Study on Filled XLPE Insulation Material for HVDC Cables, Part. 1

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The High Voltage Direct Current (HVDC) cables developed by our company are highly regarded for their excellent direct current (DC) characteristics. These include a permissible conductor temperature of 90°C under normal conditions and the ability to operate under polarity reversal. These characteristics are achieved by adding inorganic fillers to cross-linked polyethylene (XLPE). Our cables are widely adopted in domestic and international projects. Through collaborative research with the university, we are working to understand how adding inorganic fillers improves DC characteristics. As part of these efforts, we report the development of a novel technique for evaluating charge trap depth, which is believed to significantly influence DC characteristics, using approaches such as X-ray photoelectron spectroscopy (XPS) and X-ray absorption spectroscopy (XAS).

Keywords: HVDC, XLPE cable, nanocomposite, insulation material

1. Introduction

As renewable energy sources become increasingly utilized, the demand for direct-current (DC) cables is rising for applications such as transmitting electricity from offshore wind farms to the mainland and facilitating international interconnections for wide-area electricity exchange. Cross-linked polyethylene (XLPE),*1 which is free from oil-leakage concerns, is currently the predominant insulation for DC cables. However, conventional XLPE cables utilized in alternating-current applications have been observed to accumulate substantial space charge*2 under DC voltage. This makes XLPE insulation problematic for many DC cable applications. Sumitomo Electric Industries, Ltd. has historically prioritized the incorporation of inorganic fillers, such as talc and clay, into XLPE, with the objective of enhancing its insulating properties. As a consequence, the company has a strong track record domestically and abroad; examples include the world's first 250 kV DC-XLPE cables supplied to Electric Power Development Co., Ltd. for its Kitahon High Voltage DC (HVDC) Link in 2012, 250 kV DC-XLPE cables delivered to Hokkaido Electric Power Co., Inc. for installation in a long tunnel for the Hokuto-Imabetsu HVDC Link in 2019, and the world's highest-voltage 400 kV DC-XLPE cables, shipped to NEMO Link Limited for connection between the UK and Belgium in 2019. These cables incorporate insulation made of a material produced by adding an inorganic additive to XLPE to have high DC characteristics, enabling operation at high temperatures (a high continuous permissible conductor temperature of 90˚C) and with reversed polarity. Furthermore, to prevent the inorganic filler from coagulating in XLPE and turning into foreign matter defects, Sumitomo Electric has cultivated material technologies for utilizing finely dispersed nanoscale particle-size fillers. This paper reports on our efforts to develop a method of evaluating charge trap depth. Charge trap depth is considered important for understanding the DC characteristics of DC-XLPE cables.

2. Polymer Nanocomposites and DC Characteristics

2-1 Polymer nanocomposites

Materials produced by adding a filler with a nanoscale particle size to a polymer to improve its characteristics are generally known as polymer nanocomposites. Nanocomposites have a large interface area between the polymer and filler, therefore even a small amount of filler can drastically improve the polymer's performance. Nanocomposites are particularly attracting great interest as an insulation material because they have been found to surpass polymers in breakdown strength and partial-discharge resistance.[1), 2)] Nanocomposites have also been reported to improve DC characteristics by suppressing space charge accumulation and reducing electrical conductivity.[3), 4)] Figure 1 shows a comparison of the volume resistivity for nanocomposites containing small amounts of various inorganic fillers added to the polymer. Note that these are relative values, with the volume resistivity of the polymer alone set to 1. It can be seen that adding any of the fillers A to C improves the volume resistivity compared to the polymer alone. Furthermore, as seen when filler C is added, it was confirmed that even with the same constituent elements of filler, changing its surface treatment can result in significant differences in volume resistivity. Therefore, it is

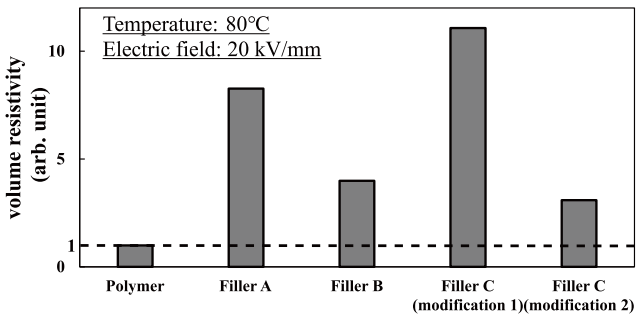

Fig. 1. Volume resistivity of different nanocomposites

necessary to understand the effects of constituent elements and surface treatment of fillers on DC characteristics.

2-2 Charge trap

The reasons why electrical conductivity and space charge accumulation characteristics change with filler addition include increased charge carrier migration paths and alterations in polymer morphology such as crystallinity. Another plausible explanation frequently reported is the effect of "charge traps" formed at the interface between the polymer and filler.[5], [6]

Several models have been proposed regarding the mechanism of charge trap formation and the effects of charge traps on electrical properties such as electrical conductivity and space charge accumulation. For example, as shown in Fig. 2, trap levels for charges (holes/electrons) are generated at the interface between the polymer and filler. It is explained that trapping of charges at these levels causes a decrease in the overall electrical conductivity of the material and relaxation of the local electric field.

Traditionally, charge trap depths have been estimated using thermally stimulated depolarization currents (TSDC) and photo-stimulated discharge currents (PSDC). However, since TSDC does not account for the potential effect of temperature changes on the polymer's molecular structure during the measurement process, and since PSDC makes it difficult to assign the obtained spectra, these methods may not accurately evaluate charge trap depth. Therefore, as a novel method for evaluating charge trap depths, we developed a technique, termed X-Ray spectroscopic Trap Depth Profiling (X-TDP), that assesses the charge trap depth within nanocomposites by evaluating the band alignment at the interface between the polymer and filler.

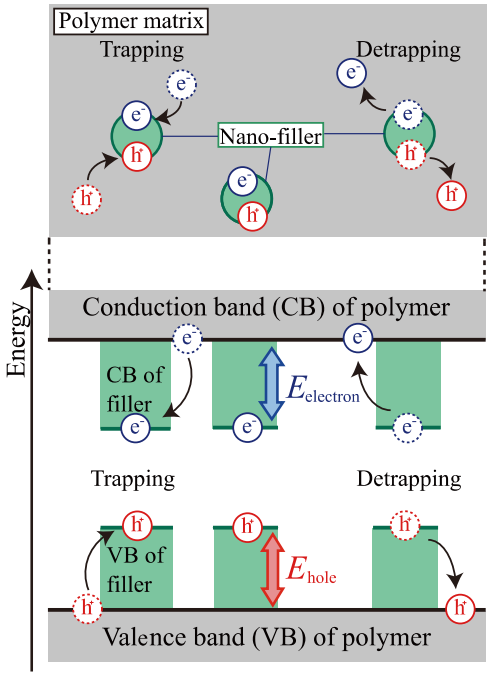

Fig. 2. Schematic diagram of the structure and energy levels in nanocomposites

3. Development of a Method for Evaluating the Charge Trap Depth Formed by Fillers

This chapter first briefly explains the principles of two types of analysis required for the evaluation and then describes a method for calculating charge trap depth.

3-1 X-ray photoelectron spectroscopy (XPS)

XPS is a technique for analyzing the electronic states and chemical bonding states of atoms present within a few nanometers of a material's surface. Figure 3 shows a schematic diagram of XPS. Electrons within atoms in a material are bound to specific electron orbitals, each possessing a characteristic binding energy E_B. When X-rays with an energy greater than E_B are irradiated, the photoelectric effect causes these electrons to be emitted as photoelectrons with a certain amount of kinetic energy. Here, the energy conservation law expressed by Eq. (1) holds true.

$$E_B = h\nu - E_K - \phi \quad \cdots\cdots (1)$$

In this equation, E_K is the kinetic energy of the photoelectron entering the spectrometer; $h\nu$ is the X-ray energy; and ϕ is the spectrometer's work function. XPS detects the energy of the emitted photoelectrons. Since $h\nu$ is constant, determining ϕ from standard samples, such as gold, allows one to determine the binding energy E_B of the electron orbitals within the sample. Varying the measurement range of E_K while irradiating with X-rays yields a spectral distribution showing the relationship between the kinetic energy of the emitted photoelectrons and their intensity.

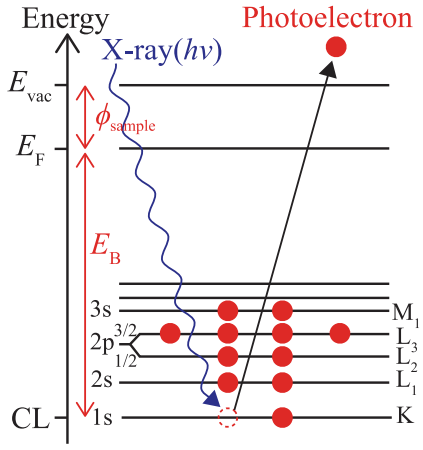

Fig. 3. Schematic diagram of measurement of bond energy E_B by XPS

3-2 X-ray absorption spectroscopy (XAS)

XAS is a technique that analyzes the electronic and chemical bonding states of a sample. It utilizes the phenomenon in which electrons in the core levels of elements within the sample absorb part of the X-rays and become excited into unoccupied orbitals when X-rays are irradiated onto the sample. Figure 4 presents a schematic diagram of XAS. Scanning the energy of the X-ray irradiating the sample reveals a sharp increase in X-ray absorption at the energy level corresponding to the bond energy

of the core electrons, i.e., differential energy between core level and the lowest unoccupied level. The peak of this increase is known as the X-ray absorption edge. Detailed measurement of absorption spectra at a certain energy level close to the X-ray absorption edge reveals an oscillation structure known as the X-ray absorption fine structure (XAFS). For this measurement, it is a general practice to use a synchrotron light source that can continuously radiate a high-intensity X-ray. Light of the required energy is extracted from this source using a spectrometer and irradiated onto the sample.

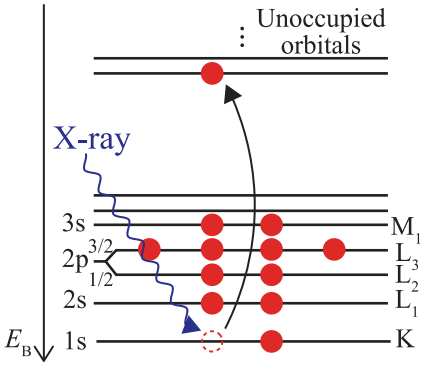

Fig. 4. Schematic diagram of XAS measurement

3-3 Evaluation of charge trap depth by X-TDP

Figure 5 presents a schematic diagram of band alignment at the interface between the polymer and filler. This section describes techniques used to evaluate the hole trap depth E_{hole} and the electron trap depth $E_{electron}$ as charge trap depths.

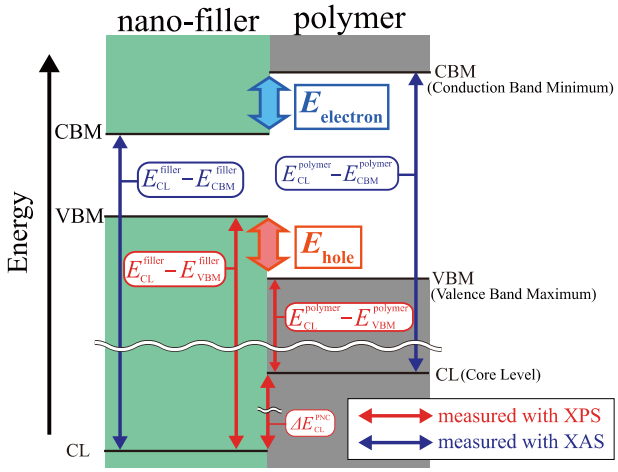

Fig. 5. Band alignment at polymer / inorganic filler interface

(1) Evaluation of hole trap depth

The hole trap depth E_{hole} formed by inorganic fillers is determined as the energy difference between the valence band maximum (VBM) originating from the inorganic filler and the VBM originating from the polymer within the nanocomposite material. However, in measurements using only the nanocomposite, it is difficult to distinguish between the VB spectrum originating from the polymer and the VB spectrum originating from the filler. Furthermore, XPS measurements of insulating samples are affected by sample charging, causing shifts in the absolute energy values. Therefore, a method was developed to evaluate the hole trap depth from individual samples of polymer and inorganic filler, as shown in the following Eq. (2).

$$E_{hole} = \Delta E_{CL}^{PNC} + \left(E_{CL}^{polymer} - E_{VBM}^{polymer}\right) - \left(E_{CL}^{filler} - E_{VBM}^{filler}\right) \quad \cdots\cdots (2)$$

In this equation, $\Delta E_{CL}^{PNC} = E_{CL-filler}^{PNC} - E_{CL-polymer}^{PNC}$ is the difference between the energy of the inner core level of the inorganic filler constituent atoms in the nanocomposite sample and the energy of the core level of the polymer constituent atoms. Similarly, $E_{CL}^{polymer} - E_{VBM}^{polymer}$ is the difference between the energy of the core level of the polymer constituent atoms itself and the VBM energy, and $E_{CL}^{filler} - E_{VBM}^{filler}$ is the difference between the energy of the core level of the filler constituent atoms itself and the VBM energy. As seen in Eq. (2), this method utilizes only the energy differences between the core levels and the VBM, and between the core levels themselves for each sample. Therefore, shifts in the absolute energy values due to sample charging do not affect the evaluation results.

(2) Evaluation of electron trap depth

The electron trap depth $E_{electron}$ formed by inorganic fillers can be determined as the energy difference between the conduction band minimum (CBM) originating from the inorganic filler within the material and CBM originating from the polymer. Since XPS measures photoelectrons emitted from occupied orbitals, it cannot directly measure the energy of the CBM, which is an unoccupied orbital. Therefore, we developed a method to evaluate the electron trap depth by combining XPS and XAS measurement results, as shown in the following Eq. (3).

$$E_{electron} = \Delta E_{CL}^{PNC} + \left(E_{CL}^{polymer} - E_{CBM}^{polymer}\right) - \left(E_{CL}^{filler} - E_{CBM}^{filler}\right) \quad \cdots\cdots (3)$$

In this equation, $E_{CL}^{polymer} - E_{CBM}^{polymer}$ represents the difference in energy between the core level of the constituent atom in the polymer unit and the CBM, while $E_{CL}^{filler} - E_{CBM}^{filler}$ represents the difference in energy between the core level of the constituent atom in the filler unit and the CBM. These values are obtained by analyzing the XAS measurement results for each sample.

4. Example Study: Using LDPE with TiO_2

4-1 Measurement samples and conditions

The X-TDP method was used to evaluate the charge trap depth formed by titanium dioxide (TiO_2) in low-density polyethylene (LDPE).

A monochromatic Al Kα line (1486.6 eV) was used as

the XPS measurement light source, with charge neutralization performed as necessary using an Ar ion gun.

XAS was measured in the soft X-ray region using the total electron yield method at the beamline BL17 of Kyushu Synchrotron Light Research Center (SAGA-LS). (Project Numbers: SEI2023C-019, SEI2024A-019)

4-2 Measurement results

From the XPS and XAS measurements, the band alignment at the LDPE-TiO_2 nanocomposite interface was determined as shown in Fig. 6. Since the VBM of the TiO_2 is higher than that of the LDPE, TiO_2 can trap holes within LDPE, with a trap depth of 0.6 eV. Furthermore, since the CBM of TiO_2 is lower than that of LDPE, it was found that TiO_2 can trap electrons in LDPE, with a trap depth of 3.7 eV.

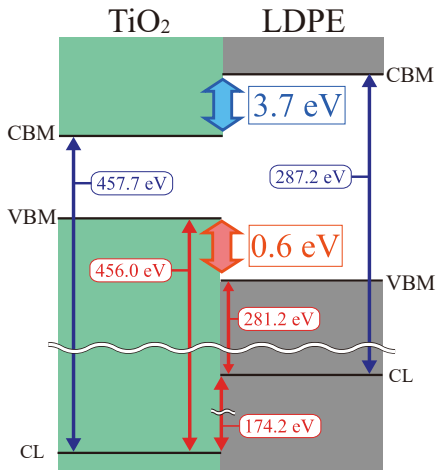

Fig. 6. Band Alignment of TiO_2 / LDPE nanocomposites

4-3 Discussion

The results of this study are consistent with previous studies. One of such studies[7] indicates that the direct current electrical conductivity decreases with the addition of TiO_2 compared to LDPE alone. The other studies[8], [9] indicate that space charge accumulation is suppressed. This confirms the improvement effect of TiO_2 addition on direct current characteristics. Regarding the suppression of space charge accumulation by charge traps, the following factors are generally considered. One is that charge traps formed by TiO_2 inhibit the mobility of ionic charges generated by impurity ionization, thereby suppressing local charge accumulation and reducing the heterocharge*3 density near the electrode. Another factor is that the homocharge*3 injected from the electrode into the nanocomposite is trapped by the filler near the electrode-nanocomposite interface, increasing the homocharge density near the interface. These two factors are thought to have suppressed space charge accumulation in the nanocomposite by relaxing the charge at the electrode-nanocomposite interface and inhibiting subsequent charge injection.

Comparing the trap depths for holes and electrons, since deeper traps are formed for electrons, differences in macroscopic properties such as electrical conductivity and space charge accumulation behavior may arise depending on the polarity of the applied voltage. Therefore, further investigation is warranted. Furthermore, the charge trap depths evaluated in this study were found to be consistent with first-principles calculation results.[10]

5. Conclusion

Sumitomo Electric's DC-XLPE cables exhibit exceptional DC characteristics, including a continuous permissible conductor temperature of 90°C and the ability to operate under polarity reversal, achieved through the addition of inorganic fillers. These cables have been successfully applied in numerous domestic and international projects. This paper reports an evaluation method for charge trap depth, considered crucial for elucidating the mechanism behind the characteristic of DC-XLPE cables. We will continue to utilize this method to investigate these mechanisms further.

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Technical Terms

*1 Cross-linked polyethylene (XLPE): A polymeric insulation material made by strengthening intermolecular bonds of polyethylene through crosslinking reaction for improved heat resistance. XLPE is most widely used as insulation in power transmission cables.

*2 Space charge: Electric charge accumulated in an insulation material under the application of an electric field to the material. When space charge is present, the electric field is locally distorted.

*3 Heterocharge/Homocharge: If the polarity (positive/negative) of the charge injected from an electrode differs from the polarity of the space charge produced in front of the electrode, the space charge is termed heterocharge; if identical, the charge is termed homocharge.

References

(1) Roy, M., Nelson, J. K., MacCrone, R. K., Schadler, L. S., Reed, C. W., and Keefe, R., "Polymer nanocomposite dielectrics-the role of the interface," IEEE transactions on dielectrics and electrical insulation, vol. 12, no. 4, pp. 629-643 (2005)

(2) Tanaka, T., Dielectric nanocomposites with insulating properties, IEEE Transactions on Dielectrics and Electrical Insulation," vol. 12, no. 5, pp. 914-928 (2005)

(3) Murakami, Y., Nemoto, M., Okuzumi, S., Masuda, S., Nagao, M., Hozumi, N., Sekiguchi, Y., and Murata, Y., "DC conduction and electrical breakdown of MgO/LDPE nanocomposite.," IEEE Transactions on Dielectrics and Electrical Insulation, vol. 15, no. 1, pp. 33-39 (2008)

(4) Hayase, Y., Aoyama, H., Matsui, K., Tanaka, Y., Takada, T., and Murata, Y., "Space charge formation in LDPE/MgO nano-composite film under ultra-high DC electric stress," IEEJ Transactions on Fundamentals and Materials, vol. 126, no. 11, pp. 1084-1089 (2006)

(5) Smith, R. C., Liang, C., Landry, M., Nelson, J. K., and Schadler, L. S., "The mechanisms leading to the useful electrical properties of polymer nanodielectrics," IEEE Transactions on Dielectrics and Electrical Insulation, vol. 15, no. 1, pp. 187-196 (2008)

(6) Li, S., Min, D., Wang, W., and Chen, G., "Linking traps to dielectric breakdown through charge dynamics for polymer nanocomposites," IEEE Transactions on Dielectrics and Electrical Insulation, vol. 23, no. 5, pp. 2777-2785 (2016)

(7) Fleming, R. J., Pawlowski, T., Ammala, A., Casey, P. S., and Lawrence, K. A., "Electrical conductivity and space charge in LDPE containing TiO2/ nanoparticles," IEEE Transactions on Dielectrics and Electrical Insulation, vol. 12, no. 4, pp. 745-753 (2005)

(8) Wang, Y., Xiao, K., Wang, C., Yang, L., and Wang, F., "Effect of nanoparticle surface modification and filling concentration on space charge characteristics in TiO2/XLPE nanocomposites.," Journal of Nanomaterials, vol. 1 (2016)

(9) Gao, J. G., Liu, H. S., Lee, T. T., Schachtely, U., Kobayashi, H., and Li, L. L., "Effect of hydrophilic/hydrophobic nanostructured TiO2 on space charge and breakdown properties of polypropylene.," Polymers, vol. 14, no. 14, 2762 (2022)

(10) Katase, D., Onoda, T., Kubo, Y., Uemura, S., Sekiguchi, Y., Umemoto, T., Kumada, A., and Sato, M, "X-Ray Spectroscopic Trap Depth Profiling (X-TDP) for Charge Trap Analysis in Polymer Nanocomposites," IEEE Transactions on Dielectrics and Electrical Insulation, vol. 99, no. 1-1 (2025)

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