Deep trap sites suppressing space charge injection in polycyclic aromatic compounds doped XLPE composite

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Abstract: In this study, the space charge characteristics in the polycyclic aromatic compounds doped cross-linked polyethylene (XLPE) composite were analysed by integration current (Q(t)) method and quantum chemical calculation. Experimentally, the space charge behaviours of XLPE composites modified by the three selected polycyclic aromatic compounds during polarisation and depolarisation process at 25 and 80°C were measured by Q(t) method, respectively. The energy levels and 3D potential distributions of the three polycyclic aromatic compounds were calculated by density functional theory. The experimental and calculation results indicate that the polycyclic aromatic compound C with deep carrier traps and stronger polarity exhibits outstanding ability to reduce space charge injection than the others at both 25 and 80°C. Generally, 4,4′-bis (dimethyl amino) benyil has great potential as the organic additive for DC cable insulation from the view of space charge suppression.

1 Introduction

Space charge accumulation in cross-linked polyethylene (XLPE) is always one of the most serious problems in high-voltage direct current (HVDC) insulation applications, especially for HVDC cables [1, 2]. In recent years, many methods have been proposed to suppress space charge injection. Nanocomposites are one of the most concerned and widely studied methods [3–6]. However, the uniform dispersion of inorganic nanoparticles in the XLPE matrix cannot be guaranteed even after surface treatment, which greatly limits the application of nanocomposites in practical engineering [7].

The polycyclic aromatic compound is one of the earliest reported special additives in XLPE insulating materials for power cables. Some research results have shown that polycyclic aromatic compounds can improve the DC breakdown strength and space charge characteristics of polyethylene [8, 9]. However, the physical mechanism of polycyclic aromatic compounds on the suppression of charge injection has not been fully understood. Over the past few years, researchers have gradually focused on the molecular simulation and the quantum chemistry studies of small size molecules or particles to reveal the charge transport characteristics [10, 11]. This greatly facilitates the efficiency of polycyclic aromatic compounds selection for HVDC cable insulation and assists the analysis of their physical mechanism in XLPE composite.

This paper focuses on the space charge injection of the polycyclic aromatic compounds modulated XLPE composites and its quantum calculation analysis. The modification of XLPE was achieved by three selected polycyclic aromatic compounds. The space charge characteristics of different samples were measured by a Q(t) system. The energy levels and 3D potential distributions of the additives were calculated and discussed to reveal the mechanisms of charge transport modulation.

2 Experimental setup

2.1 Test sample

The polycyclic aromatic compounds, 4,4′-difluorobenzophenone, 4,4′-dihydroxybenzophenone, 4,4′-bis (dimethyl amino) benyil, were purchased from J&K Scientific Ltd, and denoted by PAC-A, B, C, respectively (Fig. 1). The neat XLPE serving as control, which was supplied by Borealis Company, was made by low-density polyethylene containing antioxidant and dicumyl peroxide. The different polycyclic aromatic compounds with additive content of 0.5 wt% were dispersed into the XLPE matrix by the Bunbury mixer at the processing temperature of 110°C. The samples were made by a stainless-steel mould at 180°C for 30 min under a pressure of 30 MPa to produce films with a diameter of 10 cm and thicknesses of 250 μm.

2.2 Current integration measurements

The basic principle of $Q(t)$ method is to insert an integrating capacitor $(C_{INT})$ between a high-voltage terminal and the test target [12, 13]. $Q(t)$ is defined as follows:

$$Q(t) = Q_0 + \int_0^t I_{ab}(t) \, dt + \int_0^t I_{leak}(t) \, dt$$

where $Q_0 = C_s V_{dc}$ is the initial amount of charge on $C_{INT}$, $C_s$ is the capacitance of the test sample and $V_{dc}$ is the applied voltage. $I_{ab}(t)$ is the absorption current due to the trapping and de-trapping process during space charge injection, and $I_{leak}(t)$ is the leakage current. This measurement was carried out at 25°C and 80°C.

Fig. 1 Chemical structural formula of polycyclic aromatic compounds
(a) PAC-A, (b) PAC-B, (c) PAC-C
current after the equilibrium of carrier migration. Dividing (1) by $Q_0$ yields the charging ratio $\lambda$, which depends on the measuring time but shows the charge injection behaviour

$$\lambda = \frac{Q(t)}{Q_0} = 1 + \frac{\int_0^t I_{abs}(t) \, dt}{Q_0} + \frac{\int_0^t I_{leak}(t) \, dt}{Q_0}$$

(2)

In this work, the basic space charge accumulation characteristics of the different XLPE samples under various electric fields ranging from 10 to 60 kV/mm at 25°C and 5 to 30 kV/mm at 80°C were measured, respectively.

3 Results and analysis

3.1 Space charge injection

The experimental results of the charge injection characteristics are shown in Fig. 3. The space charge injection in pure XLPEs increases significantly with elevating applied electric field at 25°C. The charging ratio $\lambda$ is 1.27 under the electric field of 10 kV/mm, and it turns to be 1.9 for 60 kV/mm, which indicates that space charges are gradually injected into the XLPE under higher electric field, shown in Table 1. Similarly, the amount of the space charge accumulated in the PAC modified XLPEs increases with the applied electric field. However, it is obvious that the ability of the PAC modified XLPEs to inhibit space charge accumulation is stronger than that of the neat XLPE under various electric fields. Especially for the XLPEs modified by the PAC-C, the charging ratio at the end of the polarisation process is only 1.11 at the electric field of 60 kV/mm.

Comparing the $Q(t)$ data of XLPE samples at 25 and 80°C, it can be seen that space charge is more easily injected and accumulated in XLPEs at a higher temperature. For the neat XLPEs, the charging ratio can be boosted to 4.14 at 80°C under 30 kV/mm, which is much higher than that at 25°C under 60 kV/mm. For the PAC-C modified XLPE, the $\lambda$ is as low as 1.26, which means much less charge injection. It can be seen that the selected polycyclic aromatic compound has a significant ability to suppress space charge accumulation at even elevated temperature. Compared with the neat XLPE, the higher the temperature is, the more prominent the effect of the polycyclic aromatic compound on suppressing space charge accumulation is, shown in Table 2.

3.2 Quantum chemical calculation

In this work, the kinetic energy distribution and molecular orbitals were calculated using density functional theory with the B3LYP Hamiltonian and the 6–31G basis function in Gaussian 09 software [13]. Here, XLPE structure including three PE molecular chains with an orientation by crosslinking was built and shown in Fig. 4.
The calculation results of the energy level distribution of the XLPE and the different polycyclic aromatic compounds are shown in Fig. 5. The highest occupied molecular orbital and lowest unoccupied molecular orbital (LUMO) levels are marked with red and blue lines, respectively [10, 14]. The electron affinity $\chi$ of the XLPE molecular is $-1.21$ eV, while for the chosen PAC-A, B, and C, the electron affinity of them are 2.37, 1.66, and 1.8 eV, respectively. The polycyclic aromatic compounds with positive $\chi$ are easier to attract mobile electrons, meaning that polycyclic aromatic compounds can play a voltage-stabilising role in XLPE matrix, which attenuate the energy of high-energy electrons and leave the polymer matrix unharmed under high electric field [15].

In the trap point of view, the polycyclic aromatic compounds introduce new energy levels into the composite, forming local trap sites, which is similar to the effect of nanoparticles [1]. As shown in Fig. 5, there is a big energy difference between the LUMO level and its next level, which means that electrons at the LUMO level need more energy from the electric field or thermal source to hop over the next level for conduction. It was introduced that the mentioned energy difference between the LUMO and the next level can be regarded as a trap depth [16]. As is the same for holes. For the PAC-A, electron trap sites among 1.6–1.7 eV but no obvious hole traps are generated. Electron and hole trap levels of PAC-B doped XLPE are about 1.3 and 0.4 eV, respectively. Compared with the former two kinds of voltage stabilisers, PAC-C introduces more hole trap sites with a deep level ranging from 0.5 to 0.9 eV. To suppress bipolar charge injection into DC cable insulation materials, it is evident that PAC-C with both deep electron and hole traps are the ideal choice.

Fig. 6 shows the 3D static potential distributions and equivalent dipole moments of different PACs. It can be seen that the potential range of the PAC-C is much larger and its polarity of equivalent dipole moment is much higher than that of the PAC-A and PAC-B. The potential well around the equivalent dipoles obtained from the PACs can also be considered as the introduced traps [17]. This indicates that the PAC-C can introduce more traps or deeper traps in XLPE than the PAC-A and PAC-B. In this way, XLPE doped with the PAC-C possesses a stronger capacity to capture charges, which makes it easier to block carrier injection and releases the field distortion by space charge accumulation. This further ensures the ability to suppress space charge injection simultaneously in the PAC-C modulated XLPE sample.

4 Conclusions

The space charge characteristics of XLPEs modified by different voltage stabilisers were measured using a $Q(t)$ system and analysed by quantum chemical calculation. The experimental and theoretical results of space charge behaviours show that the voltage stabiliser C with high electron affinity, various deep traps, and large potential range exhibits a good ability to suppress space charge injection in XLPE, which is also the basic principle of voltage stabiliser selection for advanced dielectrics composites for HVDC insulation.

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### Table 2 Charging ratio of PAC modulated XLPEs at 80°C

| Electric field, kV/mm | XLPE | PAC-A | PAC-B | PAC-C |
|-----------------------|------|-------|-------|-------|
| 5                     | 1.24 | 1.07  | 1.09  | 1.04  |
| 10                    | 1.77 | 1.08  | 1.09  | 1.04  |
| 20                    | 3.25 | 1.52  | 1.44  | 1.08  |
| 30                    | 4.14 | 2.59  | 2.42  | 1.26  |
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