In the present study, the excluded volume and the Monte Carlo simulation are carried out. The concept of excluded volume is efficient in treating the problem of percolating systems in which the objectives possess a large aspect ratio. However, the Monte Carlo simulation presented here is not only applicable to large aspect ratio but also to very small one.

2.1 Excluded volume method

The exclude volume (excluded area in two dimensions) of an object is defined as the volume (area) around an object into which the center of another similar object is not allowed to enter if overlapping of the two objects is to be avoided. The exclude volume for an elongated objective is very different in shape from the actual object. Thus, the total excluded volume can be obtained by multiplying this volume by N_c, which is the critical number density of objects in the system. If $\langle V \rangle$ defines an average excluded volume, the total excluded volume $\langle V_{ex} \rangle$ is given by

$$\langle V_{ex} \rangle = \langle V \rangle N_c \tag{1}$$

and similarly, the total excluded area is:

$$\langle A_{ex} \rangle = \langle A \rangle N_c . \tag{2}$$

Note that $\langle V \rangle$ or $\langle A \rangle$ of an object with different shapes is very different, and its value can be calculated according to the shapes such as cylindrical rods in three-dimensions (3D) and line segments and narrow strips in two-dimensions (2D).

The average excluded volume $\langle V \rangle$ for a carbon nanotube (CNT), modeled as a cylinder of length L and diameter D, is given by [6]

$$\langle V \rangle = \frac{4}{3}\pi D^3 + 2\pi D^2 L + 2DL^2 \langle \sin\theta \rangle_\mu \tag{3}$$

where $\langle \sin\theta \rangle_\mu$ is the average value of $\sin\theta$, and θ is an angle between two CNTs.

The term $\langle \sin\theta \rangle_\mu$ describes the degree of CNTs alignment. The calculation of $\langle \sin\theta \rangle_\mu$ is complicated. However, it is easy to obtain $\langle \sin\theta \rangle_\mu = 0$ when the CNTs are perfectly aligned. In the case of random distribution, the value of $\langle \sin\theta \rangle_\mu$ is calculated to be $\pi/4$.

The average excluded area in the uniform and randomly orientated system is given as

$$\langle A \rangle = 4WL + \pi W^2 + \left(L/2\theta_\mu\right)^2 \left[4\theta_\mu - 2\sin\left(2\theta_\mu\right)\right] \tag{4}$$

where W is the width of fibers, and θ_μ is the orientation angle.

The critical volume fraction of CNTs is associated with total excluded volume $\langle V_{ex} \rangle$.

In the three-dimensional system, the critical volume fraction can be estimated by

$$\phi_c = 1 - \exp\left(- \frac{\langle V_{ex} \rangle v}{\langle V \rangle} \right) \tag{5}$$

where v is the volume of CNTs capped at each end with a hemisphere.

Substituting Eq. (3) into Eq. (5), we have

$$\phi_c = 1 - \exp\left(- \frac{\langle V_{ex} \rangle \left[(\pi/4) D^2 L + (\pi/6) D^3 \right]}{(4\pi/3) D^3 + 2\pi D^2 L + 2DL^2 \langle \sin\theta \rangle_\mu} \right) \tag{6}$$

Similarly, we obtain the critical area fraction in the two-dimensional system:

$$\phi_c = 1 - \exp\left(- \frac{\langle A_{ex} \rangle \left[WL + (\pi/4) W^2 \right]}{4WL + \pi W^2 + (L/2\theta_\mu)^2 \left[4\theta_\mu - 2\sin(2\theta_\mu) \right]} \right) \tag{7}$$

2.2 Monte Carlo simulation

In the present simulation, we only obtain the 2D solution of percolation problem on orientated short-fiber composites [12]. Using Eq. (2), the critical volume fraction can be given by

$$\phi_c = 1 - \exp\left(- \frac{\langle A_{ex} \rangle a}{\langle A \rangle} \right) = 1 - \exp(- N_c a) \tag{8}$$

The product $N_c a$ is defined as the average number of objects within the system at the percolation threshold. For a model of fiber with a finite-width, we can obtain

$$N_c A = \frac{4}{\pi (L/D)} \left(\frac{L_c}{2r_s} \right)^2 \tag{9}$$

where L/D is the fiber aspect ratio. L_c is the critical length, and r_s is the average lattice constant normalized by

$$r_s = 1/\sqrt{\pi N_s} \tag{10}$$

and N_s is the number of planted and randomly distributed sites.

Bonding criterions for two sticks with a finite-width can be analyzed by the schematic diagrams shown in Figs 1 and 2. Sites are planted by generating random coordinates (x_k, y_k), $k = 1, 2, \cdots, N_s$. Each stick of length L_k is centered on a site and has an assigned orientation angle θ_k. Figure 1 illustrates the relationship between two different coordinate systems that are fixed on fibers. The axes y' and y'' indicate the orientation angles of θ_i and θ_j, respectively. According to the translation relationship between the Cartesian coordinates, we can easily obtain the coordinates of overlapped two fibers:

$$y' = \frac{(\Delta x \cos\theta_j - \Delta y \sin\theta_j) + x' \cos(\theta_i - \theta_j) - x''}{\sin(\theta_j - \theta_i)}, \tag{11}$$

$$y'' = \frac{(\Delta x \cos\theta_i - \Delta y \sin\theta_i) + x' - x'' \cos(\theta_i - \theta_j)}{\sin(\theta_j - \theta_i)}, \tag{12}$$

where

$$\begin{Bmatrix} \Delta x \\ \Delta y \end{Bmatrix} = \begin{Bmatrix} x_i^0 - x_j^0 \\ y_i^0 - y_j^0 \end{Bmatrix}. \tag{13}$$

Let us consider the case of a finite-width stick, as shown in Fig. 1. Since bonding

occurs when two fibers overlap, the bonding criterions are satisfied by the following both conditions:

$$|x'| \le D/2\,, \quad |x''| \le D/2\,, \tag{14}$$

$$|y'| \le L/2\,, \quad |y''| \le L/2\,, \tag{15}$$

where D and L are the stick width and length, respectively.

When two fibers are parallel with the same orientation angle (Fig. 2), the bonding criterions are given by

$$A_{ij} = d_{ij}\left|\sin\left(\theta_i + \gamma_{ij}\right)\right| \le \frac{L_i + L_j}{2}, \tag{16}$$

and

$$B_{ij} = d_{ij}\left|\cos\left(\theta_i + \gamma_{ij}\right)\right| \le D\,, \tag{17}$$

where

$$d_{ij} = \sqrt{\left(x_i - x_j\right)^2 + \left(y_i - y_j\right)^2}\,, \tag{18}$$

$$\gamma_{ij} = tg^{-1}\left(\frac{y_i - y_j}{x_i - x_j}\right). \tag{19}$$

For widthless fibers $\left(x' = x'' = 0\right)$, we can obtain the bonding criterions from Eqs. (11), (12) and (15) as follows

$$\left|\frac{\left(\Delta x\cos\theta_j - \Delta y\sin\theta_j\right)}{\sin\left(\theta_j - \theta_i\right)}\right| \le \frac{L}{2}, \tag{20}$$

$$\left|\frac{\left(\Delta x\cos\theta_i - \Delta y\sin\theta_i\right)}{\sin\left(\theta_j - \theta_i\right)}\right| \le \frac{L}{2}. \tag{21}$$

3. Experimental

Two types of CNTs used to fabricate the nanocomposites in this study are VGCF and VGNF (Showa Denko.Co., Ltd.). VGCFs were analyzed by scanning electron microcopy (SEM), and their average diameter was about 150 nm and the length was 10-20 μm. The diameter of VGNFs was about 80 nm. The resin used as matrix was unsaturated polyester resin (UPR), and the hardening agent was PERMEK, produced by NOF Co., Ltd.

The nanocomposite sheets were fabricated by a solution-evaporation method. Ethanol solution was used to obtain uniform dispersion of VGCFs. According to the volume fraction, a fixed quantity of VGCF was added to the ethanol solution and stirred well with a glass rod. Next, UPR was added to prepared composite solutions and the mixture was ultrasonicated at room temperature for 3 hours. In order to remove the ethanol solution by evaporation, the composite solutions were heated in a furnace at 80^{o}C for 4 hours. After that, the hardening agent was poured and a sheet with 1 mm thickness was modeled under heat treatment of 100^{o}C for 1 hour.

The specimens were made in the form of a rectangular bar ($30\times5\times1$ mm^3). The electrical resistances of 5 specimens for each volume fraction was measured at room

temperature by using a digital multi meter VOAV7510 (IWATSU Co., Ltd. Japan). The morphology of the nanocomposites was observed using scanning electron microscopy techniques (SEM). In order to clearly observe the fracture surfaces, the specimens were sputtered with gold using an S-510 (HITACH, Co., Ltd. Japan).

4. Results and discussion

Figure 3 (a) and (b) shows SEM micrographs of the fracture surface of unsaturated polyester resin filled with 4 wt% of VGCF and VGNF, respectively. The darker regions correspond to the unsaturated polyester resin and the brighter regions to the carbon nanotubes. The SEM image of fracture surface shows that nanotubes are distributed uniformly in the polymer matrix. In addition, the nanotubes appear interconnected at this weight fraction (4 wt%) and the nanotube-nanotube junctions are formed. The observation can prove that the nanocomposites filled with nanotubes have lower percolation behavior with the weight fraction less than 4 wt%.

Figure 4 shows the influence of CNT volume fraction on the volume electrical resistivity of the nanocomposites. It is found that both UPR/VGCF and UPR/VGNF nanocomposites exhibit a typical percolation behavior. Sharp drops in the curve of volume fraction versus volume electrical resistivity are observed between 2 and 3 vol.%

and the nanocomposites exhibit low percolation threshold. This is partly because VGCFs or VGNFs have larger fiber aspect ratio. On the other hand, the conducting pathways in nanocomposites filled with CNTs not only are physical contacts between themselves, but also can be connected between the conducting elements with very small distances across which electrons can tunnel [12, 13]. The electrical conduction in composite system can also be performed through the electron hopping mechanism. Figure 5 shows the schemata for the formation of conducting pathways. If the electron hopping mechanism applies to the electrical conductivity of the nanotube/unsaturated polyester nanocomposites, the electrical conductivity will increases due to effective electron hopping distance between nanotubes. The required nanotube-nanotube distances are soft, penetrable shell of thickness (tunneling distance) less than 5 nm for the nanocomposites to be electrically conductive [14]. This suggests that nanocompostes exhibit lower percolation threshold of fiber volume fraction because of tunneling effect.

A high surface-to-volume ratio of CNTs results in percolation threshold occurring at lower volume fraction. VGCF/UPR nanocomposites are found to have a slightly lower percolation threshold, and a slightly higher resistivity than VGNF/UPR above the percolation threshold. We do not quite understand the reason why the critical fraction

volume of VGCF/UPR is slightly lower than that of VGNF/UPR, but this may suggest an additional effect due to the aspect ratio and agglomeration of CNTs. The dispersion process of VGNFs is more difficult than that of VGCF since the van der Waals (vdW) interactions among VGNFs due to smaller diameter may be stronger.

According to our computational simulation [10], the total excluded area $\langle A_{ex} \rangle$ and total excluded volume $\langle V_{ex} \rangle$ were obtained to be 4.1 and 1.4 for randomly aligned long fibers, respectively. Using Eq. (6) and (7), thus, the critical volume fraction of VGCFs are predicted to be 4.5-8.5 vol.% for 2D simulation and 0.5-1.0 vol.% for 3D simulation. For the average length of VGCFs used in this study being approximately 15 μm (the aspect ratio of 100), the critical volume fraction is estimated to be 5.9 and 0.7 vol.% for 2D and 3D simulations, respectively. Based on the two-dimensional Monte Carlo simulation in this study, the relationship between the percolation threshold and aspect ratio of the fibers is shown in Fig. 6. It is found that the critical volume fraction shows logarithmically linear dependence on the aspect ratio when they are larger than 40. The critical volume fraction of VGCF is predicted to be 2.9-5.5 vol.%, which is larger than the results predicted by the excluded area method. As shown in Fig. 6, there is a reasonably good agreement between predicted values and the experimental data although the predicted results are slightly larger than the experimental ones.

In the early work [15], standard percolation theory predicts that the electrical (the density of dependence of the) conductivity has the following relationship:

$$\sigma \propto (\phi - \phi_c)^t, \quad \text{for} \quad \phi \geq \phi_c, \tag{22}$$

where σ is the electrical conductivity. ϕ is the volume fraction, and ϕ_c is the critical volume fraction corresponding to the percolation threshold. t is the critical exponent of conductivity, which governs the scaling behavior in the region of ϕ_c. Figure 7 shows the electrical conductivity versus volume fraction of the nanocomposites. It is found that plot experimental data follow typical percolation behavior. Using a least square method, the values of the critical exponents (t) are obtained to be 0.93 and 0.91 for VGCF and VGNF, respectively. For a film in two dimensions, the critical exponent is predicted to be 1.33 [16]. The experimentally measured values of the critical exponent are close to but somewhat lower than that of theoretical prediction.

5. Conclusions

Unsaturated polyester resin composites filled with VGCF and VGNF are fabricated to study the percolation behavior. Two analytical models based on the excluded volume approach and the Monte Carlo simulation are presented to predict the critical concentration of the nanocomposites. The composites show the electrical conductivity

with low percolation threshold between 2 and 3 vol.%. Reasonably good agreement can be observed between the predicted and measured values of the critical volume fraction in percolation systems containing high aspect ratio nanotubes.

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Figure captions

Figure 1 Diagram of the relationship between orientated fibers in different coordinate systems

Figure 2 Diagram of determining bonding criterion of fibers with the identical orientation angle

Figure 3 SEM micrographs of fracture surface of unsaturated polyester resin filled with carbon nanotubes composites at room temperature. (a) 4wt% VGCF/UPR nanocomposites; (b) 4wt% VGNF/UPR nanocomposites.

Figure 4 Changes in the electrical resistivity vs. volume fraction for VGCF/UPR and VGNF/UPR nanocomposites

Figure 5 Scheme for the formation of conducting pathways

Figure 6 The influence of aspect ratio (*L/D*) on the critical volume fraction

Figure 7 Conductivity of nanocomposites as a function of $\phi - \phi_c$

Figure 1

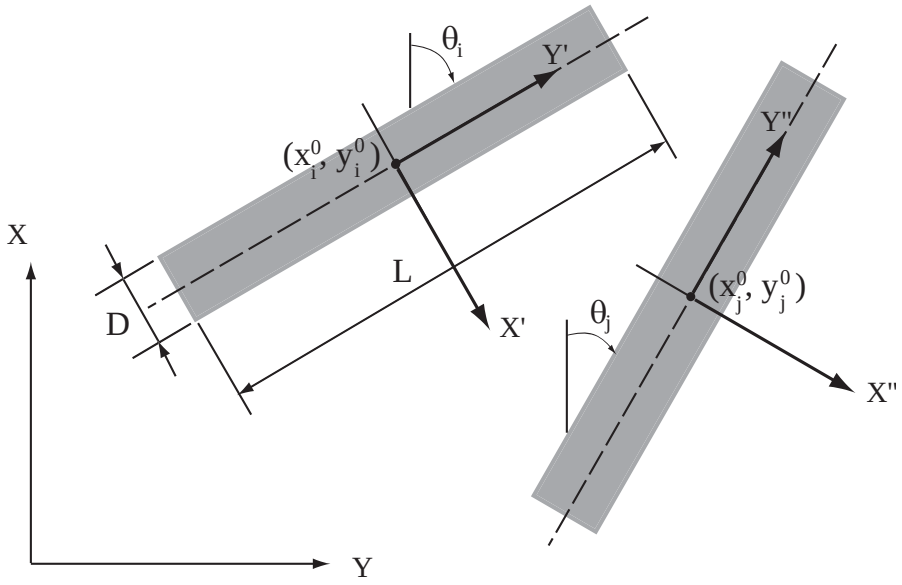


Figure 2

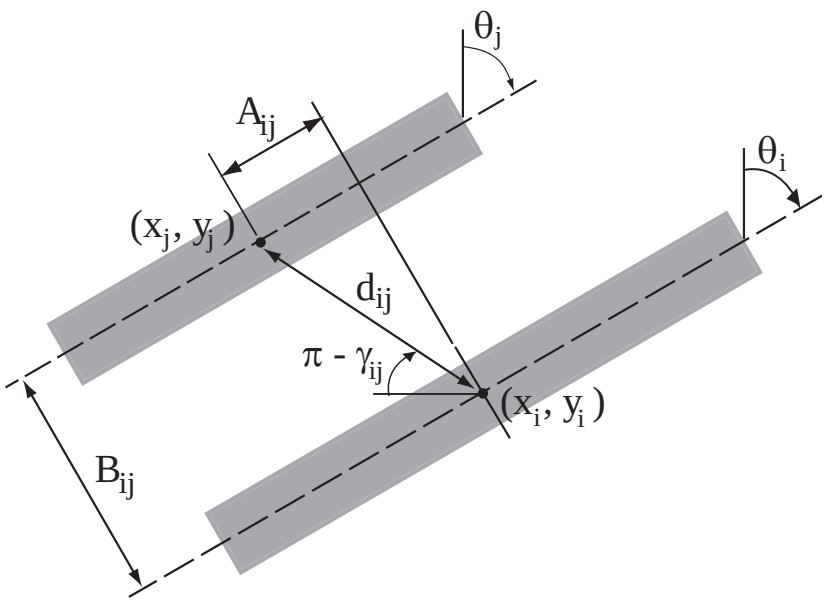


Figure 3

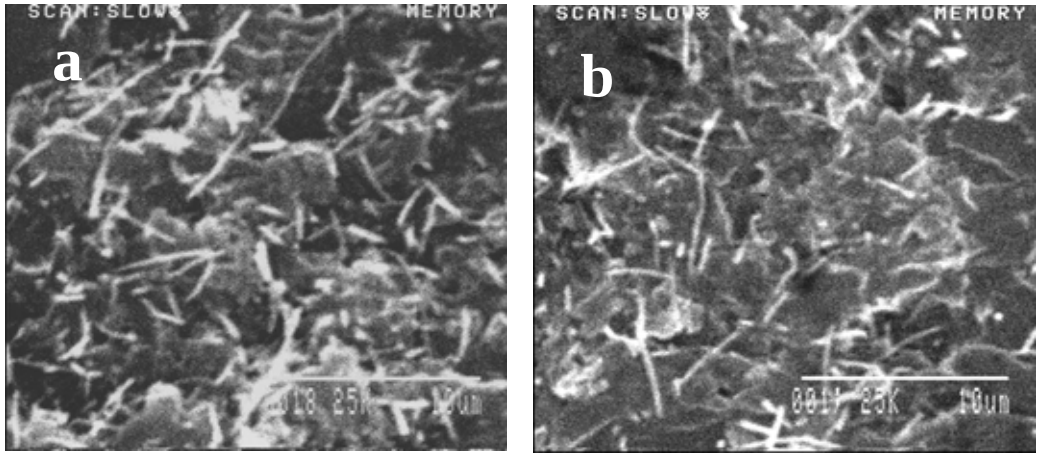


Figure 4

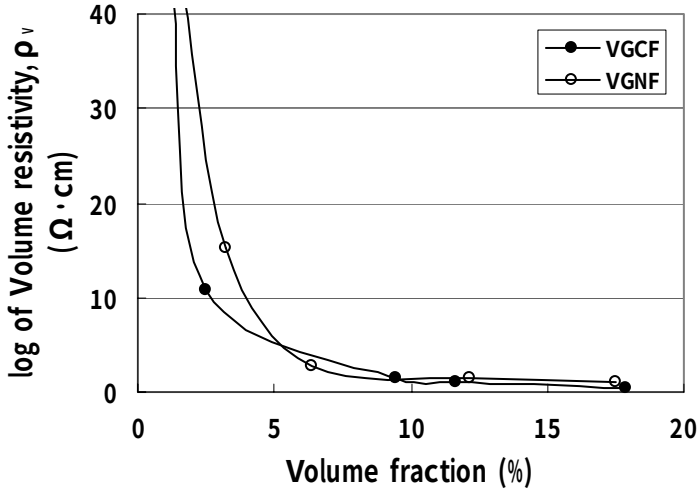

log of Volume resistivity, ρv
(Ω·cm)
40
30
20
10
0
0
5
10
15
20
Volume fraction (%)
VGCF
VGNF

Figure 5

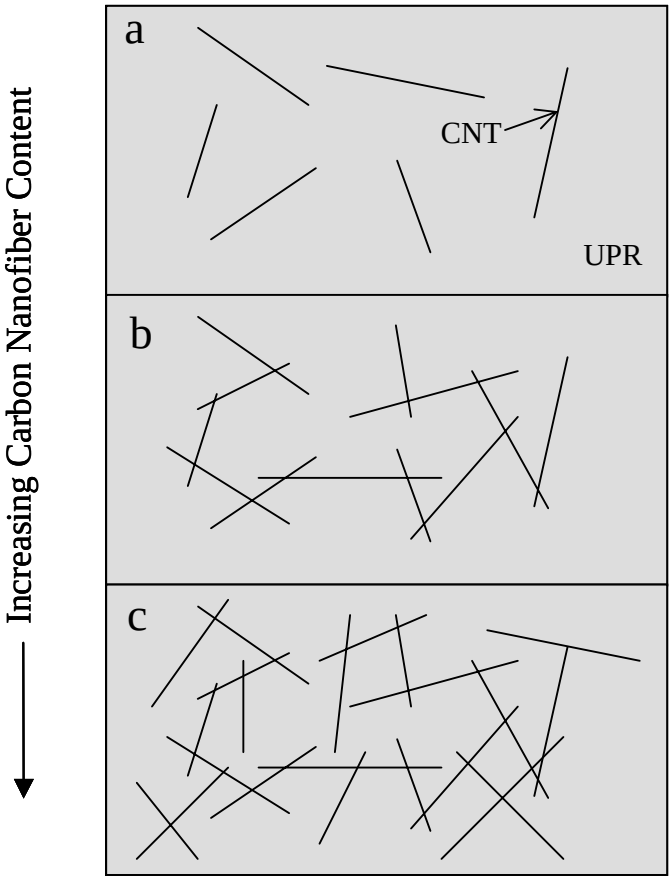


Figure 6

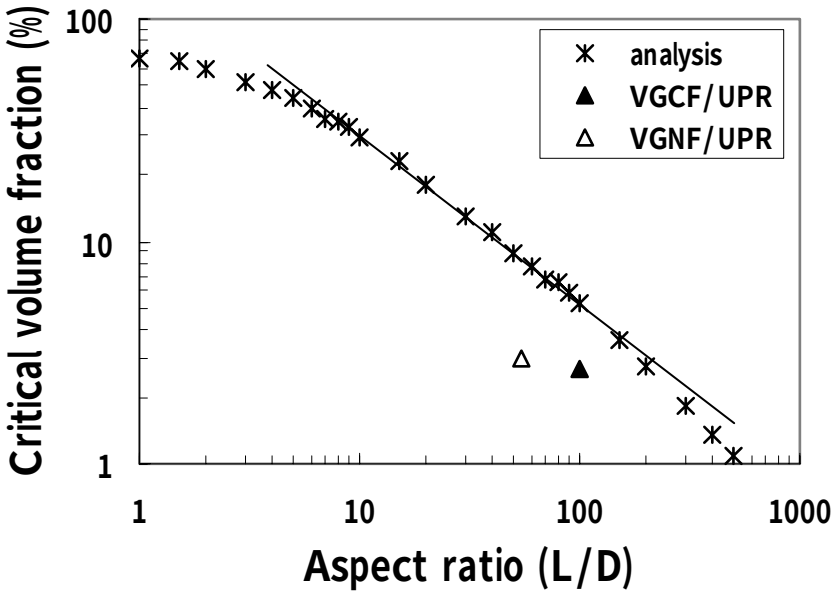
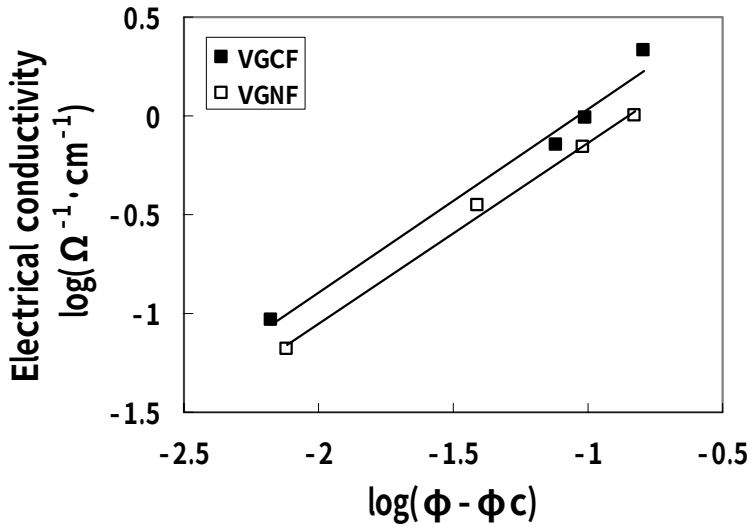

Critical volume fraction (%)
100
10
1
1
10
100
1000
Aspect ratio (L/D)
analysis
VGCF/UPR
VGNF/UPR

Figure 7


Electrical conductivity
log(Ω⁻¹·cm⁻¹)
VGCF
VGNF
0.5
0
-0.5
-1
-1.5
-2.5
-2
-1.5
-1
-0.5
log(φ - φc)