Volume Resistivity, Specific Heat and Thermal Conductive **Properties of the Semiconductive Shield in Power Cables**

Kyoung-Yong Lee[†], Yong-Sung Choi* and Dae-Hee Park*

Abstract - To improve the mean-life and reliability of power cables, we have investigated the volume resistivity and thermal properties demonstrated by changing the content of carbon black, an additive of the semiconductive shield for underground power transmission. Nine specimens were made of sheet form for measurement. Volume resistivity of the specimens was measured by a volume resistivity meter after 10 minutes in a preheated oven at temperatures of both 25 ± 1 [°C] and 90 ± 1 [°C]. As well, specific heat (Cp) and thermal conductivity were measured by Nano Flash Diffusivity and DSC (Differential Scanning Calorimetry). The ranges of measurement temperature were from 0[°C] to 200 [℃], and heating temperature was 4 [℃/min]. From these experimental results, volume resistivity was high according to an increase of the content of carbon black. Specific heat was decreased, while thermal conductivity was increased according to a rise in the content of carbon black. Furthermore, both specific heat and thermal conductivity were increased by heating temperature because the volume of materials was expanded according to a rise in temperature.

Keywords: Semiconductive Shield, Specific Heat, Thermal Conductivity, Volume Resistivity

1. Introduction

Until recently, most studies involving the electrical phenomena and systematic properties of the quality improvement and lifetime enhancement of underground transmission power cables have been limited to the insulating layer. However, this study, through the in-depth analysis of the power cable's semiconductive shield, attempts to instill new recognition on the importance of the role and the function of the semiconductive shield.

Since the usage purpose of the semiconductive shield differs from the interior to the exterior of the XLPE insulator, the required property differs. Therefore, for the semiconductive shield to perform its necessary role in the power cable, it needs to have an adequate amount of carbon black, which provides optimum thermal, electrical and mechanical properties. In this study, the electrical and thermal properties are dealt with, with particular emphasis on the volume resistivity, specific heat and heat conductivity.

First of all, the ultimate reason for using the semiconductive shield material is to ease the uneven electric field between the conductor and the neutral line of the power cable. If any void or impurity exists within the XLPE or the electric field is distorted, field convergence could take place causing damage to the insulator. The semiconductive shield material relieves such distortion phenomenon, allowing an even electric field to maintain. In fact, it is the carbon black within the semiconductive shield material that carries out this role. The carbon black forms a conductive network within the semiconductive shield material, and relieves high electric fields from the conductor shield of the XLPE insulator. However, since the power cable is operated at $90[^{\circ}C]$ continually, it could give rise to other effects on the shield material. For example, it could result in the PTC (positive temperature coefficient) phenomenon, in which the semiconductive shield material's resistance drops dramatically due to the temperature increase, or it could bring about thermal damage to the XLPE insulator due to the increase of specific heat and thermal conductivity. Here, if the thermal conductivity of the semiconductive shield material increases, heat transfer to the exterior will obviously occur. Therefore, it is just a matter of time when the heat is transferred to the XLPE insulator before the oxidation reaction begins. The oxidation reaction occurs as long as there is sufficient temperature and oxygen.

In fact, for the XLPE, molecular level oxygen arises from the process of compounding the material. Thus, oxidation brings about the aging effect, which proceeds over a long period of time [1, 2]. Therefore, through the measurements of volume resistivity, specific heat and thermal conductivity according to carbon black content and temperature, the best base resin will be assigned and the optimum carbon black content will be decided, while maintaining the given role as a semiconductive shield material.

[†] Corresponding Author: School of Electrical, Electronic and Information Engineering, Wonkwang University, Korea. (leeky@wonkwang.ac.kr)

School of Electrical, Electronic and Information Engineering, Wonkwang University, Korea.(biochips@wonkwang.ac.kr, parkdh@wonkwang.ac.kr) Received: January 22, 2005 Accepted: May 19, 2005

2. Experimental

2.1 Materials

In this study, EVA (Ethylene Vinyl Acetate, Hyundai Petrochemical Co. Ltd.), EEA (Ethylene Ethyl Acrylate, Mitsui Dupont) and EBA (Ethylene Buthyl Acrylate, ARKEMA) were used as the basic materials, and their composition ratio is given in Table 1. As shown in Table 1, the content of conductive carbon black (acetylene black) was the variable, and their contents were 20, 30, 40[wt%], respectively.

Table 1 Composition of specimens

(Unit: %)

| (91111111 | | | | | | |
|-----------|---------------------------|---------------------------------------|---|---|---|---|
| EVA | EEA | EBA | Carbon Black Additive | | Agent | Total |
| 78.2 | - | - | 20 | 1.3 | 0.5 | 100 |
| 68.6 | - | - | 30 | 0.6 | 0.5 | 100 |
| 58.9 | - | - | 40 | 0.6 | 0.5 | 100 |
| - | 78.2 | - | 20 | 1.3 | 0.5 | 100 |
| - | 68.6 | - | 30 | 0.6 | 0.5 | 100 |
| - | 58.9 | - | 40 | 0.6 | 0.5 | 100 |
| - | - | 78.2 | 20 | 1.3 | 0.5 | 100 |
| - | - | 68.6 | 30 | 0.6 | 0.5 | 100 |
| - | - | 58.9 | 40 | 0.6 | 0.5 | 100 |
| - | - | - | - | , | - | - |
| - | - | - | - | - | - | - |
| - | - | - | - | - | - | - |
| | 78.2 68.6 58.9 - | 78.2 - 68.6 - 58.9 78.2 - 68.6 - 58.9 | 78.2 - 68.6 - 58.9 - - 78.2 - 68.6 - 58.9 - 78.2 - - - 68.6 | 78.2 - - 20 68.6 - - 30 58.9 - - 40 - 78.2 - 20 - 68.6 - 30 - 58.9 - 40 - - 78.2 20 - - 68.6 30 | 78.2 - - 20 1.3 68.6 - - 30 0.6 58.9 - - 40 0.6 - 78.2 - 20 1.3 - 68.6 - 30 0.6 - 58.9 - 40 0.6 - 78.2 20 1.3 - 68.6 30 0.6 | 78.2 - - 20 1.3 0.5 68.6 - - 30 0.6 0.5 58.9 - - 40 0.6 0.5 - 78.2 - 20 1.3 0.5 - 68.6 - 30 0.6 0.5 - 58.9 - 40 0.6 0.5 - - 78.2 20 1.3 0.5 - - 68.6 30 0.6 0.5 |

As presented in Fig. 1, the sheets were primarily kneaded in their pellet form material samples for 5 minutes on rollers ranging between 70[°C] and 100[°C]. Then they were produced as sheets after being pressed for 20 minutes at 180[°C] with a pressure of 200[kg/cm]. The specimen used for measuring volume resistivity was a sheet of 1[mm] in thickness, 30[mm] in width and 64[mm] in length. Fig. 2 indicates the chemical structure of each of the base resins used in this study. As shown, ethylene polymer chains are copolymerized with olefin chains such as VA, EA, BA.

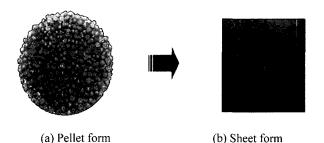


Fig. 1 Shape of semiconductive materials

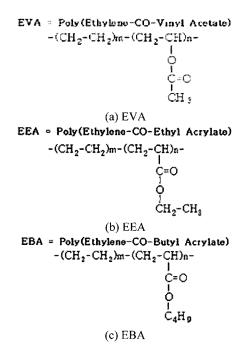
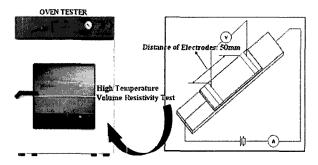


Fig. 2 Chemical structure of base resins

2.2 Experimental devices and methods

The volume resistivity measurement of specimens according to carbon black content was performed in conditions as given in Fig. 3. As shown in Fig. 3, silver paint was applied so that the two ends of each specimen were 50[mm] apart. Afterwards, the specimens were put in ovens that were preheated to $25\pm1[^{\circ}\text{C}]$ and $90\pm1[^{\circ}\text{C}]$ for 10 minutes, and their resistivity was measured.



. Fig. 3 Volume resistivity experimental equipment

The specific heat (Cp) was measured by DSC (TA Instrument, DSC 204F1) with a μ -Sensor, mainly used for specific heat. The temperature range of DSC was from 20[°C] to 60[°C], and the heating rate was 10[°C/min]. The thermal conductivity was measured by Nano Flash Diffusivity (NETZSCH, LFA 447). The measured temperatures were 25[°C] and 55[°C]. Since the melting temperature of the semiconductive shield material was near 60[°C], the thermal conductivity was measured below

55[°C]. This instrument is suitable for ASTM E1461 standards, utilizing the Xenon Flash lamp as the light source. The Xenon Flash lamp is located and operates below the specimen. The heat transferred to the upper part of the specimen is measured by the infra red sensor (IR detector) located above.

3. Results and Discussion

3.1 Volume resistivity

Generally, the electric conductivity can replace the volume resistivity, and typical semiconductive shield materials have values of $10^{\sim} 10[\Omega]$. In fact, every carbon black has a certain range of electric conductivity. When carbon black is mixed with polymers, they show conductivity. Although this conductivity is very complex, the related two theories are general.

The first is the structure theory, which assumes that the conduction occurs through the chain structure of carbon chains. The second is the jumping theory, which assumes that the electrons jump between the dispersed carbon elements. This latter theory is known as the "Tunnel Effect". As shown in Fig. 4 (a), in the conduction system via carbon chains, a sufficient amount of carbon black is necessary to form the chain structure. However, the conduction between widely dispersed carbon elements cannot be explained by the structure theory (Fig. 4 (b)), because it can only occur when the electron hops across gaps that are small in size [nm] (max. gap: 100[Å], when the gap is more than 100[Å] apart, it becomes nonconductive.). Thus, the so called "Tunnel Effect" system is proposed [1-3].

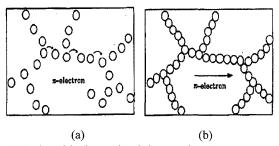


Fig. 4 Carbon black conductivity mechanism: (a) structure theory (b) jumping theory

The first important property for the carbon black to have excellent electric conductivity is the minuteness of the particle. That is, when the size of the particle becomes finer, the amount of carbon black per unit volume increases, thereby decreasing the distance between particles and increasing the conductivity. Secondly, carbon

black with high structure enlarges the path for electron transfer, allowing conductivity to rise. Thirdly, if the porosity is high, the amount of carbon black per unit mass goes up, lowering the distance between particles and increasing conductivity. Fourthly, carbon black with low volatility is needed since volatile elements prevent the tunneling of electrons, thereby decreasing conductivity [3-4].

Fig. 5 shows the measurements of volume resistivity at $25[^{\circ}C]$ of semiconductive shield materials according to the content of carbon black. The volume resistivity decreased in the range of $15^{\circ}218[\Omega]$. cm] as the carbon black content increased. Thus, the conductivity increased according to the structure theory, which allows the distance between particles to shorten as the carbon black content increases.

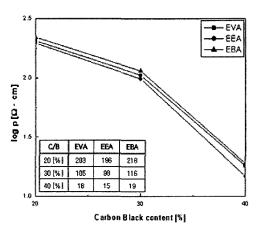


Fig. 5 Volume resistivity of semiconductive materials by carbon black content (at 25° C)

Fig. 6 presents the measurements of volume resistivity at $90[^{\circ}C]$ of semiconductive shield materials according to content of carbon black. The volume resistivity decreased in the range of $135^{\circ}561[\Omega]$. cm] as the carbon black content increased.

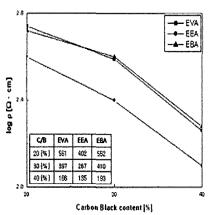


Fig. 6 Volume resistivity of semiconductive materials by carbon black content (at 90 °C)

Just like at 25[°C], the volume resistivity decreased as the carbon black content increased, but the volume resistivity increased more dramatically than at 25[°C]. This is due in part to the PTC (positive temperature coefficient) phenonmenon, which is the increase in the distance between the carbon black particles after the volume expansion due to temperature rise in the base resin below the melting temperature, and in part to the NTC (negative temperature coefficient) phenomenon, which is the formation of a new conductive network by the rearrangement of carbon black above the melting temperature.

Thus, according to the PTC phenomenon, when the temperature reaches melting point, the distance between the carbon black particles increases within the base resin, damaging the conductive network. Such destruction of the conductive network blocks electron hopping, resulting in an increase in volume resistivity. On the other hand, according to the NTC phenomenon, as the melting of resin crystals occurs, all carbon black with fluidity are free to rearrange themselves, forming new conductive networks, increasing electron passageways, and therefore explaining how the volume resistivity value decreases. The melting range of the semiconductive shield materials used in this study is between $63[^{\circ}C]^{\sim}73.61[^{\circ}C]$. Therefore, until this range is approached, the volume resistivity of the semiconductive shield materials will steeply increase due to volume expansion. However, after this temperature, the volume resistivity will somewhat decrease as the carbon black rearranges into a fresh conductive network [6-8].

As a matter of fact, the volume resistivity value is not provided in Fig.s 5 and 6 between $25[^{\circ}C]^{\sim} 90[^{\circ}C]$. Therefore, according to the reference in Fig. 7, most specimens with the melting temperature of $130[^{\circ}C]$ show increase in volume resistivity until $130[^{\circ}C]$, and decrease after that. Thus, it is evident that the PTC phenomenon occurs prior to the melting temperature and the NTC phenomenon occurs after it.

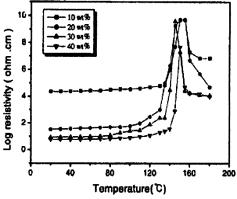


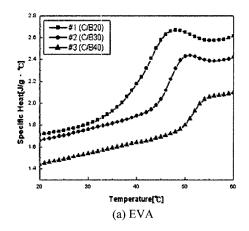
Fig. 7 PTC and NTC properties of CB/HDPE composite by carbon black content

Hereby, according to the melting temperature of the semiconductive shield materials used in this study, the PTC phenomenon occurs from the point of 25[°C] until the melting temperature is reached, and then the NTC phenomenon occurs. According to the results, volume resistivity was lowest when the carbon black content was in the range of 30~40[wt%]. Also, among the semiconductive shield materials, EEA resin, which demonstrated the least effect of PTC and NTC, exhibited excellent electric conductivity.

3.2 Specific heat and thermal conductivity

Fig. 8 indicates the changes of specific heat of the semiconductive shield materials according to carbon black content. As known from Fig. 8, as the carbon black content rises, the specific heat is lowered. Also, within the highlighted circle, as the temperature increases, most materials show dramatic increase of their specific heat after about 30 [°C]. The tendency is readily identified in Table 2, which lists the specific heat of Fig. 8 at 25[°C] and 55 [°C]. That is, as the carbon black content increases at 25 [°C], the specific heat decreases in the range of $1.48869 \sim 1.88374[J/g. \degree C]$. Also, as the carbon black content increases at 55[$^{\circ}$ C], the specific heat decreases in the range of $2.05849 \sim 2.57447 [J/g. \degree]$. However, as the temperature increases, it is evident that the specific heat of the materials is increasing. There are two possible explanations for such phenomena.

First, specific heat lessens according to the carbon black content because the mass of semiconductive shield materials have amplified. Generally, specific heat is defined as the thermal energy [J] needed to heat a 1[g] substance by 1[$^{\circ}$ C] in temperature. The unit is written as [J/g $^{\circ}$ C]. Therefore, as the mass of the material increases, the thermal energy needed to heat the inner temperature of the material decreases.



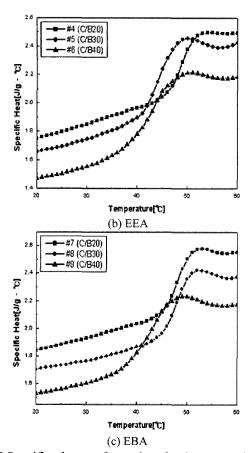


Fig. 8 Specific heat of semiconductive materials by carbon black content and temperature

Particularly in the case of carbon black used as the filling material for the semiconductive shield, since it already possesses excellent thermal conductivity by itself, it is obvious that the used thermal energy within the semiconductive shield material diminishes as the carbon black content rises [9-11].

Second, the specific heat of most semiconductive shield materials increased rapidly as the temperature increased after 30[°C]. The specific heat values of semiconductive shield materials measured in this study are constant-pressure specific heat values. That is the thermal energy when the pressure is constant and the heat is applied.

Table 2 Specific heat of semiconductive materials by carbon black content and temperature

| Specimens | Specific heat [J/g ⋅ ℃] | | | |
|-----------|-------------------------|---------|--|--|
| Specimens | 25[℃] | 55[℃] | | |
| #1 | 1.75051 | 2.57447 | | |
| #2 | 1.70432 | 2.38927 | | |
| #3 | 1.48869 | 2.05849 | | |
| #4 | 1.79656 | 2.49502 | | |
| #5 | 1.69282 | 2.39703 | | |
| #6 | 1.50342 | 2.18059 | | |
| #7 | 1.88374 | 2.56049 | | |
| #8 | 1.73263 | 2.39790 | | |
| #9 | 1.56017 | 2.17554 | | |

Under constant pressure, the materials will expand in size as the temperature goes up. Thus, part of the heat is being used to perform the work of volume expansion. Therefore, in order to boost the temperature, more heat should be applied. This is why the specific heat of the materials soared after $30[\,^{\circ}\mathrm{C}]$ [9, 10].

The peak of specific heat reaches its maximum point around $50[^{\circ}C]$ as the temperature for the semiconductive shield materials rises. After this point, the materials exhibit slight decrease in specific heat, and then increase again. In fact, this temperature range is where the melting point of the materials appears. Therefore, this is the region when the materials are taking in heat in order to change their state from solids to liquids and not for volume expansion. In addition, more thermal energy is required for their state transition because of their latent heats. This is why there is the rising tendency in the specific heat values.

Fig. 9 shows the changes in thermal conductivity of the semiconductive shield materials according to carbon black content and temperature change. Thermal conductivity defines the extent of heat (=energy) transferred from one point to another within a certain object. As shown in Table 3, polymers and ceramics have less thermal conductivity than metals. This is because metal materials produce free electrons by forming metal bonds. These free electrons do not play their roles only in electric conductivity, but in heat transfers as well. In this type of instance, the free electrons are called thermal electrons. Thermal electrons receive energy from the active vibration of the atom when they inter-collide. As the entropy movement of the thermal electrons amplifies, active thermal electrons transfer energy to the colder side by the vibration and collision of the atoms. Thus, this is in agreement with the second law of thermodynamics (=law of entropy) [10].

Conversely, non-metals do not contain the free electrons necessary to transfer thermal energy from high temperature to low temperature. However, these non-metals transfer their heat by the vibration of the atom. As the atom begins vibrating, the heat is transferred as the nearby atoms start vibrating from the affect of the first one. This form is known as phonon. As a reference, the semiconductive shield materials used in this study are semiconductive complex materials that contain both non-metal polymers and conductive carbon black.

As previously mentioned, Fig. 9 presents the changes in thermal conductivity of the semiconductive shield materials according to the carbon black content and temperature. As evident from Fig. 9, thermal conductivity of the materials at 25[°C] increases in the range of 0.406~0.721[W/mK], and the materials at 55[°C] increases in the range of 0.469 ° 0.807[W/mK]. Thus, thermal conductivity of the materials goes up as the carbon black

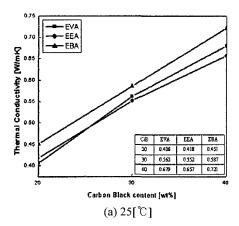
content increases or the temperature rises. This tendency has already been explained by the prior explanation on specific heat. As mentioned, specific heat is the thermal energy needed to increase 1[g] of the material by $1[^{\circ}\mathbb{C}]$. This could be phrased to say that the particles within the material are storing the thermal energy [10-14].

Table 3 General thermal conductivity of materials at 25 [°C] [10].

| Pure metal | Nb | Fe | Zn | W | Al | Cu | Ag |
|----------------------------|-----------------------|-----------------------|-------------------|------------------|-------------------|---------------------|---------|
| k [W/mK] | 52 | 80 | 113 | 178 | 250 | 390 | 420 |
| Ceramics and glasses | Glass borosilicate | Silica-fused (SiO) | SN | Alumina (AlO) | Sapphire (AlO) | Rerylliuum (BeO) | Diamond |
| k [W/mK] | 0.75 | 1.5 | 20 | 30 | 37 | 260 | ~ 1000 |
| Polymers | Poly propylene | PVC | Poly carbonate | Nylon 6.6 | Teflon | LDPE | HDPE |
| k [W/mK] | 0.12 | 0.17 | 0.22 | 0.24 | 0.25 | 0.3 | 0.5 |

From the specific heat measurement, the materials do not use all the heat they acquire for increasing their inner temperature. Thus, the particles within the material store the permitted thermal energy until the critical point (=the thermal equilibrium temperature within the material), and once it has been reached, they transfer the thermal energy to another point as they cannot afford the energy. Thus, the semiconductive shield materials store the thermal energy from the continuous temperature rise until thermal equilibrium is reached, and transfer the leftover heat to other points. In addition, as the content of carbon black, which has an excellent thermal conductivity, increases, their distance between particles decreases. This promotes the movement of thermal electrons between carbon black particles, and the thermal vibrations of base resin atoms and carbon black thermal electrons rises. Therefore, it is obvious to say that the thermal conductivity increases as the carbon black content increases.

From the results, EVA and EEA generally show similar curves, but at $25[\,^{\circ}C]$, EVA has increased by $1.7{\sim}3.2[\text{wt}\%]$ than EEA and at $55[\,^{\circ}C]$, EEA by $0.9{\sim}2.7[\text{wt}\%]$. Also, EBA shows more thermal conductivity than EVA and EEA.



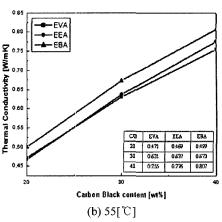


Fig. 9 Thermal conductivity of semiconductive materials by carbon black content and temperature

This demonstrates the property of EBA, which had the biggest specific heat value. Therefore, EEA exhibits excellent thermal conductivity in general.

4. Conclusions

In this study, the thermal and electrical properties of semiconductive shield materials according to carbon black content and temperature have been measured, and by appointing the optimal base resin and carbon black content the possibility of improving the reliability of power cable has been investigated.

As the result, many specimens' volume resistivity decreased as the carbon black content increased in the electrical property experiments. This is due to the shortening of the distance between the particles as the carbon black content rose, leading to improvement in electrical conductivity. Also, among the volume resistivity investigated at 25 [°C] and 90 [°C], there was a much more dramatic increase at 90[°C] compared to that at 25[°C]. This is due in part to the PTC phenomenon, which occurs by the temperature rise below the melting temperature, volume expansion of the base resin and the increase in the distance of carbon black particles resulting from it, and also to the NTC phenomenon, which occurs by the rearrangement of carbon black within the base resin after the melting temperature, forming a new conductive network, leading to the decrease of volume resistivity. In this experiment, the semiconductive shield material was mostly unaffected by PTC and NTC, with the EEA resin showing an outstanding degree of electrical conductivity.

In the specific heat measurement, according to the mass increase due to the boost of carbon black content within the materials, the specific heat diminished. Also as the temperature rose, it could be seen that most materials had a rapid increase in their specific heat after 30[°C], due to the

increase in thermal energy consumption, resulting from the volume expansion within the materials. The specific heat, which exhibited a gentle decline, demonstrates a tendency to increase again after 50[°C]. This was because additional thermal energy was needed for the state transition of the materials.

Lastly, when measuring thermal conductivity, it increased as the carbon black content and temperature became higher. This was because the particles within the materials stored the permitted thermal energy until a certain critical point (=thermal equilibrium temperature within the materials), only transferring the thermal energy to other points when it could hold no more. Thus, the materials stored the thermal energy from the continuous temperature rise, and transferred the leftover thermal energy to other points. Also, the increase of carbon black, which has an outstanding thermal conductivity, led to shortening of particle distances and an increase in thermal conductivity.

From the results, EEA was an outstanding base resin with electrical conductivity among the materials, and the optimal carbon black content was 30~40[wt%]. EBA showed the best thermal conductivity. EEA and EVA displayed similar properties. Therefore, considering both electrical and thermal properties, EEA was assigned to be the best base resin.

Acknowledgment

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Kyoung-Yong Lee

He received his B.S. degree in Electrical, Electronic and Information Engineering from Wonkwang University. Since his graduation, he has been working towards his M.S. degree at the same university. His research interest is in the area of electrical

materials. His main field of study has been power cable insulating materials and polymer fields.

Tel: +82-63-850-6349. Fax: +82-63-857-6890



Yong-Sung Choi

He received his B.S., M.S. and Ph.D. degrees in Electrical Engineering from Dong-A University in 1991, 1993 and 1998, respectively. He was employed as a Post-doctoral Fellow at the Japan Advanced Institute of Science and Technology from 1999 to 2000. He

then worked with T. Kawai of Osaka University as a JSPS Fellow from 2001 to 2002. He has also worked as a Research Professor at Wonkwang University. His main research interests are in the areas of biotechnology (biochip), high voltage, and discharge and its applications.

Tel: +82-63-850-6349, Fax: +82-63-857-6890



Dae-Hee Park

He received his B.S. and M.S. degrees in Electrical Engineering from Hanyang University in 1979 and 1983, respectively, and his Ph.D. degree from Osaka University in 1989. He worked at the LG Cable Research Institute as a Senior Researcher from 1974 to 1992.

After that, he joined the School of Electrical, Electronics and Information Engineering at Wonkwang University where he is currently employed as a Professor. He was at MSU in the USA as a Visiting Professor from 1999 to 2000. His main research interests are in the areas of insulating and dielectric materials, new lighting sources and discharge. From 2004, he has been a Director at the Center for Advanced Electric Applications.

Tel: +82-63-850-6349, Fax: +82-63-857-6890