# Self-temperature-control plane heaters by polyethylene glycol–graphite systems. 3

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It is known that some polymer systems dispersed with conductive particles show switching phenomenon, the mechanism of which can be ascribed to volume expansion of the bulk polymer by Joule heat. We have reported that polyethylene glycol–graphite systems also show switching. However, the mechanism of the switching in these systems cannot be explained in terms of volume expansion, and thus a model for electric conduction in these systems has been presented. Unfortunately we later found that it was necessary to revise the model. In the present work electric properties of polyethylene glycol–graphite systems are reported with a reference of those of $n$-hexatriacontane-graphite systems. In the later systems switching can be explained in terms of volume expansion. From these results in these two systems a revised model is presented for electric conduction in polyethylene glycol–graphite systems. Copyright © 1996 Elsevier Science Ltd.

## INTRODUCTION

Various types of fillers such as carbon black, graphite, metal, etc. are dispersed into polymers for various purposes. One of these is as switching elements. These are polymer composites with electric conductive particles dispersed in them. Their electrical properties are characterized by low resistances at low temperatures (switch-on) and high resistances at temperatures higher than certain temperatures (switch-off). The first paper has been reported by Ohe *et al.* concerning the switching element composed of carbon black–polyethylene–paraffin[1] and Bueche's papers have followed this[2,3]. They ascribed the mechanism of the switching to volume expansion of the systems. Namely, at low temperatures electric current flows through network-paths composed of direct contacts of carbon particles loaded in a matrix polymer, whereas at high temperatures these network-paths are broken by the thermal expansion of the matrix polymer, which causes an increase in the electric resistance of the system. On the other hand, we found a new switching composite composed of polyethylene glycol (PG) and graphite (GC)[4] and proposed a new mechanism for the switching in this system[5]. Since then we have continued research on the mechanism of electric conduction in PG–GC systems. There is much evidence that the switching phenomenon in PG–GC systems cannot be explained in terms of volume expansion. However we found that the proposed model[5] is only

empirical and the mechanism of electric conduction is not fully clarified. Therefore it is necessary to reconstruct the model. At the same time it is also necessary to contrast the electrical properties in a PG–GC system with those in other switching systems, because the former is only one exceptional case for which the mechanism by volume expansion cannot be applied. In the present work $n$-hexatriacontane ($n$HTC)–GC systems were used as a reference. These show a switching phenomenon, the mechanism of which can be, of course, explained in terms of volume expansion of the system. In the present work the effect of GC concentration on resistivity is compared between PG–GC and $n$HTC–GC systems in order to investigate the role of PG matrix in electric conduction in PG–GC systems. The relation between electric current and applied voltage is also compared in these two systems, especially at temperatures near switching temperatures (the temperature at which a sharp increase in resistance appears). In addition, the effect of GC concentration on resistivity is compared between these two systems, from the view point of percolation threshold. Taking these results into consideration, the previous model is reconstructed.

## EXPERIMENTAL

Polyethylene glycol was no. 6000 from Dai-ichi Kogyo Seiyaku and the number average molecular weight was 8200. $n$-Hexatriacontane was guaranteed grade reagent from Nacalai Tesque. Graphite was 90–300 M from

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Nishimura Kokuen. Samples were made by mixing the desired amount of GC into PG or *n*HTC in a molten state and casting those mixtures in small Teflon$^R$ containers. In the present work two types of samples were made. One is disc-shaped, of which the diameter and thickness were 20 mm and 2 mm, respectively. The other is micropillar-shaped, of which the diameter and height were 1.5 mm and 1 mm, respectively. These samples were used to obtain a relation between resistivity and field strength using a different procedure from that for disc samples as described below. Electrodes were made with silver paint (Dotite D-550) on the top and the bottom surface.

Resistivities were obtained with a digital multimeter (Advantest TR6841) for samples with lower resistances. For samples with higher resistances DC voltages were applied for samples with a power source (Kikusui PAB-250) and the electric currents through the samples were measured with a picoammeter (Advantest TR8641). In order to obtain the relation between an applied voltage and a current the latter procedure was employed. However, in every case care was taken not to apply higher voltages for samples with lower resistances in order to avoid the increase in temperature by Joule heat.

The relation between resistivity and field strength was obtained with micropillar samples. Resistivities were obtained as follows[5]: A series circuit was made with a sample and reference resistors of known value. A one shot DC pulse was supplied for this circuit with the DC power source through a made-to-order pulse switch, of which switch-on time was 10–30 ms. Resistivities were obtained by measuring voltages applied across the sample and the reference resistor with a digital oscilloscope (Nicolet 2090-204).

Temperatures of samples were controlled with an air bath (Komatsu-Yamato Coolnics CRT-520) and monitored with a thermistor (Takara Digimulti D611).

## RESULTS AND DISCUSSION

### *Effect of GC concentration on resistivity*

It is well known that an abrupt decrease in electrical resistance is observed when a certain amount of conductive particles are loaded in a polymer system. The critical amount of particles is called the 'percolation threshold'. In *Figure 1* resistivities of *n*HTC–GC systems are shown as a function of temperature for various GC concentrations. Resistivities do not differ too much when GC concentration is 0–10 wt%. Namely, the *n*HTC–GC (10 wt%) system behaves as an insulator, and so does the pure *n*HTC system. However the increase in GC concentration from 10 wt% by only 1 wt% causes a dramatic decrease in the resistivity, as is shown in *Figure 1* (compare □ and ●). Therefore, we could say that ~11 wt% is the percolation threshold in the *n*HTC–GC system. The increase in GC content by 1 wt% causes not only an abrupt decrease (eight orders of magnitude) as described above, but also the appearance of the switching phenomenon, an abrupt increase in resistance at higher temperature, as seen in *Figure 1*.

The results in *Figure 1* can be explained as follows. At lower GC concentrations (0–10 wt%) GC particles dispersed in *n*HTC are isolated with each other and thus the resistance of the bulk *n*HTC is the main contributor to that of the total system. However, when
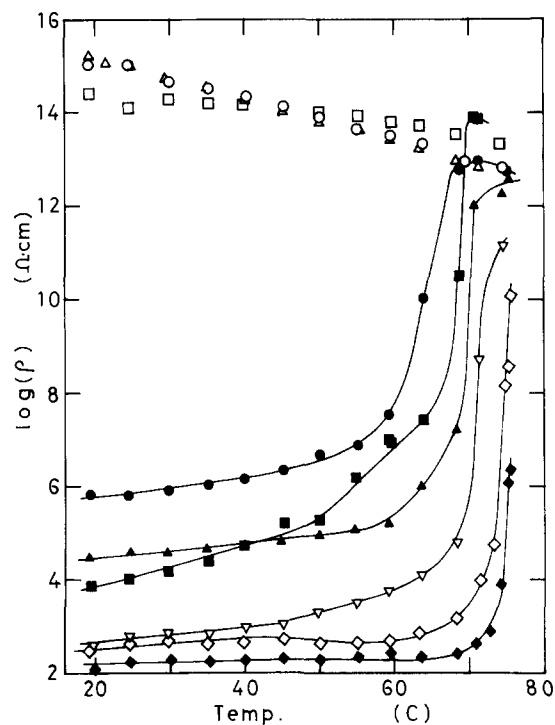


**Figure 1** Logarithm of resistivity vs. temperature in the *n*HTC–GC systems. Graphite concentrations are: ○, 0; △, 5.00; □, 10.0; ●, 11.0; ▲, 13.0; ■, 15.0; ▽, 20.0; ◇, 25.0; ◆, 33.83 wt% respectively
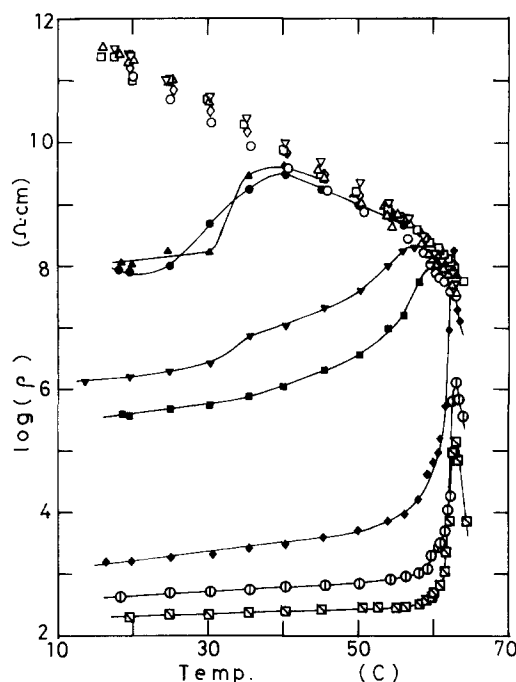


**Figure 2** Logarithm of resistivity vs. temperature in PG–GC systems. Graphite concentrations are: ○, 0; △, 5.00; ▽, 10.0; □, 15.0; ◇, 16.0; ●, 17.0; ▲, 18.0; ▼, 19.0; ■, 20.0; ◆, 25.0; ◐, 30.0; ▨, 35.0 wt% respectively

GC concentration reaches 11 wt%, electric paths can be formed between two electrodes through the bulk *n*HTC by a kind of chain composed of GC particles contacting directly with each other. These particle chains can be cleaved at temperatures near the switching temperature by the thermal expansion of the bulk *n*HTC, which results in the increase in resistivity. This could be the

mechanism of the switching phenomenon in the nHTC-GC systems. Therefore the mechanism of the volume expansion is fully applicable for nHTC-GC systems.

*Figure 2* shows resistivities of PG–GC systems of various GC concentration vs. temperature. As for the systems with lower GC concentrations (0–16 wt%), a similar result is seen as that for nHTC–GC systems with 0–10 wt% GC. Namely, resistivities at a specified temperature are almost the same among these systems within experimental errors. Comparing the result of the PG–16 wt% GC system with that of the PG–17 wt% GC system, the resistivity is decreased by four orders of magnitude at ~20°C. This decrease is not as extraordinary as that for the nHTC–GC systems (eight orders of magnitude) described above. There are two important points that should be noted. One is that resistivity in PG–GC systems at a lower temperature (20°C, for example) decreases with increasing GC concentration more moderately than that in nHTC–GC systems. The other concerns the temperature at which resistance shows a maximum. In the PG–17 wt% GC and PG–18 wt% GC systems resistances show maxima at around 40°C. In the PG–19 wt% GC system the temperature at which resistance shows a maximum peak shifts to the higher temperature. The peak temperature also shifts to a much higher temperature in the PG–20 wt% GC system. In these four systems with GC concentrations of 17, 18, 19 and 20 wt%, the peak temperatures shift to higher temperatures in this order and the rates of the increase in resistance with increasing temperature are lower than those in usual switching systems such as nHTC–GC. Therefore in this sense the experimental results of these four systems differ from those in other systems which show the switching phenomenon by volume expansion. In PG–GC systems with GC concentration ≥20 wt% sharp peaks are seen at the switching temperature around 62.5°C.

In PG–GC systems characteristic features appear at a GC concentration 17–20 wt%. The moderate decrease in resistance at ~20°C with increasing GC concentration implies that bulk PG plays a role for electric conduction. This will be discussed later.

*Effect of applied voltage on electric current*

As is described already, in a switching system other than PG–GC, electric paths by continuous chains of conductive particles which contact directly with each other are cut by the thermal expansion of the matrix polymer at temperatures near the switching temperature. Therefore the mechanism of the electric conduction at these temperatures is explained by tunnelling current. The importance of tunnelling conduction in carbon-filled polymer systems was given by Miyauchi and Togashi[6]. On the other hand, a theoretical approach was made by Stratton[7] and Simmons[8]. Tunnelling current through a thin potential barrier, the width of which is $d$ and the height of which is $\phi(x)$, is given as

$$J = \int_0^{E_m} P(E_x)dE_x\{(4\pi me/h^3)$$

$$\times \int_0^\infty [f(E) - f(E + eV)]dE_r\} \qquad (1)$$

where $P(E_x)$ is the probability for an electron with a

kinetic energy of $E_x$ can pass through the potential barrier, $\phi(x)$, and is given as

$$P(E_x) = \exp\{(-4\pi/h)\int_0^d [2m(\phi(x) - E_x)]^{1/2}dx\} \qquad (2)$$

where $m$ and $e$ are the mass and the charge of an electron, respectively, h is the Planck constant, $f(E)$ is the Fermi-Dirac distribution function, $E_x$ and $E_r$ are kinetic energies of an electron of X direction and r direction, respectively and the r is the direction perpendicular to the X axis. Simmons and Stratton[7,8] made various approximations and gave different expressions for tunnelling current as a function of voltage. However, they have shown the same result, that although tunnelling current is ohmic when lower voltage is applied, current turns to be strongly voltage dependent when the voltage exceeds a certain value.

In *Figure 3* logarithms of current in the present nHTC–GC system are plotted as a function of electric field. Currents are almost ohmic at 20°C over the whole range of field studied. At 74.5°C (approximately the switching temperature) currents are ohmic at lower field. However strong field dependence of current is also seen when the electric field exceeds 2 V cm$^{-1}$. A similar strong field-dependence is also seen in the carbon black–SBR rubber–wax system[3] if data are replotted. These experimental results agree well with the theoretical results[7,8]. Therefore it can be concluded that the mechanism of the switching in *Figure 3* is due to volume expansion of the bulk systems and that tunnelling currents dominate near the switching temperatures.

In *Figure 4* logarithms of current in the PG–25 wt% GC system are plotted as a function of logarithm of electric field at various temperatures. In this case strong field-dependence of current is not clearly visible, as is
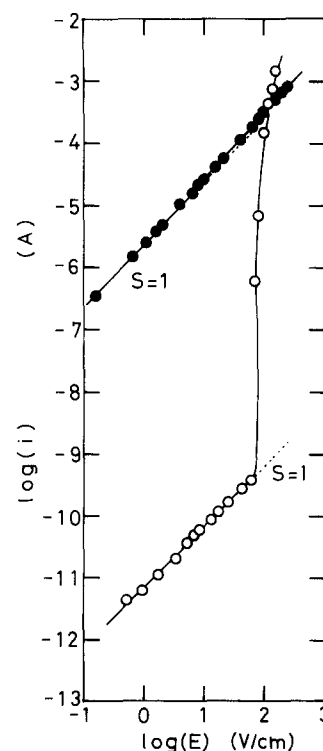


**Figure 3** Logarithm of current vs. logarithm of voltage in SBR-wax-HAF system at 85°C. Data are taken from ref. 3 and recalculated
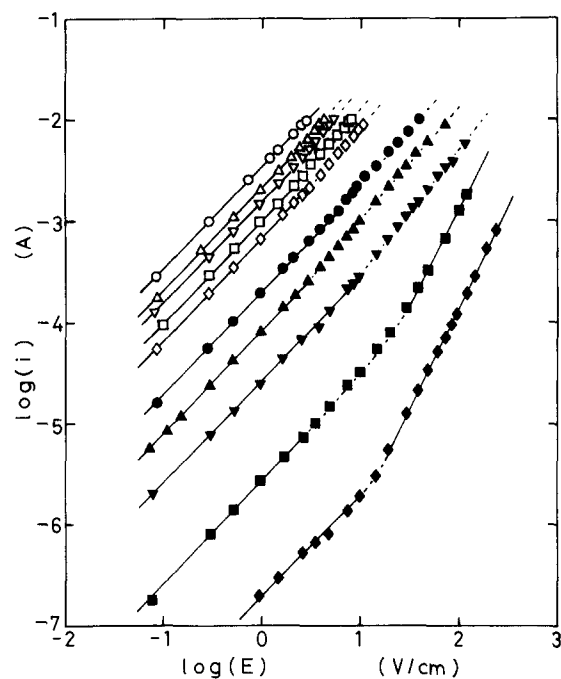
**Figure 4** Logarithm of current vs. logarithm of field in PG-25.0 wt% GC system. Temperatures are: $\bigcirc$, 19.1; $\triangle$, 29.7; $\triangledown$, 40.0; $\square$, 49.7; $\diamond$, 54.9; $\bullet$, 57.6; $\blacktriangle$, 58.7; $\blacktriangledown$, 60.0; $\blacksquare$, 61.0; $\blacklozenge$, 61.9°C respectively

seen in *Figure 3*. At lower fields the slopes of current in *Figure 4* are one. However at higher fields the slopes of current turn out to be 2 at temperatures close to the switching temperature. Slopes change smoothly from 1 to 2 at these temperatures. Thus, the results in *Figure 4* cannot be explained by tunnelling current. This means that volume expansion is not the major mechanism for the switching phenomenon in PG–GC systems.

*Mechanism of electric conduction in PG–GC systems*

In the earlier paper[5] we have used the following equation for the conductivity in PG–GC systems:

$$\sigma = \sigma_0 \exp(-\phi(x)/kT) \qquad (3)$$

where $\phi(x)$ is the barrier height of the thin PG layer between GC grains. We have assumed electron transfer from GC to PG and obtained the potential, $\phi(x)$, with the use of Poisson's equation. However later on we have noticed that it is necessary to integrate $\phi(x)$. This is not done in ref. 5. In order to calculate the conductivity, it is necessary to obtain the density of trapped electrons at the specified position (distribution function). A computational work has been made in order to obtain the relationship between the logarithm of current and the logarithm of voltage, assuming several types of distribution function for trapped electrons. In spite of this work the results obtained were similar to those in *Figure 3*, whatever type of distribution function was used. Therefore no results like those in *Figure 4* are obtained so long as we take a potential barrier in PG.

In order to discuss electric conduction in PG–GC systems we must consider a model circuit composed of two GC grains between which a thin PG layer resides. As in the previous work[5] it is assumed that electrons are transferred from GC to PG. However, we assume here that transferred electrons reside in trapping levels in PG near the GC surface. The density of electrons in trapping
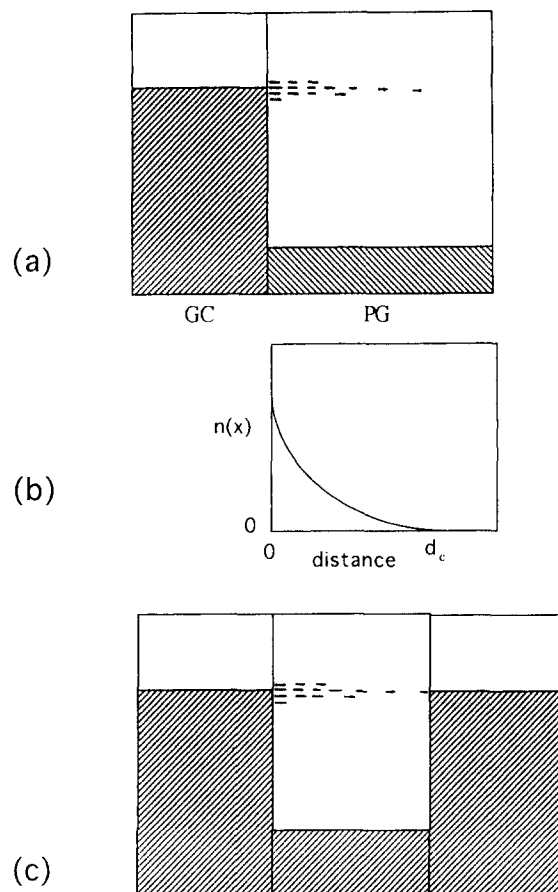


**Figure 5** Schematic picture of PG–GC junction. (a) Trapping sites in PG. The shadow parts represent valence bands. The density of occupied trapping sites is high near the GC surface. (b) Density of occupied trapping sites vs. the distance from the GC surface. The density is zero at $d_c$. (c) Model circuit for electric conduction in PG–GC systems. The distance of the gap should be less than $d_c$ so that occupied trapping sites exist in the entire region of the gap

sites could be higher at positions near the surface, and lowered with increasing distance from the surface, and zero at a certain distance ($d_c$). This is expressed in *Figures 5a* and *5b*. In this case we assume only one direction for the drift of electrons, from left to right in *Figure 6*, because the density of occupied trapping levels is higher near the surface and thus it is easier to find unoccupied levels in the right direction. In order for the model circuit to be conductive the thickness of the PG layer should be thin enough. We consider the critical thickness should be less than $d_c$ where the density of the trapped electrons decreases to zero. Namely, since trapped electrons are found in the entire region of PG layer between GC grains (*Figure 5c*), electrons can drift from one to the other GC grain through PG by hopping among trapping sites. When a voltage is applied for the model circuit, electrons starting from one GC grain, drift by hopping from one trapping site to another in the PG layer, and finally arrive at the other GC grain. When no voltage is applied, the mobility of electrons ($\mu$) can be expressed as,

$$\mu = \mu_0 \exp\{-U/kT\} \qquad (4)$$

where $U$ is the depth of the trapping level in *PG*, k is Boltzmann's constant and $T$ is absolute temperature. When voltage is applied, the mobility is changed as

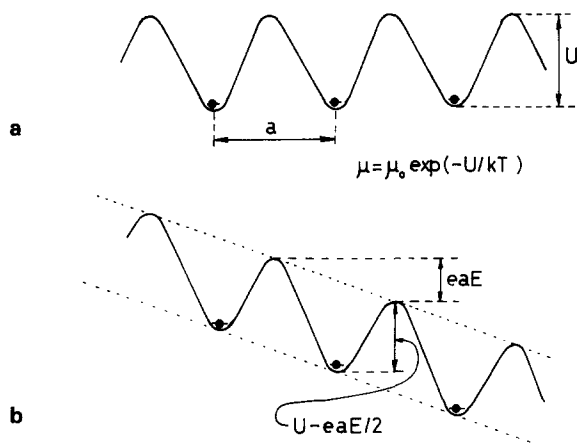$$\mu = \mu_0 \exp\{-(U - eaE/2)/kT\} \qquad (5)$$

**Figure 6** Schematic picture of electron trap in PG. (a) No field is applied. (b) Field ($E$) is applied. The potential is lowered by $eaE/2$
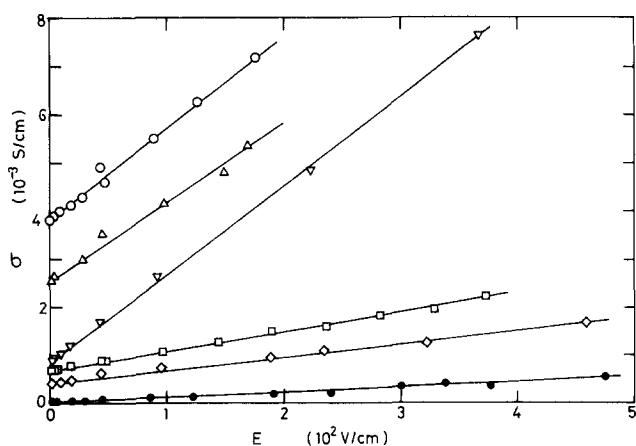


**Figure 8** Logarithm of current vs. logarithm of field in PG–GC systems. GC concentrations and temperatures are: O, 25.0 wt%, 61.0°C; △, 20 wt%, 60.8°C; ▽, 15.0 wt%, 61.3°C; ●, 10.0 wt%, 61.1°C and □, 0 wt%; 60.9°C; respectively. S denotes the slope of the straight line



**Figure 7** Conductivity vs. field in the PG–28 wt% GC system. Temperatures are: O, 19.8; △, 40.5; ▽, 54.9; □, 57.0; ◇, 58.8; ●, 60.9°C, respectively

where $E$ is the electric field between these two GC grains and $a$ is the distance between trapping site. This is shown in *Figure 6*. Then conductivity is given from the mobility as

$$\sigma = ne\mu \qquad (6)$$

where $n$ is the density of charge carriers. Therefore conductivity is given as

$$\sigma = \sigma_0 \exp\{-(U - eaE/2)/kT\} \qquad (7)$$

$$= \sigma_0 \exp(-U/kT) \cdot \exp(eaE/2kT) \qquad (8)$$

When the energy gained from the field is negligible compared with the thermal energy, namely $eaE/2 \ll kT$, conductivity is given by

$$\sigma \simeq \sigma_0 \exp(-U/kT) \cdot (1 + eaE/2kT) \qquad (9)$$

From equation (8) the relation between current density and electric field can be obtained as

$$J = \sigma E$$

$$= \sigma_0 E \exp(-U/kT) \cdot \exp(eaE/2kT) \qquad (10)$$

$$\simeq \sigma_0 \exp(-U/kT) \cdot [E + eaE^2/kT] \qquad (11)$$

Equation (11) agrees well with the experimental results in *Figure 4*. At lower fields the first term of $E$ is dominant
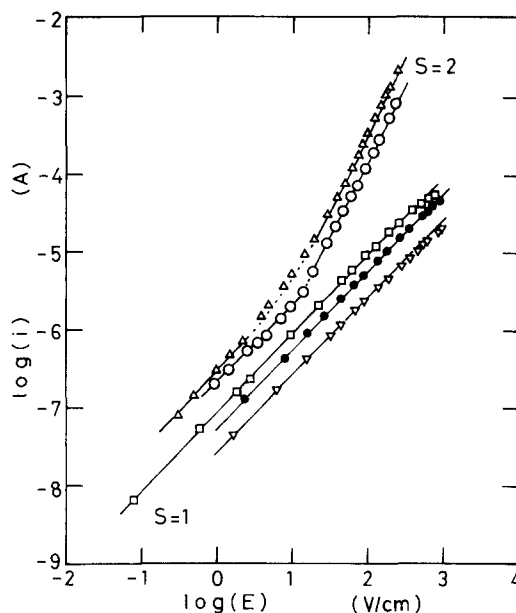
and thus current depends on $E$, whereas at higher fields the second term of $(eaE^2/kT)$ becomes dominant, so current depends on $E^2$.

The same discussion is applicable for equation (9). The second term is negligible for lower field. Thus, an Ohmic relation holds at lower fields as is seen in *Figure 4*. However at higher fields the second term cannot be neglected. In *Figure 7* conductivities of the PG–28 wt% GC system are plotted as a function of field at various temperatures. It should be noted that the abscissa of *Figure 7* is shown with a higher scale ($10^2$ V cm$^{-1}$). In the case of higher fields the second term in equation (9) cannot be neglected. As seen in *Figure 7*, experimental points fit to the straight line, suggesting the validity of equation (9). The slope of the straight line decreases with increasing temperature. On the other hand the slope is given from equation (9) as $\sigma_0(ea/2kT) \exp(-U/kT)$. The decrease in the slope in *Figure 8* could be due to an increase in the trap depth, $U$. This will be discussed later.

It is necessary to discuss field-dependence of resistivity. Generally a larger field-dependence is seen for samples with higher resistivity and this is interpreted in terms of tunnelling current through gaps between carbon particles[6]. In *Figure 7* a larger field-dependence is seen, although the resistivity is not too high. This could be explained as follows. In PG–GC systems electric conduction through thin PG layers between GC particles could play an important role even for samples with 28 wt% GC. Electric paths through continuous chains of GC particles which contact directly with each other do not seem important even in this concentration. This seems to be due to a strong interaction between PG and GC. The existence of an interaction between PG and GC is supported by the GC concentration dependence of resistivities (*Figure 2*), and the effect of dopants on resistivities of PG–GC systems, i.e. addition of small amount of dopants affects the resistivity of PG–GC systems[9].
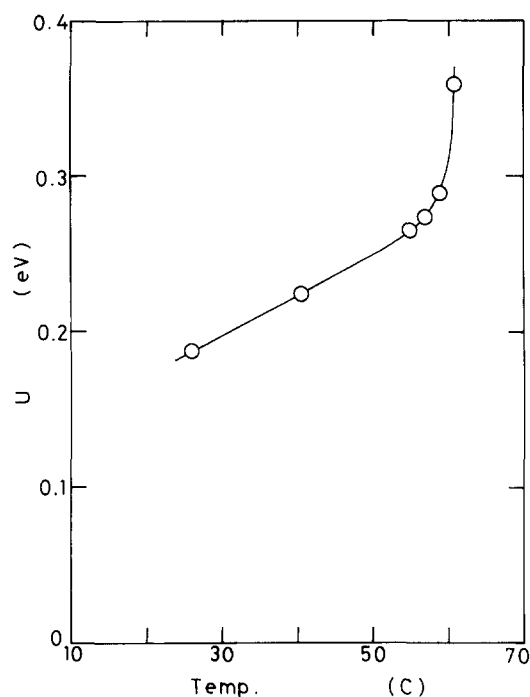
**Figure 9** Depth of trap (*U*) in PG vs. temperature

*The model for electric conduction in PG–GC systems*

It is already described that peculiar behaviours are seen in PG–GC systems as is shown in *Figures 5* and *8*. Since these cannot be explained by the volume expansion model, we have presented the model above. The first problem is the electron transfer from GC to PG and the existence of trapping sites in PG. Unfortunately no direct evidence is available at present. However, some experimental evidence supports this idea, for example, the data on electron mobilities in ethers. It is reported that mobilities of electrons in ethers are extremely low, as are those of ions[10], suggesting a strong interaction between ether molecules and electrons. It should be noted that PG is a polyether. The other is the existence of trapped electrons in r-irradiated PG at $77^\circ$ K[11]. In addition it is reported that an electromotive force is higher in a Cu/LiCl–PG/GC battery system than that in Cu/LiCl–$H_2O$/GC system, suggesting electron transfer from GC to PG[12].

The existence of trapping sites is common in the field of electronics[13]. If the interaction between electrons and surrounding molecules is strong, this favours for electron trapping. In the present case we consider that occupied trapping sites in PG exist only in the region near GC surface and that distances between GC grains should be less than $d_c$ (see *Figure 5c*). This seems to be supported by the following experimental result. *Figure 8* shows logarithm of current vs. logarithm of field in PG–GC systems with various GC concentrations. When GC concentration does not exceed 15 wt%, currents are ohmic in the entire region of field studied (slope = 1). In this region of GC concentration the average distance between GC grains is large enough so that the resistivity of the bulk PG is the major factor for the total resistivity of the system. Therefore currents in these systems are ohmic. However, when GC concentration is increased to 20 wt%, $E^2$ dependence of current (slope = 2) is clearly

seen at higher fields. It seems that 20 wt% is necessary to decrease an average distance between GC grains to the critical value of $d_c$ (*Figure 5c*). In this situation electronic conduction in PG layer between GC grains could be possible by hopping through trapping sites.

It is necessary to discuss the mechanism of the switching phenomenon in PG–GC systems. As is described above, the slope of the straight line in *Figure 7* decreases when temperature comes to close to the switching temperature. According to equation (9) the decrease in the slope is due to the increase in the trap depth, *U*. It is easily understandable that the deeper the trap the lower the probability for a trapped electron to hop into another trap. Therefore the switching, namely the increase in resistance at the switching temperature can be ascribed to the increase in trap depth in PG.

It is possible to calculate the trap depth, *U*, from the value of the intercept in *Figure 7* and equation (9). The value of $\sigma_0$ is obtained by extrapolating the conductivity value of PG–GC systems to 100 wt% GC. The obtained value, $\sigma_0$, is 0.1 S cm$^{-1}$. The value of trap depth in the PG–28 wt% GC system is shown as a function of temperature in *Figure 9*. It is seen in *Figure 9* that trap depth increases sharply at temperatures near the switching temperature. Thus, this sharp increase in trap depth is the mechanism of switching in PG–GC systems. Although the variation of trap depth in *Figure 9* is only 0.2–0.36 eV, this causes a big difference in conductivity as well as resistance because this value is effective in the exponential term.

It is necessary to describe why trap depth increases sharply near the switching temperature. We have shown before that the relationship between resistivity in PG–GC systems and temperature corresponds to that between dielectric constant of bulk pure PG and temperature[5]. It is known in radiation chemistry that electrons are produced by irradiation of liquids or glasses. These are known as solvated or trapped electrons, which show optical absorption maxima in the visible or near infra-red region. It is also known that the absorption maximum relates to the dielectric constant of the matrix. This holds also for the photoconductivity spectrum of trapped or solvated electrons. For a system with higher dielectric constant optical absorption maximum and photoconductivity maximum appear in higher energy sides. Namely the higher the dielectric constant, the deeper the trap depth. Therefore the mechanism of the switching could be due to the increase in dielectric constant of the bulk PG. It is interesting that a linear relation is obtained between logarithm of trap depth and dielectric constant of bulk PG. Although theoretical calculation has been done for trap depths[14], no trial has been made to get such a linear relation.

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