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PREDICTION OF ELECTRICAL CONDUCTIVITY OF PPLYMER FILLED BY CARBON NANOTUBES

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Abstract

In this research, we propose a 3 dimensional (3D) numerical model to predict the electrical properties of insulating polymer filled by carbon nanotubes (CNTs). In this model, with the assumption of randomly distributed CNTs in polymers, the percolation threshold is predicted at the volume fraction of CNTs when a complete conductive path connected by some CNTs is built up. Furthermore, a 3D resistor network model for electrical conduction problems of composites is proposed, in which Kirchhoff's current law is used to build up the system equations at different nodes in the network connected by CNTs, and then Ohm's law is used to predict the macroscopic electrical conductivity of composites. Also, the experiments are performed. The present experimental results plus some previous experimental results by other researchers are employed to verify the numerical results. Finally, a highly sensitive strain sensor is made by using this new nano-composite with experimental and numerical verifications.

1 Introduction

Carbon nanotubes (CNTs) of high aspect ratio possess excellent electrical conductivity. Therefore, with a little amount of CNTs, which are dispersed in insulating polymers, it is possible to produce the nano-composites with high electrical conductivity. This kind of conductive CNT/polymer composites can be applied to various fields, such as highly sensitive strain sensors, electromagnetic interference materials and etc. Generally, with the gradual increase of CNTs filled into an insulating polymer, at a specified volume fraction of CNTs, the electrical conductivity of composites will suddenly increase remarkably. This process is called as percolation process. The specified volume fraction of CNTs where the electrical conductivity increases remarkably is called as percolation threshold. After the sudden increasing stage of electrical conductivity of composites around the percolation threshold, the electrical conductivity of composites will increase very slowly, and finally will tend to be constant. Until now, there have been some studies on the electrical properties of this new nano-composite [1-8]. However, there has been no numerical model or study, which evaluates the percolation threshold or electrical behaviors of composites after the stage of percolation threshold. In the present work, a 3D numerical model for predicting the behavior of electrical conductivity in polymers filled by CNTs is proposed, which has been verified by many experimental results.

2 Theory of numerical method

The whole percolation process for the polymer filled by CNTs gradually is shown in Fig. 1. Although our model is a complete 3D model, for the clear observation, only 2D model is shown in Fig. 1. For the state *a* in Fig. 1, the electrical conductivity of composites is very low due to the low density of CNTs in polymer. With the increase of randomly distributed CNTs, the distances among CNTs becomes smaller gradually as shown in the state *b*. In this state, although a complete electrically-conducting path to transfer electric charges has not been formed, there may be a very weak electrical conductivity due to the existence of possible tunnel effect. In the state *c*, a complete electrically-conducting path is formed, which is connected by some CNTs. At this stage, the electrical conductivity of composites will increase remarkably. The volume fraction of CNTs corresponding to this state can be thought of as the percolation threshold. By further adding CNTs into polymer, a lot of electrically-conducting paths connected by CNTs can be built up like the state *d* as shown in Fig. 1. The electrical

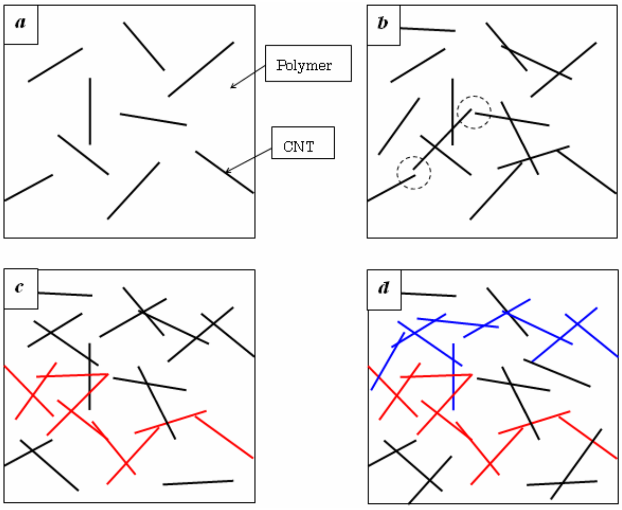


Fig. 1. Percolation process of polymer filled by CNTs

conductivity of composites will increase further, but finally tend to be constant gradually.

2.1 Percolation threshold

In this study, to predict the electrical properties of this nano-composite, we consider a 3D representative element with uniform random distribution of CNTs both in positions and orientations shown in Fig. 2. The union/find algorithm [9] was adopted to detect the first complete conductive path connecting two sides of 3D cube (red line in Fig. 2), and then the percolation threshold can be determined using the total volume of CNTs. The CNTs are considered as capped cylinders. For various lengths of CNTs, i.e. L ranging from 3.5 μm to 7.5 μm and various aspect ratios (L/D), it was found that the dimensions of $Lx/L=Ly/L=10$ and $Lz/L= 2.0$ of the 3D cube in Fig. 2 can yield sufficiently stable and isotropic results as shown in Fig. 3. Finally, a Monte-Carlo procedure of 100 simulations has been performed to obtain the average percolation threshold for one volume fraction of CNTs.

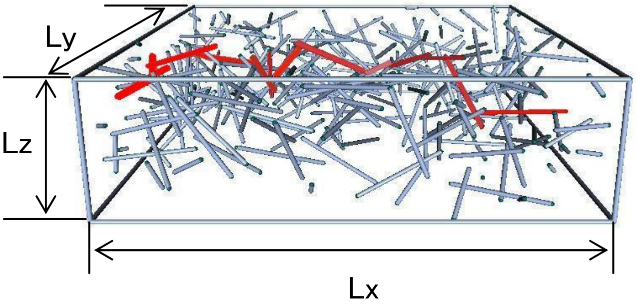


Fig. 2. Schematic of CNTs dispersion

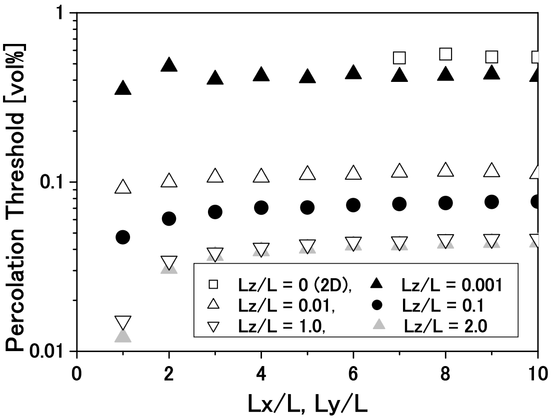


Fig. 3. Verification of convergence of unit element

2.2 Electrical conductivity of composites

In Fig. 4, a 3D resistor network [11], which contains randomly distributed CNTs in polymer, has been employed to predict the electrical conductivity of composites when the volume fraction of CNTs is higher than the percolation threshold. In Fig. 4, for the node i, which connects at least two CNTs, there is the electrical potential V_i, the electrical current can be expressed as:

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

where N is the total number of other nodes which are connected with the node i, g_{ij} the electrical conductance between ij. The potentials of electrodes of 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, from Kirchhoff's current law, the sum of all currents on one node is zero. From the above conditions and Eq. (1), the equations including all nodes can be set up. By solving these equations using ICCG method, we can obtain the total current I, and then the

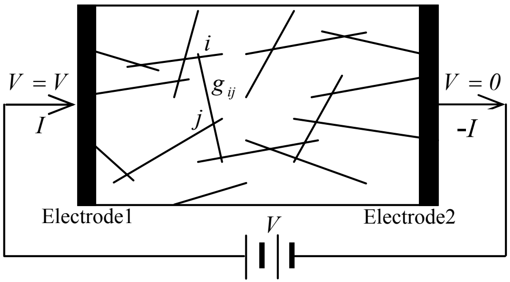


Fig. 4. Random network of resistors

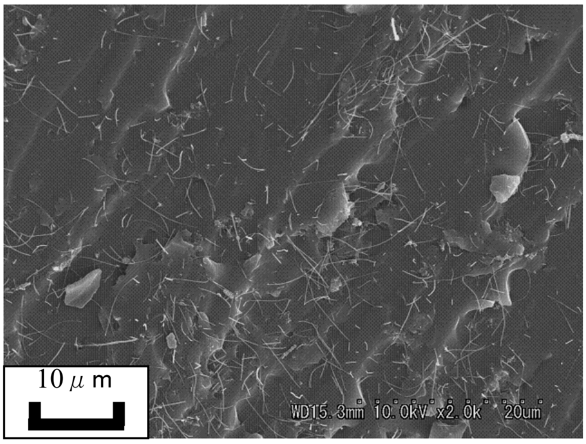
electrical conductivity of composites can be obtained from Ohm's law as follows

$$\sigma = \frac{I}{V}\frac{L_{com}}{S} \qquad (2)$$

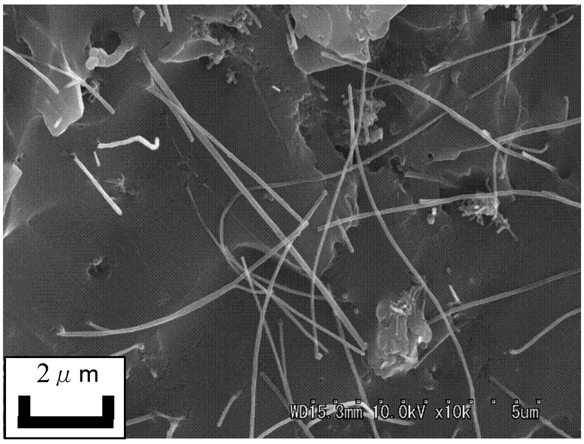
where L_{com} is the length between two electrodes, S the section area of electrode.

3 Experiments

We have performed the experiments using multi-walled carbon nanotubes (MWNTs) of high purity, which are provided by Nano Carbon Technologies Co. (NCTC) in Japan. The average diameter and average length of CNTs are 50 nm and 5μm, respectively. In our experiments, we have investigated the influences of various factors in the fabrication process on the electrical properties of nano-composites. A ruptured cross-section for the sample of 2.0wt% MWNTs was observed using a Scanning Electron Microscope (SEM) as shown in Figs 5(a) and 5(b), where the homogeneous dispersion of CNTs in polymer without obvious aggregates can be identified clearly. From our experimental results, we have found that the electrical conductivity may be 100 times different in the various samples with the same volume fraction of CNTs. Although a further observation for wider area of specimen is needed, it was found that there is almost no obvious aggregate in our various samples by different processes. Moreover, it was found that the following factors, which can remarkably decrease the electrical conductivity of nano-composites: 1) a too high mixing speed with a long time mixing process resulting in the significant increase of the mixture temperature; 2) a procedure in which we mix epoxy with MWNTs first, and then add curing agent for mixing again; 3) a long curing process. All of these factors may lead to a same result, i.e., undesirable coating of polymer on CNTs, which embarrasses the transfer of electrical charges among CNTs. Therefore, aggregates seem to be not a key factor to influence the electrical conductivity of nano-composites when using MWNTs as fillers. Finally, for our experimental specimen, the following process is employed. Initially, an epoxy (bisphenol-F resin) and an epoxy curing agent (polyaminoamides) are mixed using a planetary mixer with 2000 rpm for 30 second. Then MWNTs are added into the mixture, which is mixed again with 2000 rpm for 1 minute. After the mixing process, the liquid is cast in a silicon mold to form the nano-composites, which is cured in a vacuum oven at 80°C for 3 hours.



5a) SEM image of 2000 times magnification



5b) SEM image of 10000 times magnification

Fig. 5 SEM image for nano-composites

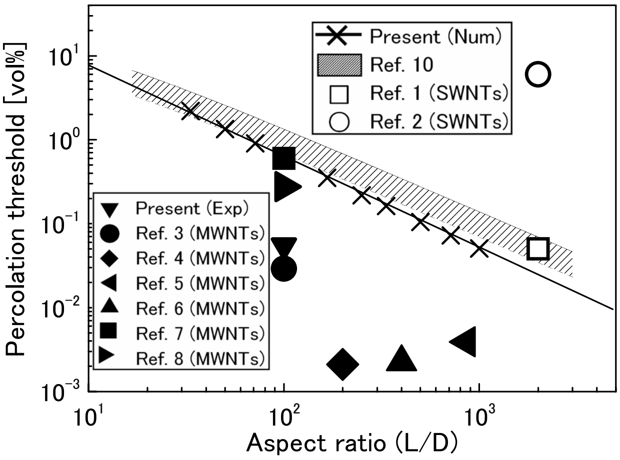


Fig. 6. Comparison of various results of percolation threshold

4 Results and discussions

4.1 Results of percolation threshold

For the case of straight CNTs of the length of 5.0 μm, the present average result of a Monte-Carlo procedure of 100 simulations, which is compared with various experimental results and the result of an empirical extruded volume approach [10], is shown in Fig. 6. From it, we can find that there is a large scattering in experimental results, which may be caused by the different properties of phase materials and different manufacturing processes. We note that the same MWNTs (NCTC) were practically used in other two experiments [7, 8]. In fact, as shown in Fig. 5b, CNTs are not perfect straight practically. The modeling of the curved CNTs is shown in Fig. 7. We divide each CNT into 10 segments. The angle in 3D space between two segments can randomly vary within a circular cone with top angle θ_{max}. For an example of curved CNTs model shown in Fig. 8(a), the influence of θ_{max} is shown in Fig. 8(b), where the percolation threshold increases as θ_{max} increases.

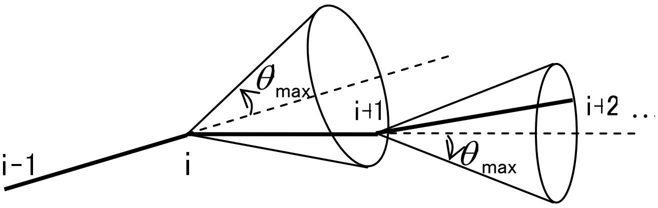
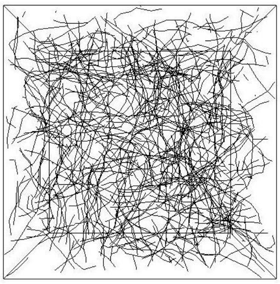
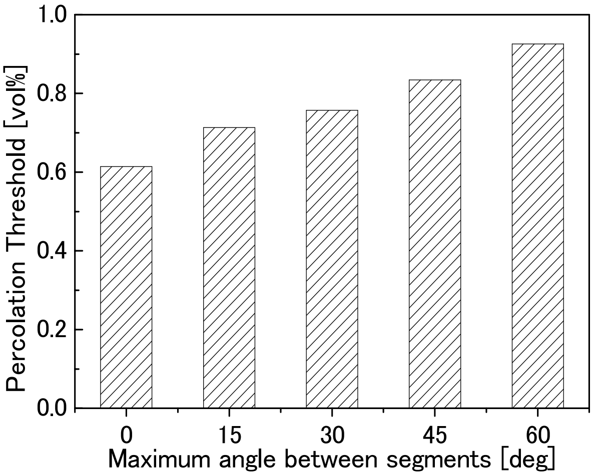


Fig. 7. Modeling of curved CNTs



8a) Model of curved CNTs with θ_{max}=30°



8b) Result of percolation threshold versus θ_{max}

Fig. 8. Influence of curved CNTs on percolation threshold

4.2 Results of electrical conductivity

Generally, the electrical conductivity of MWCNT, i.e., σ_{CNT}, ranges from 5×10^3 to 5×10^6 S/m. When CNTs possess L/D and σ_{CNT} as 100 and 10^4 S/m, respectively, the comparison of numerical and experimental results (the same L/D of CNTs) [7, 8] are shown in Fig. 9. This figure demonstrates that the numerical results agree with the experimental results very well. The influence of curvature of CNTs is insignificant. We have also numerically investigated the influence of CNTs aggregates. It was found that serious aggregates of CNTs may significantly increase the percolation threshold, but reduce the electrical conductivity. However, as stated previously, aggregates are not important for MWNTs, the results therefore are omitted.

4.3 An empirical percolation theory

Usually, the traditional percolation theory can be described as: $\sigma_{com} = \sigma_0\left(\phi - \phi_c\right)^t$, where t is the critical exponent, ϕ the volume fraction of filler, ϕ_c the percolation threshold, and σ_0 is a parameter, where ϕ_c and σ_0 are usually determined experimentally. Based on the above illustrated results, it is possible for us to establish a simple yet reliable percolation theory. By virtue of our numerical approach, for an ideal state of uniform random distribution of straight CNTs in polymer, we have investigated the electrical conductivity of

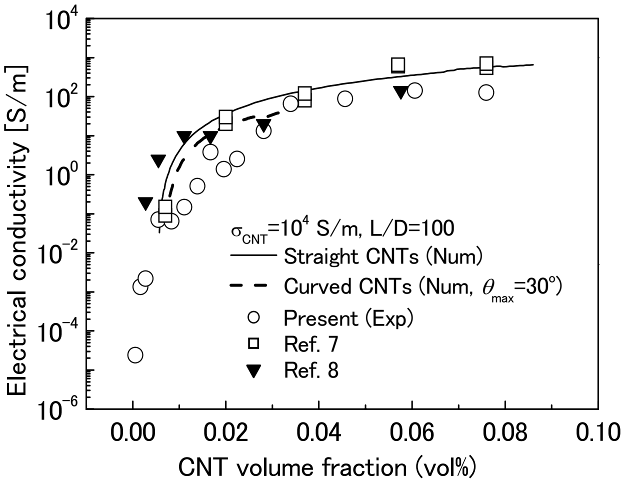
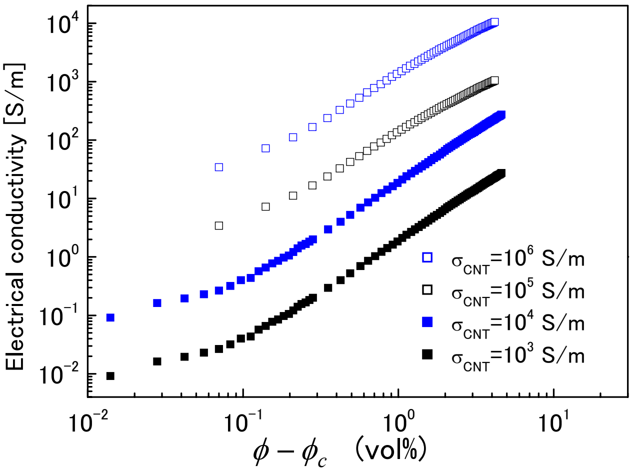
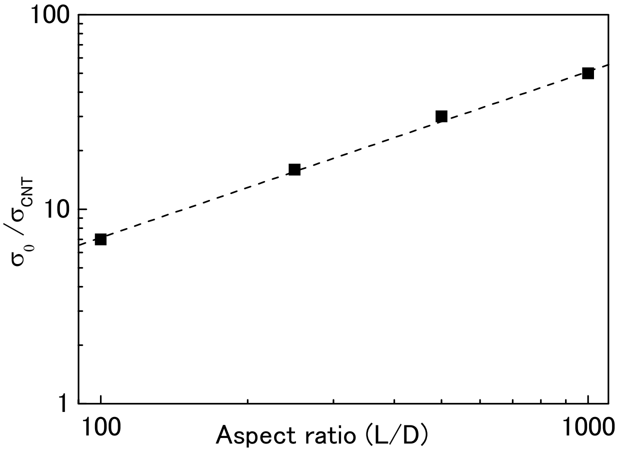


Fig. 9. Comparison of numerical results with various experimental results.



10a) Results of electrical conductivity of nano-composites for various electrical conductivities of CNTs



10b) Relationship between σ_{CNT} and σ_0

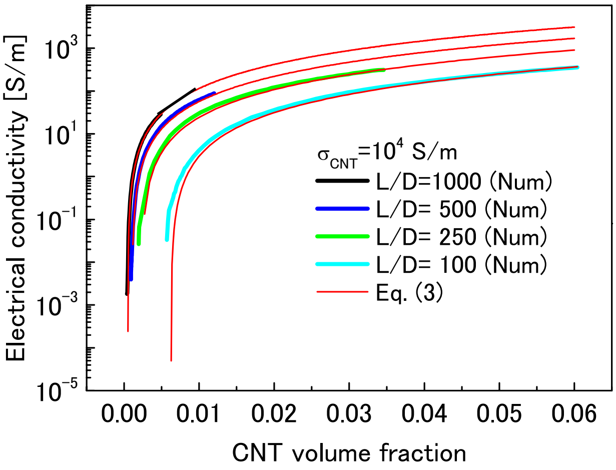
Fig. 10. Determination of σ_0 in traditional percolation theory

CNT/polymer nano-composite by considering various electrical conductivities of CNTs, i.e., σ_{CNT} (10^3 S/m~10^5 S/m) as shown in Fig. 10(a) and various L/D (100~1000) as shown in Fig. 10(b). By using the traditional percolation theory, various numerical results and the least-squares fitting, we have identified that the average value of t is 1.8 (see Fig. 10(a)), which is universal depending on the dimensionality of the system. In a 3D system, the expected value is 2. From Fig. 6, we can easily find that the relationship between the percolation threshold and L/D of CNTs. Moreover, from our various numerical results, we have surprisingly found that σ_0 is a parameter, which not only depends on σ_{CNT}, but also on L/D as shown in Fig. 10(b).

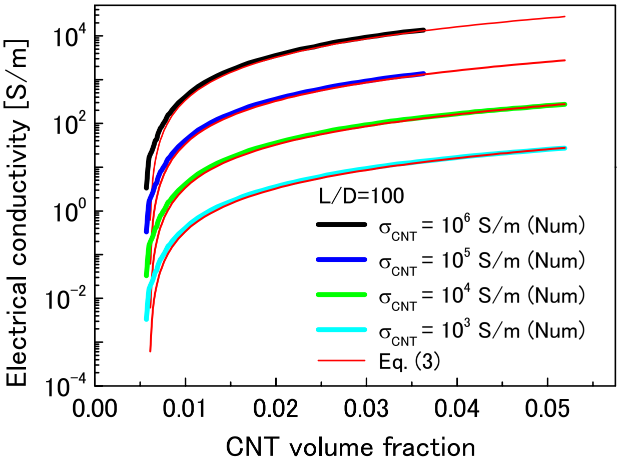
Finally, the traditional percolation theory can be re-cast into the following simple form:

$$\sigma_{com} = \sigma_{CNT} \cdot 10^{0.85\{\log(L/D)-1\}} \cdot \left\{\phi - (L/D)^{-1.1}\right\}^{1.8}$$
(3)

We note that the percolation threshold, i.e., $(L/D)^{-1.1}$ is only valid for fillers of high L/D, such as over 50. This model is of great significance by which the macroscopic electrical conductivity can be predicted simply if we know σ_{CNT} and L/D of CNTs. The theoretical predicted results by Eq. (3) are compared with those obtained numerically as shown in Figs 11(a) and 11(b) for various aspect ratio of CNTs and various electrical conductivities of CNTs. This model is also useful for predicting the electrical



11a) Comparison of theoretical results by Eq. (3) and numerical results for various aspect ratio of CNTs



11b) Comparison of theoretical results by Eq. (3) and numerical results for various electrical conductivities of CNTs

Fig. 11. Verification of proposed percolation theory by numerical results

properties of traditional composites using short-fibers of high L/D as fillers.

5 Applications as strain sensor

To study the properties of this nano-composites working as a strain sensor, our previous 3D resistor network is further extended for considering the tunnel effect on the electrical conductivity of CNT/polymer nano-composite. As shown in a SEM image for our nano-composite in Fig. 12, there are a lot of situations where there is a very short distance among CNTs. The tunnel effect means that the electrical charges can still be transferred between two CNTs without contact, if the distance between them is sufficiently small. For the tunnel effect, as shown in Fig. 13, we can approximately evaluate the resistance between two separated CNTs as:

$$R_{tunnel} = \frac{V}{AJ} = \frac{h^2 d}{Ae^2\sqrt{2m\lambda}} \exp\left(\frac{4\pi d}{h}\sqrt{2m\lambda}\right) \quad (4)$$

where J is tunnel current density, V the electrical potential difference, e the quantum of electricity, m the mass of electron, h the Planck's constant, d the barrier width (distance between CNTs), λ the height of barrier (epoxy), and A the cross-sectional area of tunnel (using that of CNTs).

When this nano-composite is under the prescribed strain, we reconstruct our 3D resistor network by considering the rigid movement of CNTs in composite. The stretch or compressive deformation in CNTs is neglected due to its much higher Young's modulus than that of epoxy (around 300 times higher for 1 TPa Young's modulus of CNTs and 3 GPa Young's modulus of epoxy). We have investigated the influence of tunnel effect. It was found that the tunnel effect leads to the increase of electrical conductivity, but its effect is limited to a very narrow band around the percolation threshold. Usually, for the volume fraction of CNTs, which is close to the percolation threshold, it is possible to create the highly sensitive sensors. In our numerical simulations, we have found that without considering the tunnel effect, our result cannot reflect the resistance change of nano-composite under the prescribed strain. Finally, this CNT/polymer nano-composite is fabricated as a strain sensor of thickness of around 100 μm. As shown in Fig. 14, this sensor is attached on the surface of a beam. Also, the traditional strain gage is employed. The experimental measured results for the resistance change of this new-type sensor is shown in Fig. 15, where the gage ratio of the traditional strain sensor is K=2. The numerical results are shown in Fig. 16. Both figures show that the sensitivity of this new-type sensor is much higher than that of the strain gage. With the decrease of volume fraction of CNTs, which gradually close to the percolation threshold, the sensitivity becomes higher. Moreover, our

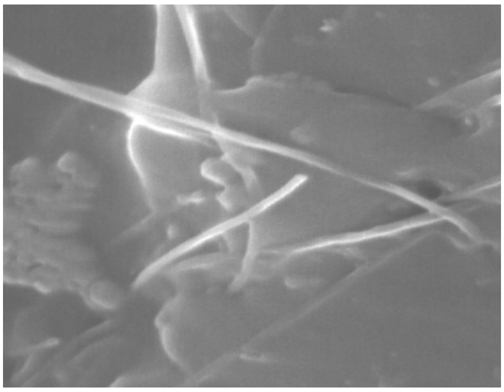


Fig. 12. A SEM image for non-contacting CNTs

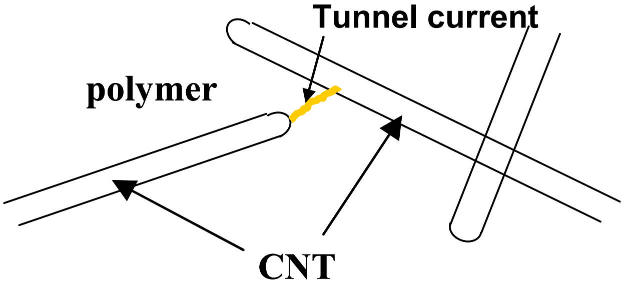


Fig. 13. Modeling of resistance for tunnel effect

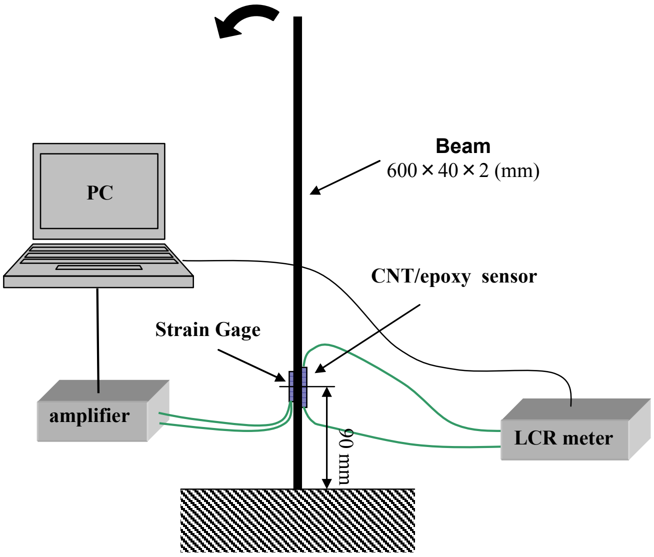


Fig. 14. Experimental setup for measuring resistance change

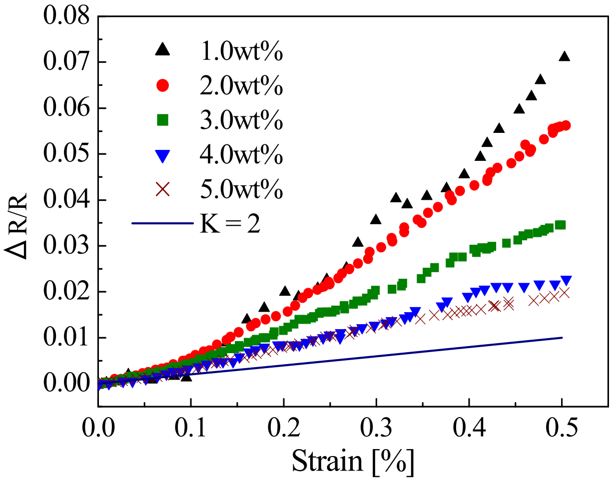


Fig. 15. Experimental results

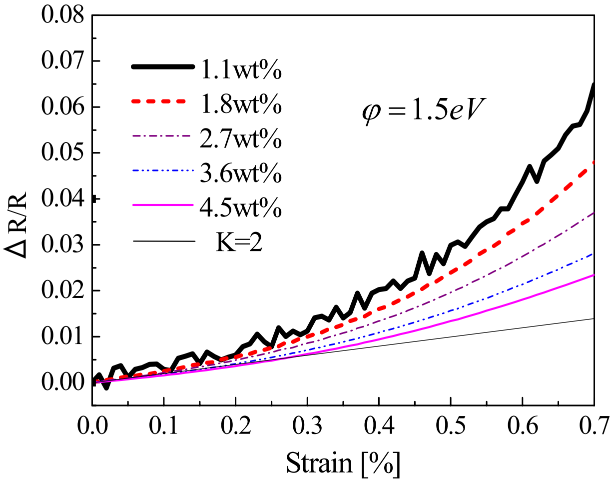


Fig. 16. Numerical results

numerical results agree well with the experimental results. The modelling of tunnel effect is very important in our numerical simulations. Without this tunnel effect, we cannot identify the change of resistance in our numerical results.

6 Conclusions

The electrical behaviour of nano-composites of polymer filled by CNTs is very complex practically, which strongly depends on the properties of phase materials and manufacturing process. The undesirable coating of polymer on CNTs formed in manufacturing process may be one of the key factors controlling the macroscopic electrical performances of nano-composites. Through a powerful numerical model, the electrical properties of nano-composites can be investigated effectively. Reliable numerical simulations plus corresponding experimental results finally help us establish a simple empirical formula for predicting the electrical properties of nano-composites with sufficient accuracy. Moreover, this nano-composite is applied as a highly sensitive sensor. Both experimental and numerical results verify its high sensitivity. An extended numerical resistor network by considering the tunnel effect is effective to predict the performance of this sensor.

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