

# The Electrical Property of Polymer Matrix Composites Added Carbon Powder

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**Abstracts** The electrical property of polymer matrix composites with added carbon powder is studied based on the temperature dependency of the conduction mechanism. The temperature coefficient of the resistance of the polymer matrix composites below the percolation threshold ( $x$ ) changed from negative to positive at  $0.20 < x < 0.21$ ; this trend decreased with increasing of the percolation threshold. The temperature dependence of the electrical property (resistivity) of the polymer matrix composites below the percolation threshold can be explained by using a tunneling conduction model that incorporates the effect of the thermal expansion of the polymer matrix composites into the tunneling gap. The temperature coefficient of the resistance of the polymer matrix composites above the percolation threshold has a positive value; its absolute value increased with increasing volume fraction of carbon powder. By assuming that the electrical conduction through the percolating paths is a thermally activated process and by incorporating the effect of thermal expansion into the volume fraction of the carbon powder, the temperature dependency of the resistivity above the percolation threshold can be well explained without violating the universal law of conductivity.

**Key words** percolation threshold, polyethylene, carbon powder, composites, resistivity.

## 1. Introduction

The composites of insulating matrix (polyethylene) and conducting phase (carbon powder) are widely applied for switching elements, conductive paint and others due to large gap of resistance value.<sup>1,2)</sup> Here, the changes of conductivity ( $\sigma$ ) and dielectric constant ( $\epsilon_r'$ ) which are based on carbon powder addition content are given by  $\sigma \propto (V_c - x)^t$  and  $\epsilon_r' \propto (V_c - x)^s$  with the respective critical exponents  $t$  and  $s$  as variables that are absolute values ( $|V_c - x|$ ) of what percolation threshold ( $x$ ) is subtracted from the volume fraction ( $V_c$ ) of carbon powder.<sup>3,4)</sup> In these equations,  $P_t$  means  $V_c$  of which the resistivity ( $\rho$ ) of polymer matrix composites is transferred from its sharp decrease to gradual decrease in accordance with the increase of carbon powder addition content. At this time, the electric field dependence of current changes from non-ohmic to ohmic.<sup>5)</sup> Although the huge cohesive bodies of carbon powder are formed in case of being less than  $x$ , a percolation path connecting between the con-

ducting phases is not made up. In this type of polymer matrix composites below  $x$ , the electric field dependence of current is explained by the tunneling conduction model.<sup>6)</sup> As the critical exponent of resistivity in the composites below  $x$  is larger than 1, and that of dielectric constant indicates 1, the temperature dependence of conductivity is explained by applying the effective medium approximation theory to the dielectric properties of these composites.<sup>7)</sup> The conductivity of polymer matrix composites higher than  $x$  is derived almost entirely from a percolation path. The changes in the conductivity of the polymer matrix composites according to the added carbon powder above  $x$  can be expressed as  $\sigma \propto (V_c - x)^2$ .<sup>5)</sup> Here, the critical exponent 2 is obtained through the infinite expansion of changing patterns in conductivity of a finite resistor network by using a scaling function, which is called the universal law of conductivity.<sup>3,4)</sup> Thus, in obtaining the critical exponent 2 as a result of experiments, such materials satisfy the universal law of conductivity.

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This research aims to examine the electrical property of carbon powder added polyethylene matrix composites.

## 2. Experimental Procedure

The polymer used as a matrix was a high density polyethylene(Mitsubishi Chemical Co., HDPE) and the carbon powder of Asahi-Thermal(Asahi Carbon Co.) of which the absorbed water was removed by heating it in air at 373 K for 3.6 ks.

As the specimens manufacture and their measurement procedures were specified in the previous study,<sup>8)</sup> here they are briefly explained. After measuring the mixture of polyethylene matrix and carbon powder, based on the measurement of their equivalent proportions, was carried out at 413 K for 0.9 ks. The composites were slowly cooled down to 353 K, and cut into 10 mm-sized pieces. These specimens for resistivity measurement were moulded by heating the pieces obtained in the processes above at 423 K for 0.6 ks with a heating presser. Sheet type specimens were manufactured in the thickness range of 0.05~2 mm; as the volume fraction of carbon powder is low, the composites were made thin in case of high resistivity, and thick in the opposite case.

Copper codes of 3 mm $\varnothing$  in diameter were used as electrodes. The volume fraction of carbon powder was obtained by using the specific gravity of HDPE (0.954 g/cm<sup>3</sup>) and carbon powder (1.8 g/cm<sup>3</sup>). It was used that the value of resistivity was calculated after connecting with a direct current voltage of 30 minutes with a vibrating reed electrometer (Taketairken Co., TR-84 type) for resistance in case of being above 20 M $\Omega$  in air. On the other hand, in case of being below 20 M $\Omega$ , a digital multi-electrometer (Kesure Co., 195A type) was used. The thermal expansion coefficients for separate specimens of 5 mm in diameter and 10 mm in length were measured with a Rigaku SS-MMA thermal stress displacement device (Rigaku Co., SS-TMA), and the same size of quartz to the specimens as a standard one was used.

## 3. Results and Discussion

Fig. 1 shows the relationships between the resistivity of the composites which was measured under the electric field 10 kV/cm, and the volume fraction of carbon powder. From this, it is observed that  $x$  at this time indicates 0.251. In other words, this value denotes the volume fraction of carbon powder, of which the current behavior is transferred from ohmic to non-ohmic.<sup>5)</sup> As the critical exponent 2 is obtained from its calculation with this value, we can see that the result satisfies the universal law of conductivity. On the other hand, it is considered that such an outcome was derived from the tunneling

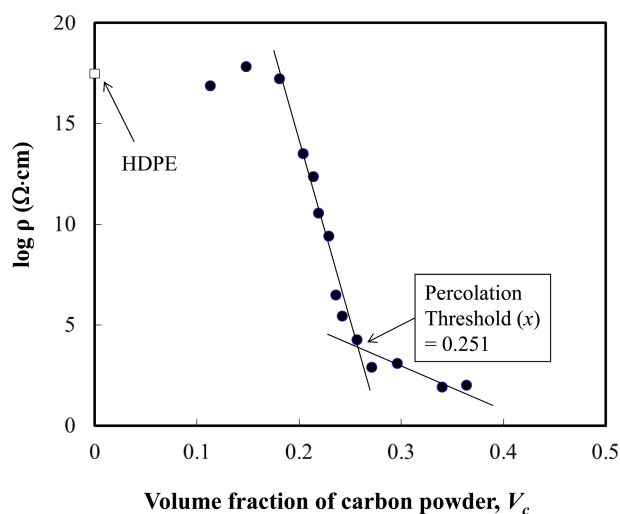


Fig. 1. Change of resistivity for volume fraction of carbon powder, including resistivity of high density polyethylene (HDPE).

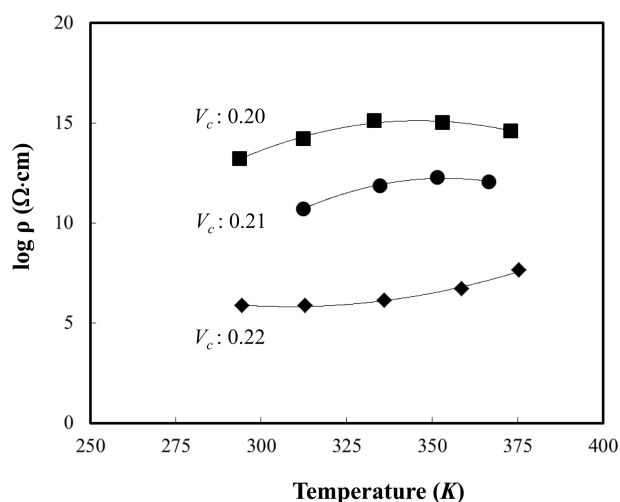


Fig. 2. Temperature dependence of resistivity of the composites with  $V_c < x$ .

conduction model because a percolation path based on carbon powder does not exist in case of the composites below  $x$  indicating the non-ohmic current behavior.<sup>5)</sup>

First of all, the temperature dependence of resistivity in composites below  $x$  needs to be explained. Fig. 2 shows that the effect of temperature on the resistivity in the specimens of 0.20, 0.21, 0.22 lower than 0.251, a  $x$  value given in Fig. 1. It is observed that at  $0.2 < x < 0.21$ , the temperature coefficient of resistivity changes from a negative (-) value to a positive (+) value. This implies that the conduction mechanism differs with temperature. Therefore, the composites below  $x = 0.20$  are not used at high temperature. Also, the gap of temperature dependence on resistivity according to the gap in the values of electric fields decreases as the volume fraction of carbon

powder increases. What should be noted here is that in case of 0.20, the temperature dependence on resistivity is a negative (-) in 1 kV/cm,<sup>8)</sup> but, in case of the field of 10 kV/cm, it indicates a positive (+) value. In addition, according to the gap of the applied electric fields, the change of resistivity at low temperature shows about itself to be about  $10^3$ , and there is almost the same value at high temperature. On the other hand, the temperature coefficient of resistance that shows a positive (+) value in case of the 10 kV/cm field decreases as the volume fraction of carbon powder increases. In case of the value of 0.22, the temperature coefficient of resistance shows a positive (+) value even in case of the field of 1 kV/cm.<sup>9)</sup>

In this regard, Sheng proposes a model of tunneling conduction in consideration of thermal voltage fluctuation with respect to the composites that is identical to those used in this research(Fig. 3).<sup>10)</sup> This model, as shown in Fig. 3, uses as a parameter the layer of polyethylene matrix existing between the carbon powder clusters. The matrix(polyethylene) layer forms a tunneling gap of length  $L$ , and the tunneling conduction is activated at the tip(area  $S$ ) of carbon powder cluster. This model makes it possible to explain the temperature dependence of resistance in the composites used in this research. At this point, based on this model, it is necessary to examine the temperature dependence of the resistivity in case of its being below  $x$  value. The current density  $j$  is obtained from the special equation proposed by Sheng.<sup>10)</sup> In the calculation using this model, the effect of thermal expansion in the composites is summarized as follows: the thermal expansion coefficient in the composites of which the volume fraction of carbon powder indicates zero to  $x$  is  $1850\sim 1400 \times 10^{-7}/K$ , and the coefficients decrease linearly as the carbon powder addition content increases.<sup>11)</sup>  $1500 \times 10^{-7}/K$  was used as the value of thermal expansion coefficient for the composites below  $x$ .

Fig. 4 shows the temperature dependence of the resistivity calculated with 2 eV as  $V_o$  and  $500 \text{ nm}^2$  as tunneling area  $S$ .<sup>5)</sup> The resistivity in this is standardized as the values of  $L = 9 \text{ nm}$  and  $T = 293 \text{ K}$ . The temperature coefficients of resistance indicating the temperature dependence of resistivity, shows a positive (+) value, and the slope increases as the tunneling gap widens. The slope shown in this is at  $0.011\sim 0.012/K$  obtained by using the equation of  $1/\rho_{293} \times (\rho(T) - \rho_{293})/\Delta T$  on the basis of resistivity ( $\rho_{293}$ ) at 293 K. This value is considered to qualitatively explain the temperature dependence of resistivity for the added carbon powder obtained in applying the electric field of 10 kV/cm shown in Fig. 2. In other words, it is considered that for the data in Fig. 2, the change(from a positive (+) to a negative (-) value) of the temperature coefficient that was observed in the specimen, of which the volume fraction of carbon powder

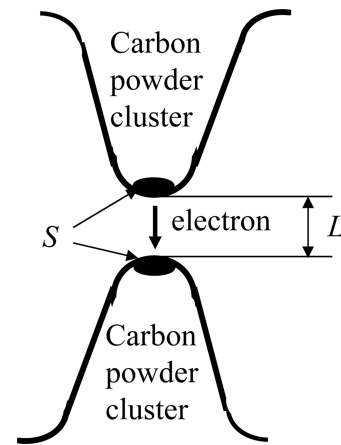


Fig. 3. A tunneling gap between carbon powder clusters in composite below percolation threshold ( $x$ ) and rectangular potential barrier approximation.

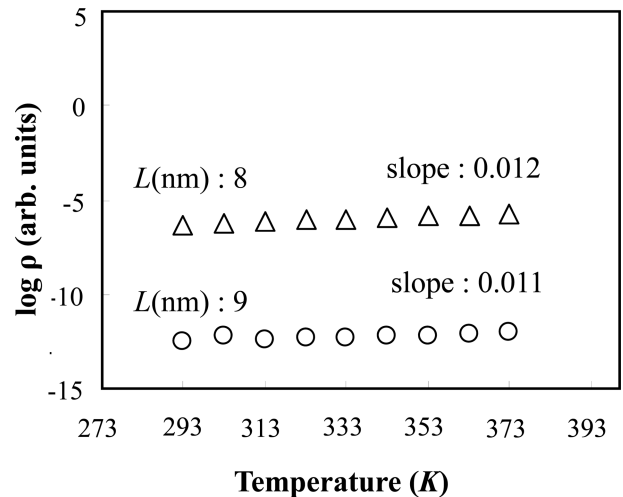


Fig. 4. Temperature dependence of resistivity obtained by calculation with the Sheng's model.<sup>10)</sup>

was 0.20 was happened in the following way: the conduction process of electrons changed to be predominant at the low electric field of 1 kV/cm on the assumption that the current of specimen containing 0.20 as the volume fraction of carbon powder was composed of the thermal activation current flowing in polyethylene and the current of tunneling conduction between the cohesive bodies of carbon powder. On the other hand, the current of tunneling conduction in the latter is considered to be predominant at the higher level of 10 kV/cm. The current of tunneling conduction, which reaches the predominant level at a high electric field changes into a positive (+) value in the thermal coefficient of resistance due to the thermal expansion of a tunneling gap. Thus, it can be understood that the temperature dependence of the resistivity below  $x$  gives

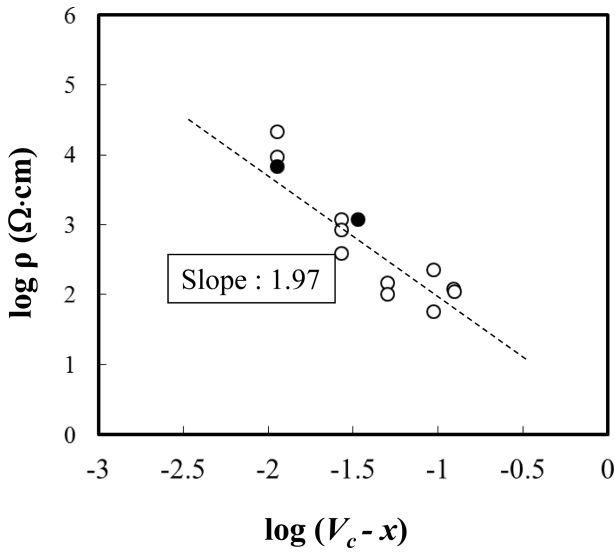


Fig. 5. Change of resistivity for the composites with  $V_c > x$  for  $\log(V_c - x)$ .

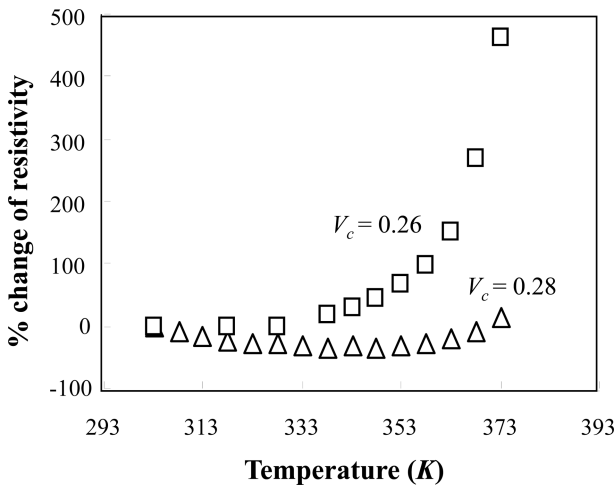


Fig. 6. % change of resistivity of the composites with  $V_c > x$  for temperature which is normalized by the value at 303 K.

the qualitative explanation with the model of tunneling conduction mechanism by introducing the thermal expansion effect of a tunneling gap.

Then, the case above  $x$  needs to be explained. Fig. 5 indicates the changes of resistivity in the composites that contain the volume fraction of carbon powder above  $x$ . In this, the slope of the straight line is 1.97. This means that the composites above  $P_t$  satisfies the universal law of conductivity.<sup>3,4)</sup> Fig. 6 shows the temperature dependence of the two specimens which is indicated by ● in Fig. 5. Here, the changes of resistivity are standardized by the 303 K resistivity values of the specimens. The changes of resistivity show negative (-) values regardless of the kinds of specimen at the temperature domains of 303 K and 323 K. As the absolute values of the slope increase

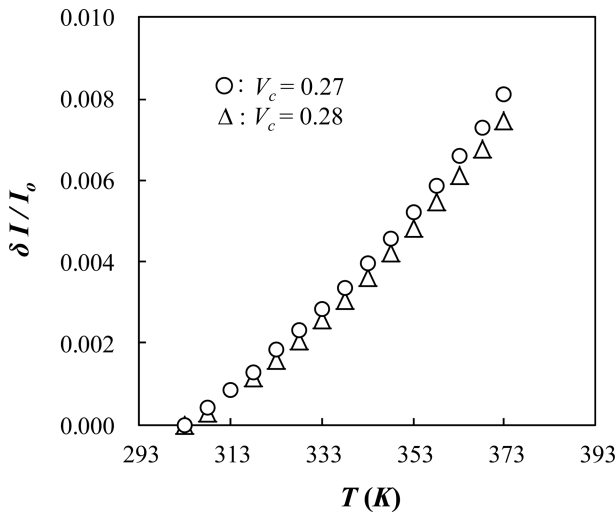
apparently in accordance with the increasing volume fraction of carbon powder, the effect of temperature on resistivity appears to be different depending on the volume fraction of carbon powder. On the other hand, as the temperature increases, the degree to changes of resistivity gets larger. This tendency gets smaller as the volume fraction of carbon powder increases. The sharp increase of temperature coefficient at high temperature is considered to be due to the effect of high density polyethylene grain melting, which induces a large positive (+) value. A percolation path determining the changing patterns of conductivity according to the volume fraction of carbon powder is formed in the composites above  $P_t$ . At this time, the change of conductivity is subject to  $\sigma \propto (V_c - x)^{2,4)}$  Here, in order to introduce the effect of temperature on conductivity, let us suppose that there exists a very thin layer of polyethylene matrix, in between the carbon powder clusters that forms a percolation path; such a layer controls the conduction process. In other words, supposing that it is the thermal activation process, the proportional constant of  $\sigma \propto (V_c - x)^2$  is  $\sigma_0 \exp(-H/kT)$ . In this equation,  $\sigma_0$  is a constant,  $H$  is activation energy,  $k$  is Boltzmann constant. And, the equation  $V_c(T) = V_0(1 + 3\delta l(T)/l_0)$  can be used to calculate the effect of thermal expansion in the composites on the volume fraction of carbon powder. Here,  $V_0$  is the volume fraction of carbon powder at 303 K, and  $\delta l(T)$  is the numerical difference between the length at temperature  $T$  and the length ( $l_0$ ) at 303 K.

Fig. 7 shows the relationships of  $T - \delta l/l_0$ . On the assumption above, the changes of conductivity based on temperature and the volume fraction of carbon powder are expressed as the equation below:

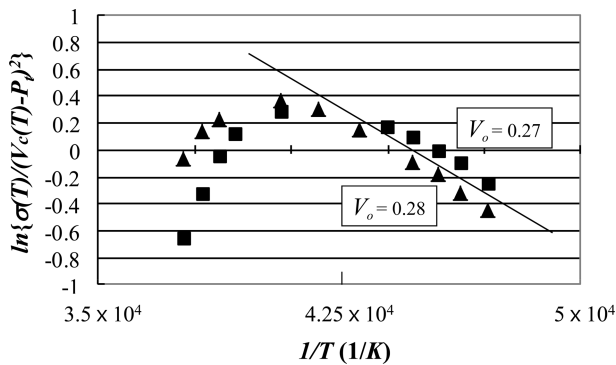
$$\sigma(T, V_c) = \sigma_0 \exp(-H/kT) (V_c(T) - x)^2 \tag{1}$$

The volume changes ( $V_c(T)$ ) of carbon powder may differ, subject to the equation,  $V_0(1 + 3\delta l(T)/l_0)$  by the thermal expansion of polyethylene matrix, but  $x$  defined at room temperature is not affected by temperature.  $H$  is activation energy, and  $\sigma_0$  is a constant. In case of being above room temperature  $x$ , equation (1) satisfies the universal law of conductivity for the changes of the volume fraction of carbon powder. It can be seen that based on the comparison of  $\sigma \propto (V_c - x)^2$  and the equation (1), in the case that  $\sigma_0$  and  $H$  in equation (1) do not have consistent values irrespective of the volume fraction of carbon powder, the equation cannot satisfy the universal law of conductivity. Accordingly, in the composites above  $x$ , the relationship of  $(1/T) - \ln[\sigma(T, V_c)/(V_c(T) - x)^2]$  should turn out to be a straight line.

Fig. 8 shows the relationship of  $(1/T) - \ln[\sigma(T, V_c)/(V_c(T) - x)^2]$ . The values of  $\ln[\sigma(T, V_c)/(V_c(T) - x)^2]$  de-



**Fig. 7.** Change of the ratio of the differential length of  $\delta I(T)$  between the length at  $T$  and the original length at  $I_0$  for temperature.



**Fig. 8.** Change of  $\ln[\sigma(T, V_c)/(V_c(T) - x)^2]$  for temperature.

creases as temperature increases due to the influence of grain melting at high temperature. This is, as shown in Fig. 5, considered to be due to the fact that at room temperature, the resistivity of the specimen, is placed above the straight line of slope 1.97, and so the value of  $\ln[\sigma(T, V_c)/(V_c(T) - x)^2]$  decreases slightly. The activation energy obtained from the straight line of slope in Fig. 8 is 0.15 eV. Thus, as shown in Fig. 6, the temperature dependence of resistivity below the temperature influenced by the melting point of grains appears to change according to the volume fraction of carbon powder. However, it can be understood that the activation energy

is consistent regardless of the volume fraction of carbon powder.

**4. Conclusion**

This study is concerned with the electrical property of carbon powder added polyethylene matrix composites. As a result of above, it is confirmed that the temperature coefficient of resistance in the composites below percolation threshold ( $x$ ) changes from negative (-) to positive (+) at  $0.20 < x < 0.21$ ; therefore, it is not used at high temperature according to the increase of volume fraction of carbon powder. As such, the tendency gets smaller as the volume fraction of carbon powder increases. This outcome can be explained by the mechanism of tunneling conduction, taking into account the voltage of heat flux by introducing the thermal expansion effect of a tunneling gap. Also, in case of the composites above  $x$ , the temperature coefficient of resistance turns into negative (-) below the temperature influenced by grain melting. Its absolute value gets larger as the volume fraction of carbon powder increases. On the other hand, the temperature dependence of resistivity above  $x$  can be explained with the universal law of conductivity by introducing the effect of thermal expansion.

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