Abstract

Carbon nanotube (CNT) has good electrical conductivity. Addition of a few percentages of carbon nanotube to polymer yields electrical conductivity but hardly affects the mechanical properties of polymer. This conductive polymer may be useful for sensing applications such as strain sensors and chem-resist sensors. Many researchers have reported on the electrical conductivity, but the electrical resistance change under strain of the carbon nanotube composites is not fully investigated.

In this study, the electrical resistance change under strain of CNT/flexible-epoxy composites was investigated experimentally and then the feasibility as large-strain sensors was demonstrated. The mechanism of the electrical resistance change under strain of CNT/polymer composites was discussed by using electrical circuit simulation based on a percolation network model and tunnelling effect between CNTs.

1 Introduction

It is well known that carbon-nanotube/polymer composites have electrical conductivity if the volume content is less than a few percent [1]. This conductive polymer may be useful for sensor applications such as strain sensors and chem-resist sensors. Many researchers have reported on the electrical conductivity, but the electrical resistance change due to strain, i.e. piezoresistivity, of carbon-nanotube/polymer composites is not fully investigated. In this study, the piezoresistivity of carbon-nanotube/flexible-epoxy composites was investigated and then the feasibility as large-strain sensors was demonstrated. The mechanism of the electrical resistance change under strain of CNT/polymer composites was also discussed by using electrical circuit simulation based on a percolation network model and tunnelling effect between CNTs.

2 Experimental

2.1 Measurement of Piezoresistivity

In this study, Vapor Grown Carbon Fiber (VGCF) supplied by Showa Denko K.K. was used as filler. VGCF is a kind of multi-walled carbon nanotube. The diameter is 150 nm, the length is 10-20μm and the electrical resistivity is $10^4$ Ωcm. Flexible-epoxy (Nippon Pelnox Corporation ME-113/XH-1859-2) was used as matrix. VGCF and flexible-epoxy was mixed by a planetary mixer and co-cured with aluminum electrodes at 80°C for 3hr. The specimen configuration is shown in Fig. 1. Quasistatic tensile tests were carried out to measure strain and the electrical resistance. Strain was measured by a clip gauge attached to the aluminum blocks, and the electrical resistance was measure by the 2-prove method using an LCR meter.

Measured electrical resistance changes are shown in Fig. 2. The horizontal axis is nominal tensile strain of VGCF/epoxy composite, and the vertical axes are the electrical resistance change (Fig.1(a)) and the measured electrical resistance normalized by the initial resistance (Fig.1(b)). The electrical resistance changes are significantly nonlinear and larger than that of metal (Gauge factor $K=2$). The fact that log-scale plots are linear represents the electrical resistance change ratio is an exponential function of strain. In addition, the nonlinearity decreases with increase of the weight fraction of VGCF.
2.2 Sensor Application

The feasibility of sensor application is demonstrated by using a patch type strain sensor. The sensor fabrication is basically the same as that described in Sec.2.1. The differences are the dimensions, the weight fraction of VGCF (6wt%) and the kind of electrodes, i.e. copper foils instead of aluminum blocks. The sensor and specimen configurations are shown in Fig. 3. Quasistatic tensile tests were carried out to measure strain and the electrical resistance. Strain was measured by using image capturing, and the electrical resistance was measure by the 2-probe method using an LCR meter.

The electrical resistance change under strain is shown in Fig.4. Up to 40 % of strain can be measured by using the composite patch sensor.

3 Mechanism of Nonlinear Piezoresistivity

The mechanism of the electrical resistance change under strain of CNT/polymer composites is discussed by using electrical circuit simulation based
on a percolation network model and tunneling effect between CNTs.

3.1 Tunneling resistance change under strain

A carbon-nanotube is a short fiber, thus the electrical conduction of carbon-nanotube/polymer composites is achieved by forming a network of carbon-nanotubes in polymer. The electrical resistance of carbon-nanotube/polymer composite consists of the electrical resistance of carbon-nanotube itself and contact resistance between carbon-nanotubes which results from tunneling current, i.e. tunneling resistance. Since the electrical resistance of carbon-nanotube itself is considerably low, the tunneling resistance is dominant over the resistance of carbon-nanotube/polymer composites. Consider the tunneling area as shown in Fig.5.

![Fig.5 Distance change between CNTs](image)

The tunneling resistance $r$ is described as [2, 3]

$$r = \frac{h^*s}{A e^{2/2m\phi}} \exp\left(\frac{4\pi e^2 \sqrt{2m\phi}}{h}\right)$$

(1)

where $h$ is Plank’s constant, $s$ is the distance between fibers, $A$ is the effective area of conduction, $e$ is an elementary charge, $m$ is the mass of electron, $\phi$ is a work function of carbon-nanotube. The tunneling resistance change under strain is derived from equation (1).

$$\frac{r_1}{r_0} = \frac{s_1}{s_0} \frac{A_0}{A_1} \exp\left(\frac{4\pi e^2 \sqrt{2m\phi}}{h}(s_1 - s_0)\right)$$

(2)

where subscript 0 and 1 represent unstrained and strained conditions, respectively. $s_1$ is described as

$$s_1 = s_0\left(1 + \epsilon(c_0^2 \theta - \nu \sin^2 \theta)\right)$$

(3)

where $\epsilon$ is an angle of the conduction path and $\nu$ is Poisson’s ratio. By substituting equation (3) into equation (2), we can obtain

$$\frac{r_1}{r_0} = \frac{s_1}{s_0} \frac{A_0}{A_1} \exp\left(\frac{4\pi e^2 \sqrt{2m\phi}}{h}(s_1 - s_0)\right)$$

(4)

Equation (4) indicates that tunneling resistance increases exponentially with increase of strain $\epsilon$, and the length of conducting path $s_0$ affects the nonlinearity of tunneling resistance change. This implies that the piezoresistivity of carbon-nanotube/polymer composite is an exponential function of strain, and the average distance of carbon-nanotubes that depends on the weight fraction affects the nonlinearity of the electrical resistance change.

3.2 Circuit Simulation

In order to discuss the mechanism of piezoresistivity, electrical circuit simulation was carried out. Circuit model for simulation is shown in Fig.6. We assumed that the formation of conductive network in resin obeys the percolation theory, the contact resistance between CNTs results form tunneling effect, and the resistance of CNT itself is much smaller than the contact resistance.

![Fig.6 Circuit model](image)

Table 1 shows the parameters for simulation. Simulated electrical resistance changes under uniaxial loading (log-scale) are shown in Fig.7. Nonlinear piezoresistivity and the dependency of gauge factor on volume fraction appear in simulation. This implies that the nonlinear behavior is caused by the combination of tunneling effect between CNTs.
and the change of the conductive network, and that the
decrease of the electrical resistance change rate
with increase of the weight fraction of CNT is
caused by the nature of the percolation network.

Table 1 Parameters for simulation

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plank’s constant</td>
<td>$h = 6.6261 \times 10^{-34}$ [Js]</td>
</tr>
<tr>
<td>Elementary charge</td>
<td>$e = 1.6022 \times 10^{-19}$ [C]</td>
</tr>
<tr>
<td>Mass of electron</td>
<td>$m = 9.109 \times 10^{-31}$ [kg]</td>
</tr>
<tr>
<td>Distance of CNF</td>
<td>$0.34[\text{nm}] &lt; d &lt; 1[\text{nm}]$ (random value)</td>
</tr>
<tr>
<td>Area of conduction</td>
<td>$A = (150[\text{nm}])^2$</td>
</tr>
<tr>
<td>Barrier height*</td>
<td>$\phi = 4.3$ [eV]</td>
</tr>
<tr>
<td>Poisson’s ratio</td>
<td>$\nu = 0$</td>
</tr>
<tr>
<td>Angle of CNF gap</td>
<td>$0&lt;\theta&lt;\pi$ (random value)</td>
</tr>
<tr>
<td>The max number of resistance $N_T$</td>
<td>80000</td>
</tr>
</tbody>
</table>

*Barrier height is assumed to be the work function of vacuum [4]

![Fig.7 Simulated electrical resistance change under loading](image)

5 Conclusions

Strain sensing by using carbon-nanotube
/flexible-epoxy was investigated. Up to 40% of
strain can be measured by using the composite patch
sensor. The mechanism of nonlinear piezoresistivity
was also discussed based on the tunneling resistance
and the percolation network.

References