Electrical Properties of Polymer Nanocomposites with Carbon Nanotube Fillers

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Abstract:

The electrical properties of polymer nanocomposites containing a very small amount of carbon nanotube (CNT) fillers, are remarkably superior to those of their conventional counterparts. Based on experimental investigation, 3D statistical percolation modelling and 3D resistor network modelling, the electrical properties of nanocomposites were successfully predicted in this work. The influence of aspect ratio, electrical conductivity, and shape of CNTs was investigated numerically. Following the success of the numerical simulations, a simple empirical formula was established to predict the electrical conductivity of the nanocomposites. This investigation highlighted the importance of theoretical and numerical modelling for the development of functional nanocomposites.

Polymer nanocomposites with carbon nanotube fillers have generated much interest among researchers, owing to the improvement of mechanical properties and electrical conductivity [1-8]. Potential applications of nanocomposites as functional materials include organic field emitting displays, photovoltaic cells, highly sensitive strain sensors, and electromagnetic-wave interference materials. Compared with conventional electronic composites containing fillers such as short carbon fibers or carbon flakes, outstanding electrical properties can be achieved with CNT nanocomposites containing far less filler material than usual, due to the much higher electrical conductivity and aspect ratio of CNTs. From the current knowledge of the electrical behavior of conventional electronic composites, the change in the electrical conductivity of composites prepared by gradually mixing an insulating polymer with traditional conductive fillers can be classified into three stages. Initially, the electrical conductivity is very low due to the low number of isolated filler particles. In the next stage, as the amount of filler particles increases, the first complete electrically conductive path of connected filler particles is formed. Consequently, the conductivity will increase remarkably, following a percolation power law. This process is referred to as percolation. Accordingly, the volume fraction of filler particles is termed the percolation threshold. In the final stage, further addition of filler particles into the polymer promotes the formation of more electrically conductive paths and a conductive network can eventually be constructed, thereby gradually increasing the electrical conductivity until it levels off to a constant value.

To date, there have been many experimental studies on the electrical properties of nanocomposites with CNT fillers. From previously published results, it was found that the percolation behavior of nanocomposites follows the same pattern as other conductive composites. For instance, the electrical properties of polymers modified by single-walled carbon nanotubes (SWNTs) [1, 2] or multi-walled carbon nanotubes (MWNTs) [3-8] were experimentally investigated. However, all the experimental

investigations have failed to provide a clear picture of the conductivity mechanisms in the nanocomposites. On the other hand, only a few theoretical or numerical studies have been performed, which were limited to the percolation threshold. For example, a numerical model was used to determine the percolation threshold for a polymer with randomly distributed CNTs [1]. An empirical formula for an extruded volume approach [9], was adopted to obtain the percolation threshold [4]. Indeed, for such a small filler as CNT, *it is still an open question whether or not the statistical percolation model can be applied to nanocomposites, although it has been successful in predicting the percolation threshold in conventional electronic composites* [9-12]. To the best of our knowledge, there has been no numerical or theoretical investigation of the electrical conductivity in nanocomposites with CNT fillers after percolation. To date, there have only been very limited numerical studies on the electrical behavior of conventional electronic composites after percolation [12]. Therefore, there has been almost no comprehensive understanding of the electrical characteristics of nanocomposites, due to the lack of systematic investigations, theoretical or numerical.

In this study, an experimental investigation was firstly carried out. Then, a 3D numerical analysis with two steps was conducted for a polymer with random distribution of CNTs. The first step, using a statistical percolation model, predicted the percolation threshold when the first complete electrically conductive path was formed. Although the experimental results were highly scattered, the present model, which corresponds to an ideal random dispersion of CNTs in the matrix, was still capable of predicting the average percolation threshold. In the second step, a 3D resistor network model was built to predict the macroscopic electrical conductivity after percolation. This model demonstrated its success in capturing the main features of the electrical behavior of the nanocomposites. The influence of aspect ratio, electrical conductivity, and shape of CNTs on the electrical properties was then numerically investigated. Finally, a simple empirical percolation model for evaluating the electrical behavior of

nanocomposites was established. This percolation model contains some new intrinsic relations, which are not reflected in the traditional percolation models.

MWNTs of high purity, provided by Nano Carbon Technologies Co., Japan, were used. The average diameter and length of the MWNTs were 50 nm and 5 μm, respectively. The specimens were prepared using *in situ* polymerization. Initially, an insulating bisphenol-F epoxy resin (jER806, from Japan Epoxy Resins Co., Ltd.) and an amine hardener (Tomaido 245-LP, from Fuji Kasei Kogyo Co., Ltd.) were mixed using a planetary mixer at 2000 rpm for 20 seconds. Then MWNTs were added into the mixture, which was mixed again at 800 rpm for 1 minute. After the mixing process, the liquid was cast in a silicon mold to form the nanocomposites, which was cured in a vacuum oven at 80^{o}C for 3 hours. To observe the dispersion of CNTs in the polymer matrix, a sample with a 2.0 wt% loading of MWNTs was intentionally fractured and then observed using scanning electron microscopy (SEM), as shown in Figs. 1(a) and 1(b). Uniform dispersion of CNTs was observed in the polymer. There was almost no apparent aggregation in most samples prepared under different fabrication processes. From these experiments, it was found that the following factors in the processing conditions could remarkably decrease the electrical conductivity of nanocomposites: 1) high shear forces in a long mixing process, and 2) curing at low temperature. The reason for this can be explained as the difficulty in the formation of a macroscopic conducting network [4]. In the narrow region around the percolation threshold, the electrical conductivity was largely dependent on the processing conditions; however, the electrical conductivity became insensitive to the processing conditions when the volume fraction of CNTs exceeded this region. The detailed experimental investigation, such as effect of processing conditions on the electrical properties of nanocomposites, will be reported elsewhere.

In the numerical analysis, shown in Fig. 1(c), a 3D representative element with a random distribution of CNTs was used. The CNTs were considered as ‘soft-core’

capped cylinders of length L and diameter D, and were allowed to penetrate each other [12]. The union/find algorithm [10] was adopted to detect the first complete conductive path spanning the 3D element (red CNTs in Fig. 1(c)), and the percolation threshold could then be determined. For various aspect ratios (L/D) ranging from 50 to 1000, it was found that 3D element dimensions of $L_x/L=L_y/L=5$ and $L_z/L= 2.0$ (Fig. 1(c)) could sufficiently achieve isotropic and numerical convergence. A Monte-Carlo procedure including 100 simulations was then conducted to obtain the average percolation threshold at each CNT volume fraction. Practically, it is not necessary for the CNTs to be perfectly straight (Fig. 1(b)). The modelling of curved CNTs is shown in Fig. 1(d). Each CNT is divided into 10 segments. The angle in 3D space between two arbitrary adjacent segments can randomly vary within a circular cone with a top angle θ_{max}. Two models of curved CNTs for $\theta_{max}=15^{o}$ and $\theta_{max}=60^{o}$ are schematically shown in Fig. 1(d), which demonstrate that the proposed method is proper to reflect the nature of curved CNTs.

The percolation threshold numerically predicted for the case of straight CNTs is compared with the experimental results and the literature data [1-9], including two other investigations using the same MWNTs [7, 8], and is shown in Fig. 2(a). There is a large scattering of experimental results, which may be attributed to the different materials and processes employed. The present percolation threshold was 0.1 wt%. As previously pointed out [4], the statistical percolation model may not be realistic enough to address inter-particle or matrix-particle molecular-scale interactions for very fine fillers, such as CNTs. Indeed, it only predicts the average probability of the formation of the first conductive path under the assumption of a uniform random distribution of straight CNTs. Nevertheless, as indicated in Fig. 2(a), the numerical predictions are still close to the experimental trend. For the curved CNTs (Fig. 1(d)), the percolation threshold increases gradually with θ_{max}, as shown in Fig. 2(b), which indicates that the formation of the first conductive path becomes more difficult compare with that of straight CNTs.

To predict the electrical conductivity after the percolation threshold, a 3D resistor network containing randomly distributed CNTs in the polymer was constructed, as shown in Fig. 2(c). Except for the work of Balberg *et al.* [12], there have been almost no numerical studies based on a fully 3D statistical resistor network model, even for conventional electronic composites with filler materials such as short fibers. As depicted in Fig. 2(c), for a CNT with two contacting points i and j with neighbouring CNTs, the conductance g_{ij} between i and j (the inverse of resistance R_{ij}) can be evaluated as: $g_{ij} = \sigma_{CNT} \frac{S_{CNT}}{l_{ij}}$, where σ_{CNT} and S_{CNT} are the electrical conductivity and cross sectional area of the CNTs, respectively, and l_{ij} is the length between points i and j. Based on the well-known matrix representation for a resistor network [13, 14] and Kirchhoff's current law, the total current I under an applied voltage can be estimated. For instance, from Fig. 2(c), the node i has an electrical potential V_i, and the electrical current between i and j can be expressed as:

$$I_i = \sum_{j}^{N_i} g_{ij} \left(V_i - V_j \right) \tag{1}$$

where N_i is the total number of nodes connected with node i. The potentials of electrodes 1 and 2 are set to be V and 0, respectively. For those nodes which are located on electrode 1, the sum of all currents is equal to I. For the nodes located on electrode 2, the sum of all currents is equal to $-I$. For other nodes within the internal area, e.g., nodes i and j in Fig. 2(c), from Kirchhoff's current law, the total current on one node is zero. From the above conditions and Eq. 1, linear algebraic equations including all nodes can be defined [13, 14]. This is a large-scale linear system, because the number of CNTs involved in the numerical model is very large, and ranges from several thousands to several tens of thousands depending on the aspect ratio of the CNTs. An iterative equation solver, i.e., the incomplete Cholesky conjugate gradient method (ICCG) has been employed to solve these linear equations. After obtaining the total current I under

an applied voltage, the macroscopic electrical conductivity of the nanocomposite can be evaluated according to Ohm's law: $\sigma_{com} = \frac{I}{V}\frac{L_{com}}{S}$, where L_{com} is the length between the two electrodes, and S is the cross sectional area of the electrode.

Generally, σ_{CNT} for MWNTs ranges from 5×10^3 to 5×10^6 S/m [15, 16]. Both the numerical prediction and experimental results for a situation where L/D=100 and σ_{CNT} =10^4 S/m are shown in Fig. 2(d). The numerical results are in very good agreement with the experimental data, indicating the effectiveness of the present numerical model in capturing the main features of the electrical conductivity in this nanocomposite, especially in the region of high volume fraction of CNTs. The difference among the three experimental results using the same MWNTs is obvious in the region around the percolation threshold. However, the three results gradually tend toward each other as the volume fraction of MWNTs increases. For straight CNTs, as the electrical conductivity and the aspect ratio of the CNTs increases, the electrical conductivity of the nanocomposite increases as shown in Figs. 3(a) and 3(b). The difference is that a higher CNT aspect ratio also leads to a lower percolation threshold. In Fig. 3(b), when the electrical conductivity of nanocomposites attains at 10 S/m, the corresponding volume fraction of CNTs for L/D=100 is around 1.3 vol%, meanwhile, the volume fraction of CNTs for L/D=1000 is only around 0.3 vol%. It means that for the applications, such as electromagnetic-wave interference materials, it is better to use CNTs with high aspect ratios under the condition of uniform dispersions. Moreover, the influence of curved shape of CNTs is insignificant as shown in Fig. 3(c) although it leads to lower electrical conductivity.

According to the traditional percolation theory [17], the electrical conductivity of electronic composites can be predicted by

$$\sigma_{com} = \sigma_0 \left(\phi - \phi_c\right)^t \quad \text{for} \quad \phi > \phi_c \tag{3}$$

where t is the critical exponent, ϕ is the volume fraction of filler, ϕ_c is the percolation

threshold, and σ_0 is a parameter depending on the electrical conductivity of filler from traditional percolation theories. Usually, ϕ_c, t and σ_0 can be determined experimentally.

To obtain an improved percolation model from Eq. 3, the following efforts have been performed. First, considering an ideal random distribution of straight CNTs in a polymer matrix, and by using Eq. 3 with a least-squares fitting, the numerical results identified that the average value of t was 1.8±0.05 as shown in Fig. 4(a) (t is the slope of curves). As previously noted [18], t is universally dependent on the dimensionality of the system. The aspect ratio and curved shape of CNTs have almost no influence on t from our numerical investigations. Second, from Fig. 2(a), the relationship between the percolation threshold and L/D of CNTs can be established as: $\phi_c = (L/D)^{-1.1\pm0.03}$. This expression is comparatively much simpler than other empirical expressions for the prediction of the percolation threshold, e.g. [9]. However, we note that this expression is only valid for filler materials of high L/D, such as those over 20. Moreover, it is interesting to note that σ_0 depends not only on σ_{CNT}, but also on L/D, as shown in Fig. 4(b), which was obtained from Fig. 3(b). *This finding is completely new, because to date σ_0 has been considered to be only dependent on the electrical conductivity of the filler, especially when the volume fraction of filler is low* [17, 18]. Finally, from the numerical results, Eq. 3 can be rearranged into the following form,

$$\sigma_{com} = \sigma_{CNT} \cdot 10^{0.85\{\log(L/D)-1\}} \cdot \{\phi - \phi_c\}^t \tag{4}$$

The predictions from Eq. 4 can accurately reproduce our various numerical results shown in Figs. 3(a) and 3(b) when we use the identified t=1.8 and $\phi_c = (L/D)^{-1.1}$. This model is also useful for predicting the electrical conductivity of other electronic composites. Naturally, for this application, we note that ϕ_c and t should be determined from experimental data, due to the strong effects of processing conditions on these two parameters. The application of Eq. 4 to composites with short carbon fibers [19] and composites with nanofibers [20] are shown in Figs. 4(c) and 4(d). The present

theoretical results are in good agreement with the experimental data [19, 20].

In fact, the electrical behavior of polymer nanocomposites filled with CNTs is very complex, especially in the narrow region around the percolation threshold, which strongly depends on the processing conditions. Based on 3D statistical percolation modelling and 3D resistor network modelling, the electrical properties of nanocomposites can be effectively estimated. Reliable numerical simulations and corresponding experimental investigations have enabled us to construct a simple formula for predicting the electrical properties of nanocomposites with sufficient accuracy. Naturally, for such a fine filler as CNT, in the light of colloid theory and solution dynamics, an improved theoretical framework that can deal with inter-particle or matrix-particle molecular scale interactions will certainly improve the prediction of the percolation threshold [4], which remains an open area of research for the future.

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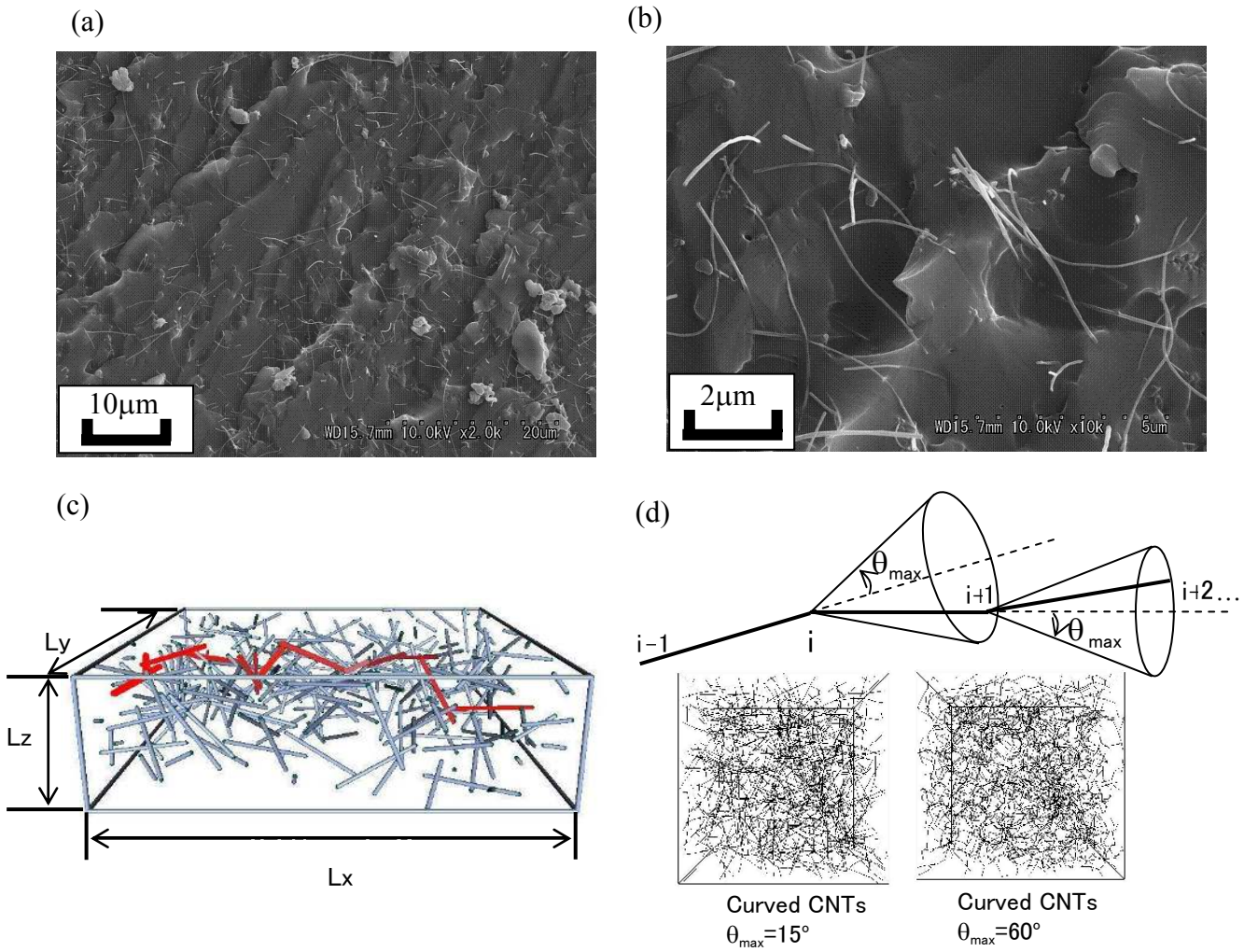
Figure legends

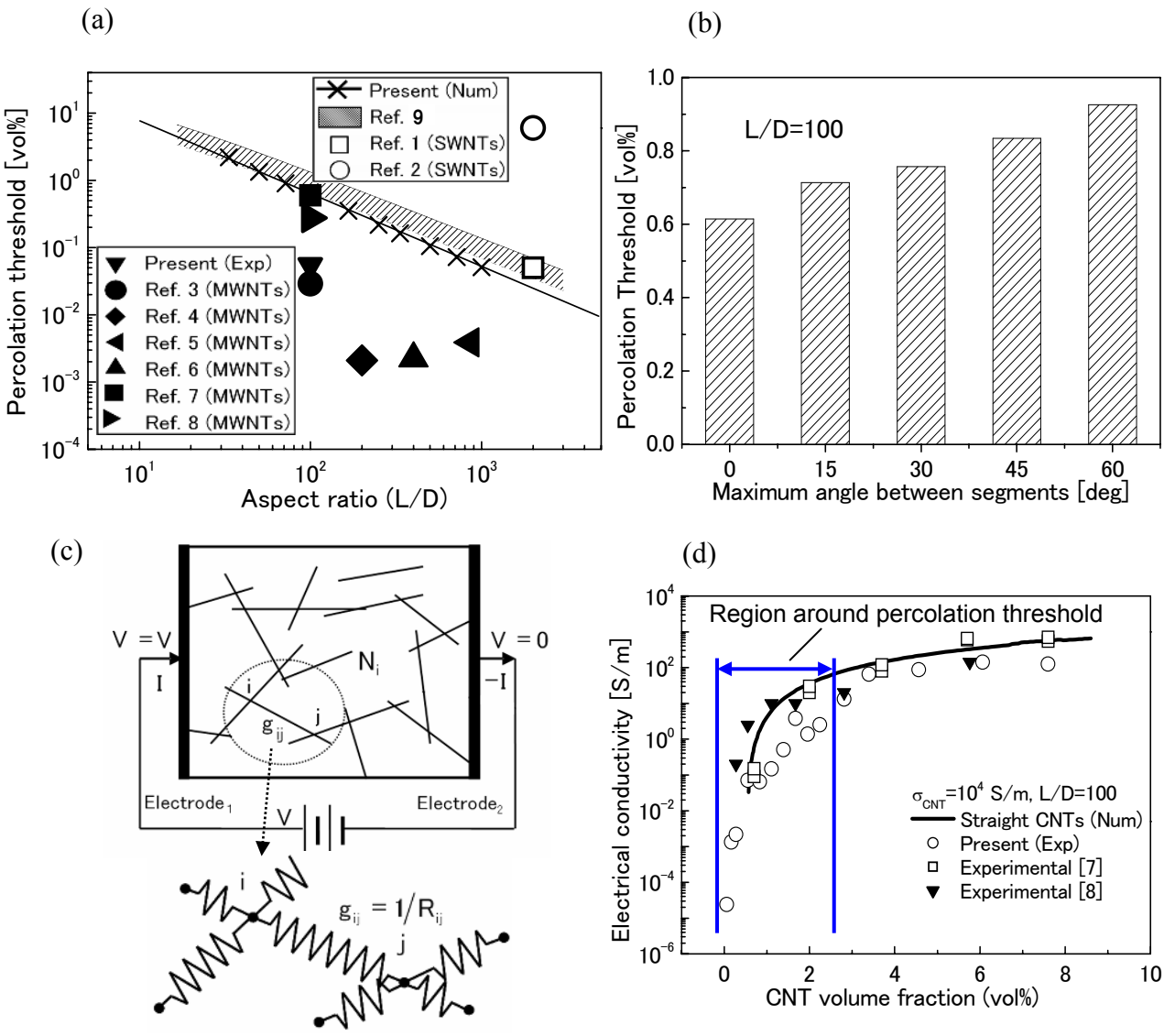
Fig. 1. (a) CNT distribution in a polymer experimental sample (SEM magnification ×2000). (b) CNT distributions in a polymer experimental sample (SEM magnification ×10,000). (c) A 3D representative element for uniform random distribution of CNTs in a polymer. (d) Numerical modelling of curved CNTs and two models for uniform random distribution of curved CNTs ($\theta_{max}=15^{o}$ and $\theta_{max}=60^{o}$) in a polymer.

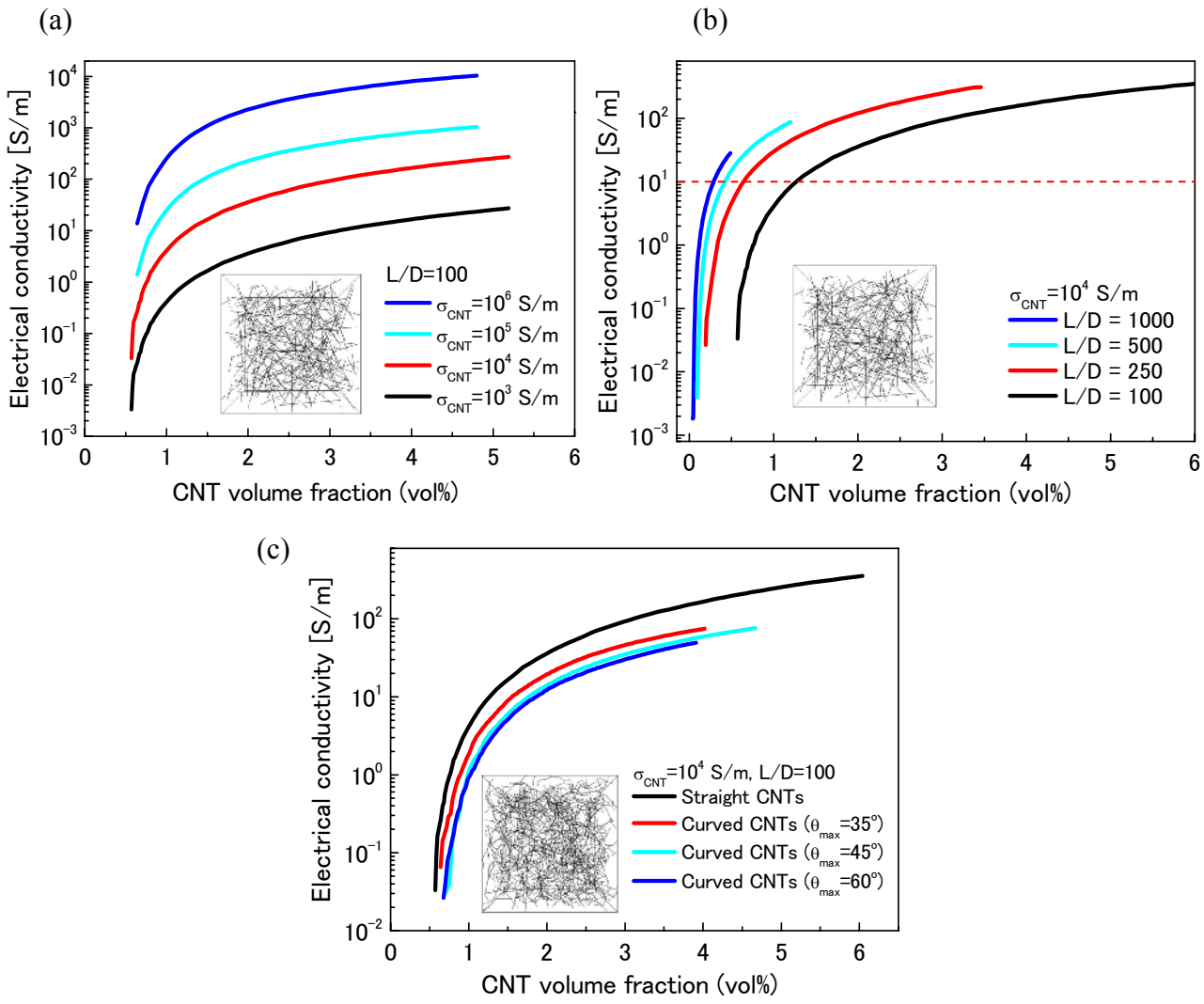
Fig. 2. (a) Comparison between the numerical and experimental percolation thresholds versus the aspect ratio of CNTs. (b) Influence of the shape of curved CNTs on the percolation threshold for L/D=100. (c) A 3D resistor model for uniform random distribution of straight CNTs in a polymer (only 2D model is shown). (d) Comparison between the numerical and experimental electrical conductivities.

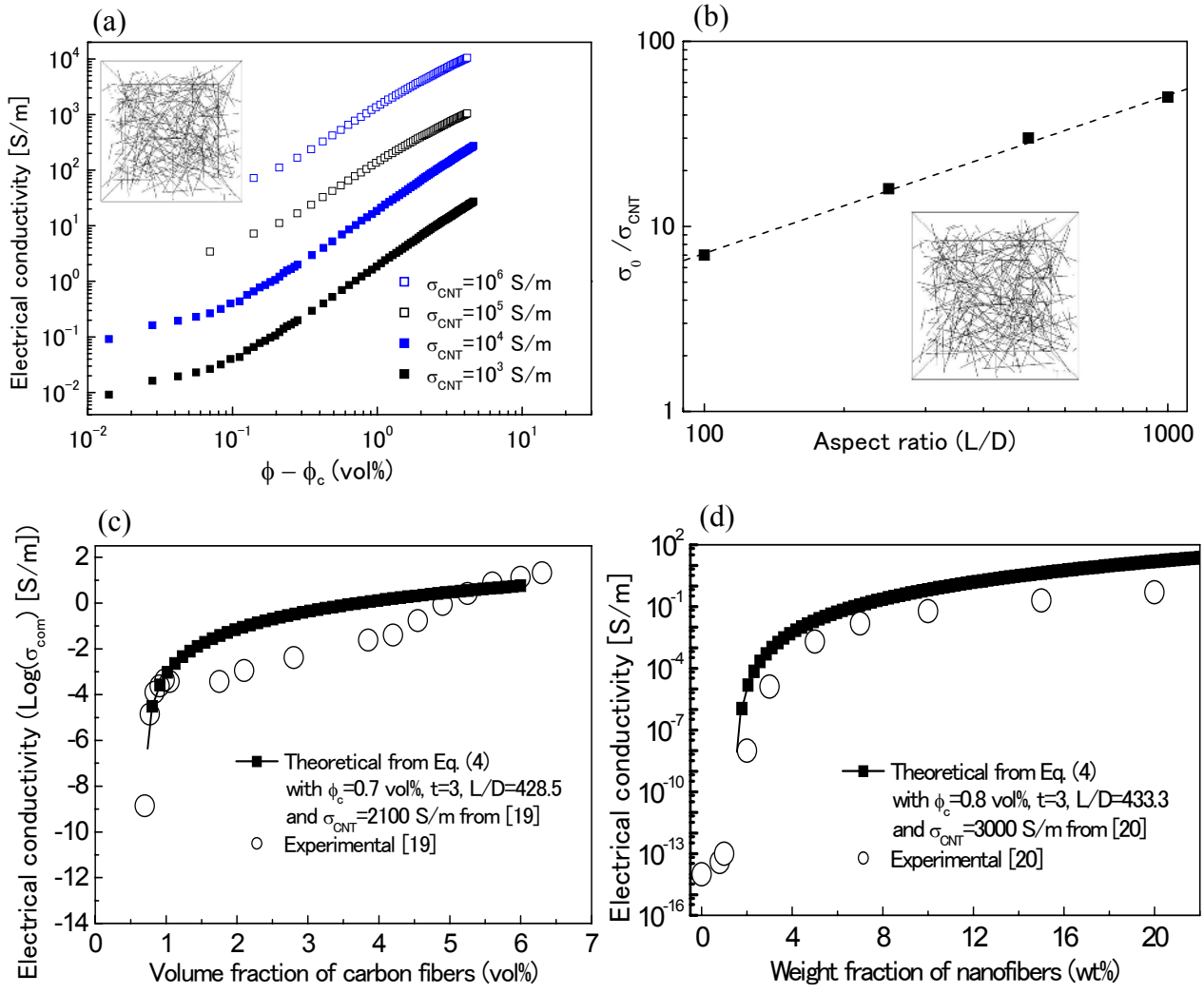
Fig. 3. (a) Influence of the electrical conductivity of CNTs on the electrical conductivity of nanocomposites. (b) Influence of the aspect ratio of CNTs on the electrical conductivity of nanocomposites. (c) Influence of the shape of curved CNTs on the electrical conductivity of nanocomposites.

Fig. 4. (a) Determination of the critical exponent t from various numerical results of different electrical conductivities of CNTs. (b) Determination of σ_0 from various numerical results of different aspect ratios of CNTs. (c) Comparison between the theoretical and experimental electrical conductivities of composites with short carbon fibers. (d) Comparison between the theoretical and experimental electrical conductivities of composites with nanofibers.


(a)
10μm
WD15.7mm 10.0kV x2.0k 20um
(b)
2μm
WD15.7mm 10.0kV x10k 5um
(c)
Ly
Lz
Lx
(d)
θmax
i+1
i+2…
i-1
i
θmax
Curved CNTs
θmax=15°
Curved CNTs
θmax=60°


(a)
Present (Num)
Ref. 9
Ref. 1 (SWNTs)
Ref. 2 (SWNTs)
Present (Exp)
Ref. 3 (MWNTs)
Ref. 4 (MWNTs)
Ref. 5 (MWNTs)
Ref. 6 (MWNTs)
Ref. 7 (MWNTs)
Ref. 8 (MWNTs)
Percolation threshold [vol%]
Aspect ratio (L/D)
(b)
L/D=100
Percolation Threshold [vol%]
Maximum angle between segments [deg]
(c)
V = V
I
V = 0
−I
N_i
i
j
g_ij
Electrode_1
Electrode_2
V
g_ij = 1/R_ij
(d)
Region around percolation threshold
Electrical conductivity [S/m]
σ_CNT=10^4 S/m, L/D=100
Straight CNTs (Num)
Present (Exp)
Experimental [7]
Experimental [8]
CNT volume fraction (vol%)


(a)
Electrical conductivity [S/m]
CNT volume fraction (vol%)
L/D=100
σCNT=10^6 S/m
σCNT=10^5 S/m
σCNT=10^4 S/m
σCNT=10^3 S/m
(b)
Electrical conductivity [S/m]
CNT volume fraction (vol%)
σCNT=10^4 S/m
L/D = 1000
L/D = 500
L/D = 250
L/D = 100
(c)
Electrical conductivity [S/m]
CNT volume fraction (vol%)
σCNT=10^4 S/m, L/D=100
Straight CNTs
Curved CNTs (θmax=35°)
Curved CNTs (θmax=45°)
Curved CNTs (θmax=60°)


(a)
Electrical conductivity [S/m]
$\phi - \phi_c$ (vol%)
$\sigma_{CNT}=10^6$ S/m
$\sigma_{CNT}=10^5$ S/m
$\sigma_{CNT}=10^4$ S/m
$\sigma_{CNT}=10^3$ S/m
(b)
σ_0/σ_{CNT}
Aspect ratio (L/D)
(c)
Electrical conductivity (Log(σ_{com}) [S/m])
Volume fraction of carbon fibers (vol%)
Theoretical from Eq. (4)
with ϕ_c=0.7 vol%, t=3, L/D=428.5
and σ_{CNT}=2100 S/m from [19]
Experimental [19]
(d)
Electrical conductivity [S/m]
Weight fraction of nanofibers (wt%)
Theoretical from Eq. (4)
with ϕ_c=0.8 vol%, t=3, L/D=433.3
and σ_{CNT}=3000 S/m from [20]
Experimental [20]