

A Study on the Percolation Threshold of Polyethylene Matrix Composites Filled Carbon Powder

Soon-Gi Shin*

Department of Advanced Materials Engineering, College of Samcheok, Kangwon National University, Samcheok-si, Gangwon 245-711, Korea

This paper investigates the percolation threshold of carbon powder-filled polyethylene matrix composites using the experimental results of the changes in resistivity and relative permittivity for filled carbon powder, the electric field dependence of current, and the critical exponent of conductivity. We found that a formation of infinite clusters is interrupted by a tunneling gap in the volume fraction section of filled carbon powder where the change in resistivity is extremely large. We also found that the critical exponent of conductivity for the universal law of conductivity is satisfied if the percolation threshold is estimated at the volume fraction of carbon powder where a nonohmic current behavior changes into an ohmic one. It is concluded that the percolation threshold should be defined at this volume fraction of carbon powder.

Keywords: percolation threshold, carbon powder, polyethylene, composites, tunneling conduction

1. INTRODUCTION

Carbon powder-polyethylene composites, applied to electronic materials, are fabricated by a mixing roll method. The mixing condition is carefully chosen to control the volume fraction of the carbon powders, which strongly affects the electronic performance of the composites. It is well known that a change in resistivity shows two break-points for filled carbon powder into insulating polymers, such as polyethylene or styrene-butadiene rubber.^[1-6] The first break-point shows a large change from insulating to non-insulating properties for filled carbon powder. The second break-point appears after the first large change and the decrease in resistivity declines with continued filled carbon powder. However, it seems that there is confusion about the percolation threshold of carbon powder-filled polyethylene matrix composites. There have been many conflicting interpretations in previous research about the percolation threshold of the composites. For example, Miyasaka^[5] and Reboul^[7] said that the percolation threshold is the first break-point. On the other hand, other researchers labelled the second break-point when they examined the critical exponent of conductivity.^[8,9]

Here we consider the percolation threshold of composites made from carbon powder and high density polyethylene, by examining the published data on the changes in resistivity, relative permittivity, and the electric field dependence of current.^[10,11] Usually, the percolation threshold is defined at the probability which is the volume fraction of conductive

phases in the random resistor network system, where an infinite cluster is formed for the first time.^[12] This percolation probability coincides with the percolation threshold of conductance. Therefore, it is necessary to determine that either the first or second break-point is the percolation threshold based on the electrical properties of the composites.^[13]

In this research, investigations of the changes in resistivity and relative permittivity for filling carbon powder, the critical exponent of conductivity, and the electric field dependence of current are presented, using two kinds of carbon powders.

2. EXPERIMENTAL PROCEDURE

The polymer used as a matrix is a high density polyethylene (HDPE: Mitsubishi Chemical Co.) and two kinds of carbon powder (#45 (Mitsubishi Chemical Co. particle size 24 nm, surface area 137 m²/g, specimen A), Asahi thermal (Asahi Carbon Co. particle size 90 nm, surface area 19 m²/g, specimen B)) are used as a conductive filler. #45 is produced by the thermal oxidative deposition process.^[14] Asahi thermal has a lower structure because the surface area is smaller than #45.

Before mixing with the polyethylene matrix, the carbon powder is heated at 373K for 3.6 ks to remove absorbed water. After the carbon powder is mixed with polyethylene at 413 K for 0.25 ks, the composite is cooled to 353 K and is cut into pieces. To improve the dispersion of the carbon powder in the matrix, the pieces of the composites are mixed at 413 K for 0.25 ks and cut into pieces again after cooling

*Corresponding author: ssg@kangwon.ac.kr

(step A). Step A is repeated 4 times. The volume fraction of the carbon powder (V) is estimated by assuming that the density of the carbon powder is 1.85 g/cm^3 .

Sheet type specimens for electrical measurements are prepared by pressing the composite pieces at 423 K for 0.25 ks. Thickness is in the range of 0.05 mm to 2 mm depending on resistivity. Copper is evaporated as electrodes of 3 cm in diameter.

Measurements of resistivity are carried out using a Takedariken TR-84M vibrating reed electrometer for resistance above $20 \text{ M}\Omega$ in air. Otherwise, measurements are conducted using a Keithely 196A digital electrometer. For measurements of the electric field dependence of current larger than $30 \mu\text{A}$, a pulse voltage of 1 ms width is applied to avoid joule heating. For currents smaller than $30 \mu\text{A}$, dc voltage is applied and almost steady state currents are taken 0.5 ks after the application of dc stress. Measurements of the relative permittivity of the composites are made at 100 kHz and 1 V ac amplitude with an HP-4284A LCR meter. Dielectric dissipation factors $\tan \delta$ larger than 10 are discarded because the readability of the phase angle of impedance for the LCR meter is above 0.01° .

3. RESULTS AND DISCUSSION

Figures 1 and 2 show the changes of resistivity (ρ) as a function of the volume fraction of the carbon powder in the carbon powder-filled polyethylene matrix composites. The resistivity is taken under the electric field 0.5 kV/cm . It is seen that there are three volume fraction sections each with a characteristic change in resistivity. At low volume fractions, from zero to the volume fraction denoted as V_1 , the resistivity is almost the same as that of polyethylene.^[10] In the range

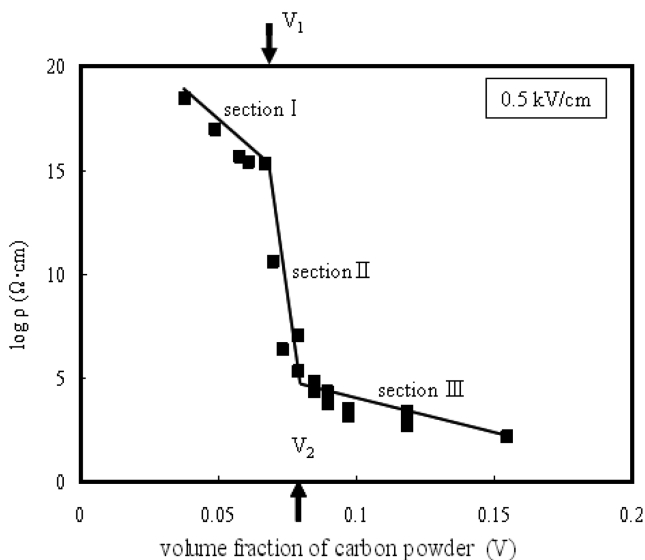


Fig. 1. Resistivity of polyethylene matrix composites with carbon powder (#45) as a function of volume fraction of carbon powder.

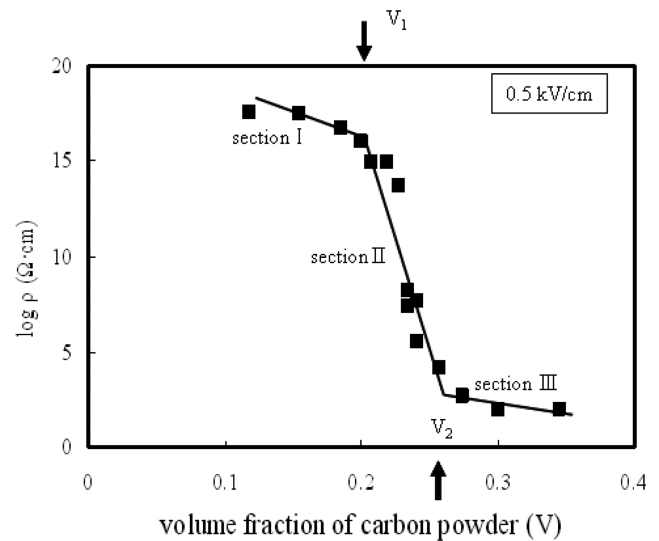


Fig. 2. Resistivity of polyethylene matrix composites with carbon powder (Asahi thermal) as a function of volume fraction of carbon powder.

of the volume fraction from V_1 to V_2 , the change in resistivity is more than 10 orders of magnitude. The change in resistivity above V_2 gets smaller for filled carbon powder than that in the range from V_1 to V_2 . Here, we shall divide the volume fraction of carbon powder into three sections according to the above discussion: section I is from zero to V_1 , section II is from V_1 to V_2 , and section III is above V_2 . Furthermore, the values of V_1 and V_2 for the two types of carbon powders are in order of the surface areas. Data for V_1 and V_2 are listed in Table 1. The feature of the dependence of V_1 and V_2 on the type of carbon powder is similar to that reported for other types of carbon powder-filled polyethylene matrix composites and has been well documented.^[9,15,16] Higher structure carbon powder shows lower values of V_1 and V_2 than lower structure carbon powder.^[9]

Figure 3 shows a typical electric field dependence of current in specimen II. Ohmic current behaviors for the electric field take place at first upon filled carbon powder. Although nonohmic current behaviors for the applied field have been presented on polyethylene films, the ohmic dependence of current on the electric field has usually been observed for low applied fields such as shown in this figure. In section II, the current is extremely small at a low electric field and show a sharp increase with an increasing applied field. The ohmic dependence of resistivity on the applied field appears again in section III, and resistivity is less than about

Table 1. Values of V_1 and V_2 in the composites

	Specimen A (filled #45)	Specimen B (filled Asahi thermal)
V_1	0.065	0.219
V_2	0.076	0.243

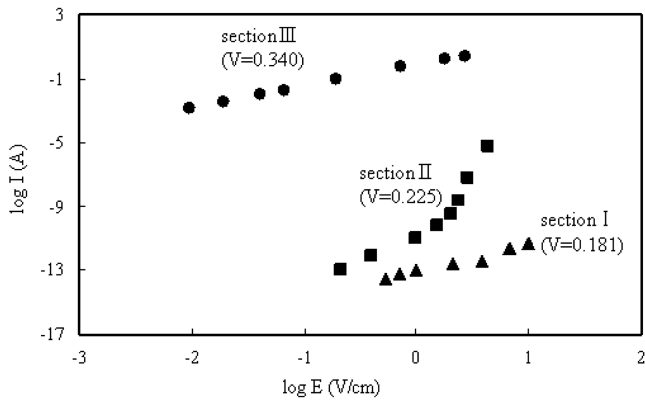


Fig. 3. Applied field dependence of current in each section in specimen B.

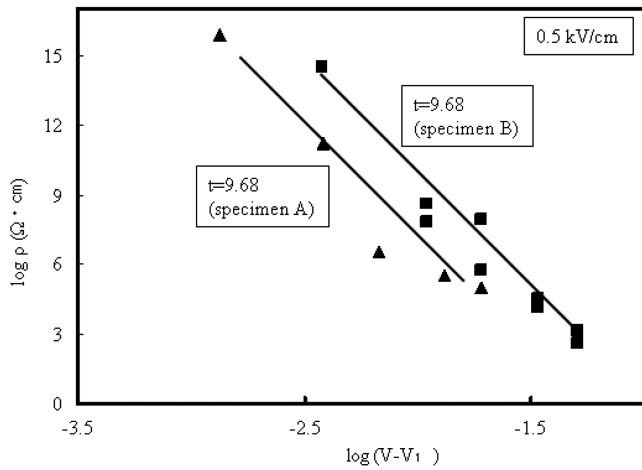


Fig. 4. Resistivity as a function of $V-V_1$ in the composites.

$10^6 \Omega \cdot \text{cm}$.

Usually, the change in conductivity (σ) after the percolation threshold (V_c) is expressed by $\sigma \propto (V-V_c)^t$, where t is the critical exponent of conductivity.^[12] In Fig. 4, ρ is shown as a function of $V-V_1$ when V_1 is assumed to be V_c . The relationship between ρ and $V-V_1$ can be expressed as a straight line on a log-log scale, as formulated by $\sigma \propto (V-V_c)^t$. The value of t is estimated from the slope and is indicated in the figure. It is seen that the estimated value of t is larger than 8.

Figure 5 shows ρ as a function of $V-V_2$, when V_2 is taken as V_c . The relationship between ρ and $V-V_2$ can also be expressed as a straight line. The values of t estimated from the slope are almost 2 and are satisfied with the universal law of conductivity.^[12,17]

Relative permittivity (ϵ_r') of the composites is shown as a function of V in Figs. 6 and 7. At first ϵ_r' for each specimen shows an increase with an increasing V up to V_1 , and rapidly increases in section II. Whether ϵ_r' increases or decreases in section III is not clear at the present time because the phase angle of the impedance of the composites above V_2 becomes

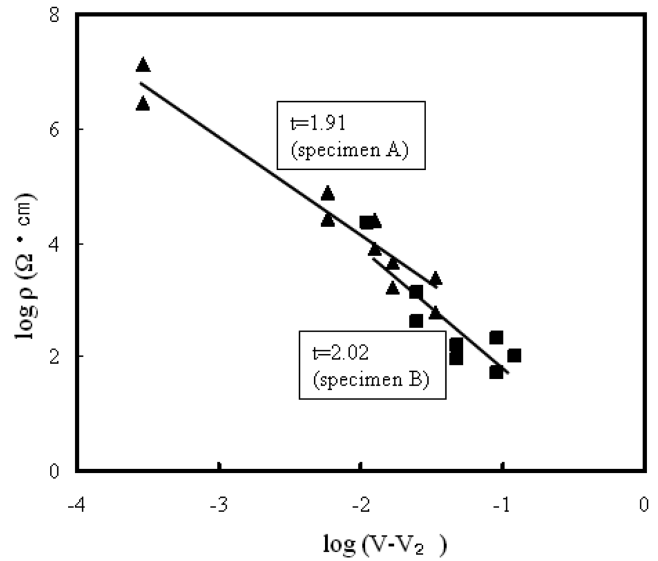


Fig. 5. Resistivity as a function of $V-V_2$ in the composites.

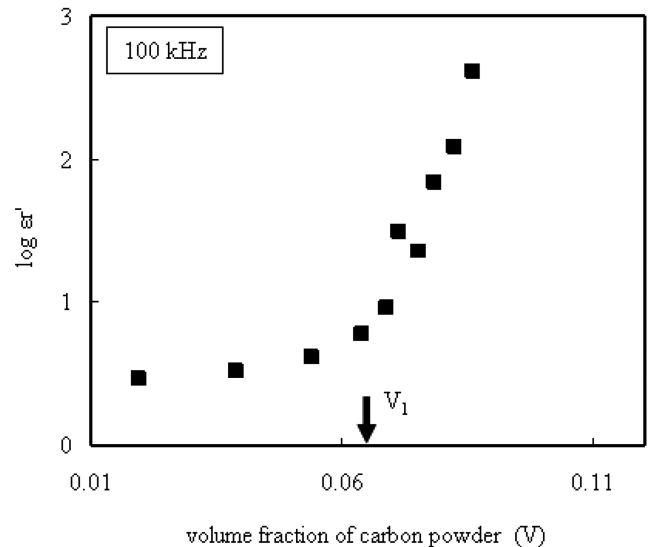


Fig. 6. Dependence of relative permittivity on volume fraction of the carbon powder in specimen A.

smaller than the readability of the LCR meter.

In section II, resistivity shows a change of more than 10 orders of magnitude and the currents present a nonohmic behavior. These behaviors may be explained by the fluctuation induced tunneling model (FT model), which was presented by Sheng.^[18] Although this model takes account of only a single tunneling junction which governs the entire conduction current, it has been successful for explaining the temperature dependence of resistivity and the electric field dependence of current for the composites of polyethylene and carbon powder.

By using this model, the nonohmic current behavior for the electric field and the sharp decrease in resistivity with

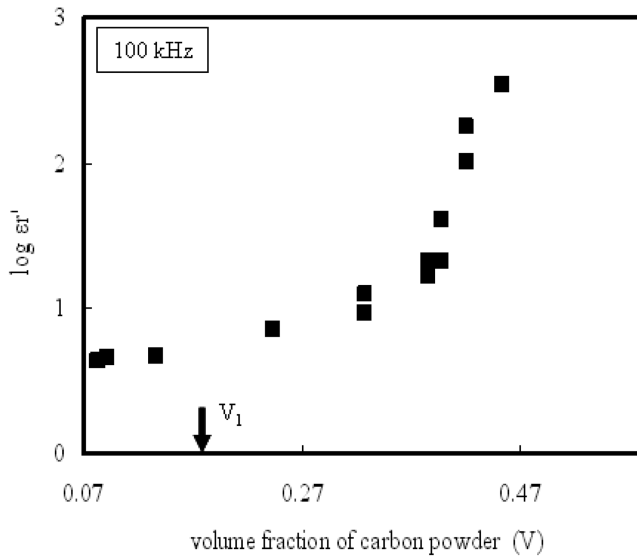


Fig. 7. Dependence of relative permittivity on volume fraction of the carbon powder in specimen B.

filled carbon powder in section II are discussed. Important parameters of tunneling conduction are barrier height (h), gap width (ω) and tunneling area (s). Recently, the work function of carbon powders is known to be 4.3 eV to 4.8 eV,^[19] and the energy gap of polyethylene is approximately 7.4 eV.^[17] If the Fermi energy of polyethylene exists at the center of the energy gap, the h of tunneling is approximately 3.7 eV. The value h decreases by the electron affinity of polyethylene, which is not well estimated. Therefore, we use the value of h in the range of 1 eV to 3 eV in order to know how h influences the magnitude of current. Other parameters of ω and s are chosen by referring to the calculated results by Sheng *et al.*^[18,21] By fitting the FT model to the temperature dependence of resistivity for the composites of polyvinylchloride and carbon powder, Sheng *et al.* estimated that $\omega = 7.5$ nm and $s = 2.5$ nm². The value of ω is assumed in the range of 2 nm to 10 nm in our calculation. Although the order of the cross section of carbon powder can be obtained from the particle size, tunneling may take place in a tiny part of a carbon powder particle. The value of s is assumed in the range of 0.1 nm² to 100 nm² as a measure to know how the tunneling area changes current.

Figure 8 shows an example of the electric field dependence of current with a parameter of ω , using following equation by Sheng.^[20]

$$J = \left(\frac{T_1}{\pi T}\right)^{\frac{1}{2}} \int_0^{E_A} d\varepsilon_T J_0(\varepsilon_A + \varepsilon_B) \times \exp\left[-\frac{T_1}{T} \varepsilon_T^2 - \frac{T_1}{T_0} \phi(\varepsilon_A + \varepsilon_T)\right] \\ + \int_{\varepsilon(E_A)}^{\infty} d\varepsilon_T J_1(\varepsilon_A + \varepsilon_B) \exp\left[-\frac{T_1}{T} \varepsilon_T^2\right]$$

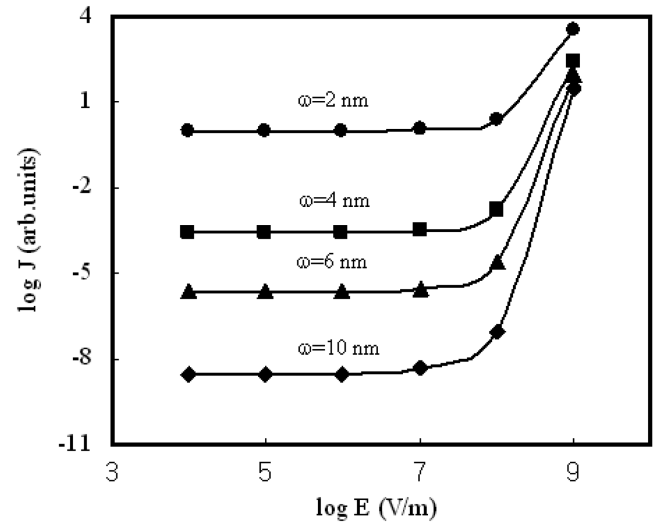


Fig. 8. Dependence of current density on electric field with a parameter of gap width. Current density is normalized with the current density at $E=10^4$ V/m and $\omega=2$ nm. (Parameters used in this calculation: $h=2$ eV, $s=1$ nm².)

$$+ \int_0^{E_A} d\varepsilon_T J(\varepsilon_A - \varepsilon_T) \exp\left[-\frac{T_1}{T} \varepsilon_T^2\right]$$

The details of the parameters required for this calculation are found in reference.^[20] In the calculation, the value of h is chosen to be 2 eV. It is seen that the current decreases by more than 8 orders of magnitude for an increasing ω and the rate of current decrease becomes smaller with a wider ω . Also, in the electric field range of 10^7 V/m to 10^9 V/m, a non-ohmic field dependence of current appears. It seems reasonable to use the FT model to explain the electric field dependence of current and the large change in resistivity for the filled carbon powder in section II. However, the electric fields used in Fig. 8 are much larger than the apparent electric field (E) shown in Fig. 3. According to Ohtsuki, a voltage ($V(\varepsilon)$) applied between adjacent clusters below the V_c is in proportion to a coherence length (ε) as $V(\varepsilon) = \varepsilon \cdot E$.^[22] This voltage becomes extremely large when V approaches V_c . From another point of view, the electric field at the tunneling gap is much larger than E because the average size of the conducting clusters is much larger than the average tunneling width.^[18] Therefore, it is reasonable to expect that the actual electric field at the tunneling gap is larger than the apparent electric field by more than 2 or 3 orders of magnitude.

The dependence of the current on h is shown Fig. 9. Although the rate of the decrement of the current for increasing h depends on the value of s , it can be seen that the current for $s = 10$ nm² changes by about 8 orders of magnitude for the range of h . The details of the parameters used in the FT model should be examined by further study of the wide tem-

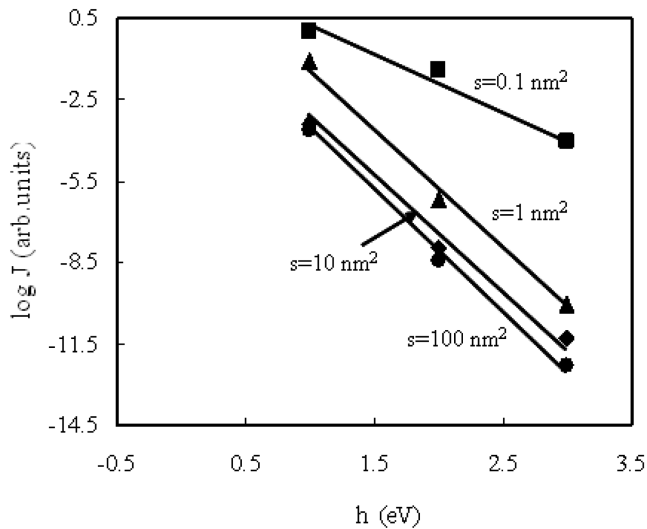


Fig. 9. Dependence of current density on barrier height with a parameter of tunneling area. Current density is normalized with the current at $h=1$ eV, $s=0.1$ nm². (Parameters used in this calculation: $E=10^5$ V/m and $d=2$ nm.)

perature dependence of resistivity in section II.

One of the points to which special attention should be paid in this part is that a tunneling gap exists in section II and seems to interrupt a formation of infinite carbon powder clusters.

As shown in Fig. 3, the ohmic dependence of current on the electric field has been observed in sections I and III. From the above discussions, a change of carbon powder dispersion in polyethylene with filling can be expressed as schematic descriptions as shown in Fig. 10. The closed circle symbol represents the carbon powder particle or its aggregate. For the low carbon powder filling in section I, carbon powder aggregates exist as in sparse distribution in the polyethylene, leading to extremely high resistivities and a small rate of growth of relative permittivity due to a Maxwell-Wagner type polarization. In section II, some of the carbon powder aggregates closely contact each other and others form with relatively large gaps. As shown in Figs. 6 and 7, a

rapid rate of growth in relative permittivity has been observed in section II, which may primarily be related to changes in the gap width and the surface area of the tunneling gap. In section III, the tunneling gaps in section II as shown in Fig. 10 start to change into ohmic contacts by eliminating the polyethylene, leading to a small resistivity. Therefore, an extremely small phase angle of the low impedance makes it impossible to measure relative permittivity.

Another point to which special attention should be paid in this part is that relative permittivity can be observed even in section II.

The values of t estimated at V_1 are larger than 8 (Fig. 4). On the other hand, the values estimated at V_2 are satisfied with the universal law of conductivity (Fig. 5). Unexpectedly, there is not much published data on the whole change in resistivity as shown in Figs. 1 and 2. However, it has been found that the values of t estimated at V_1 are larger than 2 and that those estimated at V_2 are satisfied with the universal law.^[5,6,14] V_1 is called the percolation threshold by Miyasaki^[5] and Reboul.^[7]

There are two theories for the non-universal law of conductivity. One is a model based on the tunneling conduction that incorporates the distribution of the tunneling distance. However, in this model there could not be such infinite clusters as seen by Balberg.^[9] The other theory is that a sufficiently anomalous distribution of conducting phases alters the critical exponent of conductivity.^[23] This seems to explain the large critical exponent of conductivity estimated at V_1 , leading to the conclusion that V_1 is the percolation threshold. However, the existence of the tunneling gap in section II has been experimentally confirmed and relative permittivity was observed even above V_1 .

From the point of view of the value of t , the mechanism of changing the tunneling gap and the relatively large gaps (Fig. 10) into ohmic contacts seems to correspond to that of connecting conductive phases above the percolation threshold in a random resistor network.^[10,11,24,25] Therefore, it is reasonable to conclude that the percolation threshold should be defined at the volume fraction where the break-point from

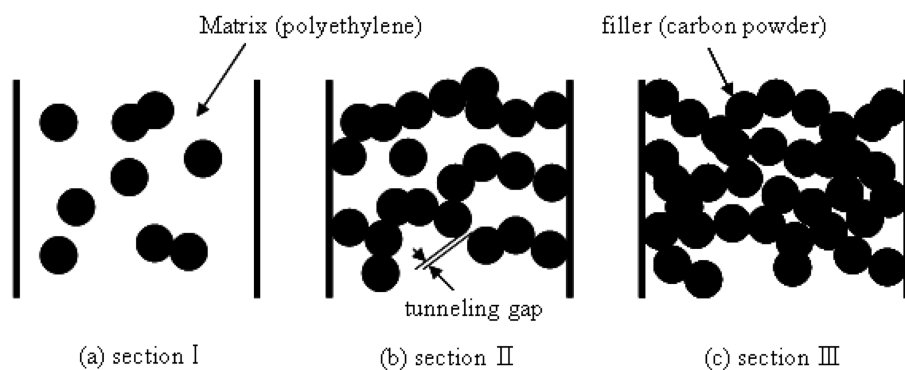


Fig. 10. Schematic descriptions of carbon powder dispersion in polyethylene matrix for each section.

tunneling to ohmic conduction mechanisms takes place.

4. CONCLUSION

Our study confirms that the percolation threshold is defined at the volume fraction where the ohmic current behavior appears after the disappearance of the nonohmic current behavior. Although the break-point of resistivity from insulating to non-insulating properties of the polyethylene matrix composites filled carbon powder is usually called the percolation threshold, was found that the tunneling gap exists even beyond this break-point and interrupts to form infinite clusters of carbon powder aggregates. Relative permittivity has also been observed even above this break-point. It is further found that the critical exponent of conductivity estimated by another break-point of resistivity from the tunneling to ohmic conduction is satisfied with the universal law of conductivity. We believe considered that the mechanism for changing the gaps between the carbon powder aggregates into ohmic contacts is the same as that of connecting conducting phases above the percolation threshold in a random resistor network system.

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