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Author(s)	Iwata, Shinya; Uehara, Hiroaki; Sekii, Yasuo et al.
Citation	電気材料技術雑誌. 2019, 28(1), p. 5-11
Version Type	VoR
URL	https://doi.org/10.18910/76112
rights	
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Electrical tree suppression mechanism using anthracene and tetracene

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Abstract : An electrical tree is known to be one of the main factors of electrical insulation degradation of polymeric materials. Suppression of the electrical tree is important from the viewpoint of prolonging the life of the insulating material or product and improving the reliability of the system. The introduction of various additives has been attempted as a method for inhibiting electrical treeing. The focus of this study is on the ultraviolet-ray absorbers (anthracene and tetracene) that have been proposed in previous works. The ultraviolet-ray absorption characteristics and aggregation of molecules, which are the grounds of the electrical tree suppression, were verified using computer simulations. Properties such as the electronic state and ultraviolet absorption spectra of the molecule were derived by quantum chemical calculation using the density functional theory, and molecular dynamics simulations were used for evaluating the aggregation of the additive molecules.

Keyword : Quantum chemical calculation; Molecular dynamics simulation; Electrical tree; Ultraviolet ray absorber

アントラセンおよびテトラセンの電気トリー抑制効果

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要旨：電気トリーは高分子材料の電気絶縁劣化の一因として知られており、その抑制は材料や製品の長寿命化や信頼性の向上という観点から重要である。抑制方法として種々の添加剤の導入が試みられている。本研究では、これまでに提唱されている紫外線吸収剤（アントラセンおよびテトラセン）に着目し、電気トリー抑制作用の一因である紫外線吸収特性や分子の凝集性について、計算機シミュレーションを用いて検証した。分子の電子状態等の特性は密度汎関数法による量子化学計算で導出し、分子の凝集性については分子動力学シミュレーションを使用し評価した。

1. Introduction

An electrical tree is a pre-breakdown phenomenon$^{1,2)}$ and is one of the main factors that lead to the degradation of polymeric material under AC and DC electric fields$^{3\text{-}6)}$. The endurance of the electrical tree is one of the major problems from the view-point of the life-time and reliability of electrical equipment and products, such as power cables and motors. Various organic and inorganic additives into the base polymeric material have been proposed for the suppression of the initiation and propagation of the electrical tree inside the materials. However, the physicochemical mechanism of the suppression of the initiation and propagation of the electrical tree is not clearly understood. In particular, the elucidation of the role of additives on a molecular size-scale is inevitable for the understanding of the suppression mechanism of an electrical tree.

Polycyclic compounds, such as anthracene and tetracene, are proposed as the additives for the suppression of electrical tree initiation$^{7)}$. In previous literature, electrical tree initiation voltage for low-density polyethylene (LDPE) with anthracene is approximately 3.5 times higher than that without anthracene$^{7)}$. The clustering of anthracene plays an important role for the absorbance of the energy of accelerated electrons, i.e., the prevention of electron avalanche in the voids of polymeric material$^{7)}$.

Additionally, anthracene and tetracene are known to act as ultraviolet (UV) absorbers. In particular, anthracene molecules absorb UV rays in making its dimer molecule8). Because UV rays are known to contribute to molecular chain scission, absorption of UV rays is effective to prevent the degradation and breakdown of polymeric materials.

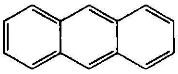
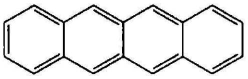
Today, in various fields, including materials science, remarkable developments are being made using computer simulations, such as quantum chemical calculations and molecular dynamics (MD) simulation methods. Research using computer simulations is being conducted in the areas of high-voltage engineering and electrical-insulating materials for the elucidation of the electrical degradation processes of materials9-11). In the present study, the molecular properties of anthracene and tetracene molecules and their dynamic behavior in polyethylene (PE) chains were evaluated by density functional theory (DFT) and MD simulation, respectively.

2. Simulation method

2-1. Quantum chemical calculations

The structures of anthracene and tetracene molecules are shown in Table 1. In this study, all the DFT calculations were computed using the Gaussian09 program$^{12)}$. The DFT calculations for the optimization of the molecules were performed at the B3LYP and 6-311++G(d,p) level. The optimized structure was

Table 1 Basic properties of anthracene and tetracene
表 1 アントラセンおよびテトラセン分子

	Anthracene	Tetracene
Skeletal formula		
Chemical formula	$C_{14}H_{10}$	$C_{18}H_{12}$
Molar mass	178.2	228.3
CAS number	120-12-7	92-24-0

determined by the absence of an imaginary solution in the frequency calculation of the ground state geometry. The atomic charge of the molecules was calculated by the Merz − Singh − Kollman (MK) scheme for molecular electrostatic potential (MEP). The UV-vis spectra were calculated using time-dependent DFT (TD-DFT). The vertical ionization potential (IP) of the molecules is an important index for evaluating their insulation properties. The total energy difference in the electrically neutral molecule E(M) and its cation E(M+) provides the IP.

2-2. Molecular dynamics simulation

The dispersion and aggregation of the anthracene and tetracene molecules in the PE chains ($C_{120}H_{242}$) was evaluated by MD simulations using the GROMACS program[13,14]. To generate force-field parameters, the restrained electrostatic potential (RESP) of molecules was determined by DFT calculations. For the anthracene and tetracene molecules, RESPs were computed by the method mentioned in Section 2-1. For the $C_{120}H_{242}$ molecule, the molecular geometry of an electrically neutral molecule was computed by DFT at the level of B3LYP/6-31G. The RESP was determined from the MK scheme.

To examine the aggregation of anthracene and tetracene molecules, it is useful to evaluate the intermolecular distance in PE chains. We evaluated the intermolecular distance of molecules using the following procedure of MD calculation. First, the low-density simulation cell, which was approximately 30 kg/m^3, with 10 anthracene (or 10 tetracene) and 50 $C_{120}H_{242}$ molecules, was made. The molecules were randomly placed. Second, an energy minimization calculation using a steepest-descent algorithm was performed to remove the inconsistent forces functioning within each molecule by yielding a displacement. Next, a 10 ns MD simulation with the constant-volume and constant-temperature (NVT) ensemble at 450 K was performed to remove the inhomogeneous structures. The temperature was controlled by using a Nosé−Hoover thermostat[15-17]. Subsequently, an MD simulation of more than 20 ns with constant-pressure and constant-temperature (NPT) ensemble at 101 kPa was performed at 300 K to obtain a relaxed initial structure. The temperature and pressure were controlled by using a Nosé−Hoover thermostat and a Parrinello−Rahman barostat18), respectively. Finally, a 20 ns MD run with the NVT ensemble at 101 kPa and 300, 340, and 380 K was conducted to obtain the final structure. The time step of the simulation was 2 fs. Trajectory data were recorded every 1,000 steps.

In all the simulations, the Lennard?Jones interaction potential for short-range intermolecular interactions with a cut-off of 1.0 nm and the particle-mesh Ewald method[19,20] for long-range electrostatic interactions were employed. The LINCS algorithm[21] was used to constrain the stretching vibrations of hydrogen atom bonding. Periodic boundary conditions for the *x*-, *y*-, and z-axes were employed.

3. Simulation results and discussion

3-1. Properties of molecules

The energies of the highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO), and IP of anthracene and tetracene

Table 2 Energies of HOMO, LUMO, H-L gap, and IP (in eV)
表 2 HOMO、LUMO、HOMO-LUMO ギャップおよびイオン化ポテンシャル（単位：eV)

	HOMO	LUMO	H-L gap	IP
Anthracene	-5.6	-2.0	3.6	7.2
Tetracene	-5.2	-2.4	2.8	6.6

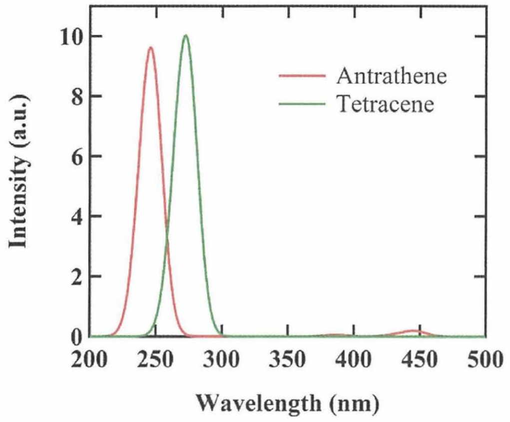


Fig. 1　UV-vis spectra of anthracene and tetracene from TD-DFT calculation at the level of B3LYP/6-311++G**

図 1　アントラセン分子とテトラセン分子の紫外可視吸収スペクトル

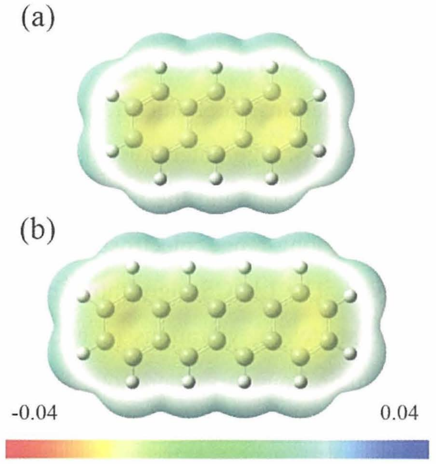


Fig. 2 Optimized geometry and MEP, in a.u., of (a) anthracene molecule and (b) tetracene molecule calculated from DFT at the B3LYP/6-311++G** level with MK scheme

図 2　アントラセンとテトラセンの安定構造と静電ポテンシャル（原子単位）

molecules are given in Table 2. For the anthracene and tetracene molecules, the H-L gap and IP energies are relatively close in value. Figure 1 shows the UV-vis spectra for anthracene and tetracene molecules. The absorption spectra appeared in the range of 225-275 nm and 250-300 nm for the anthracene and tetracene molecules, respectively. Both anthracene and tetracene show good performances as UV absorbers.

The optimized geometry and MEP of the anthracene and tetracene molecules are shown in Fig. 2. To generate force-field parameters for the MD calculation, RESP charges of molecules were determined from a B3LYP/6-311++G** basis set with the MK scheme.

3-2. MD simulation results

Snapshots of the final structure of MD simulation cells for anthracene and tetracene at 300 K are shown in Fig. 3. Some anthracene and tetracene molecules approach each other in parallel. Figure 4 shows the time evolution of the averaged intermolecular distance of anthracene and tetracene molecules during production runs at 300, 340 and 380 K. As shown in the figures, the intermolecular distances of anthracene for the 340 and 380 K model and tetracene for the 380 K model tend to increase. However, at 300 K, the intermolecular distance of anthracene and tetracene tends to decrease. The difference of the temperature dependence of the intermolecular distance is attributed to the intermolecular interaction in PE.

A previous experimental study has shown that polycyclic compound molecules aggregate in PE$^{7)}$. It is presumed that movement of molecules is likely to occur in the pressing process (compression heating process) of PE over room temperature, and molecular aggregation is caused in the cooling process. In the case of anthracene, according to the present study, an approaching of molecules was confirmed at 300 K.

3-3. Suppression mechanism of the electrical tree

Quantum chemical calculations confirmed that both anthracene and tetracene are good UV-ray absorbers. In addition, MD calculations revealed that anthracene tends to reduce the intermolecular distance at 300 K. Next, the suppression mechanism of the electrical tree is considered from two viewpoints.

First, the initiation and propagation of the electrical

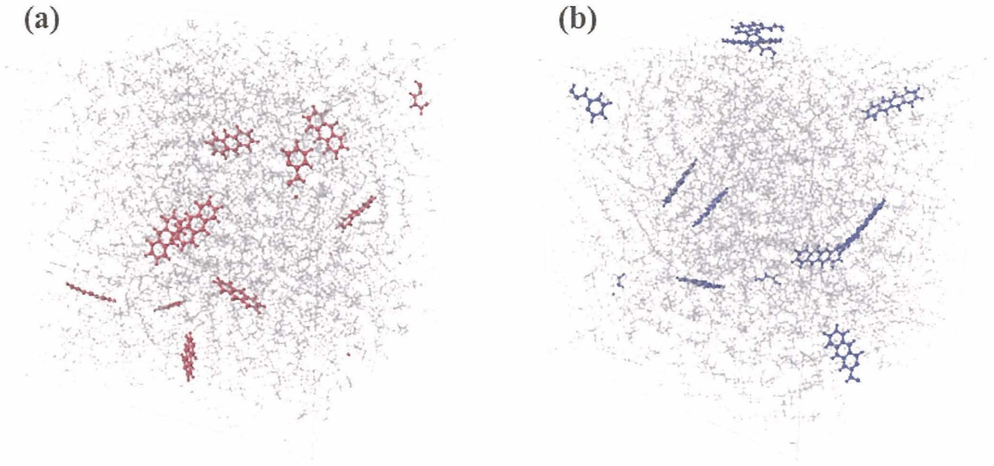


Fig. 3 Snapshot of the final structure of simulation cell at 300 K: (a) anthracene molecules and (b) tetracene molecules — the PE chains are shown in a gray wired model

図 3 300 K における計算後の構造： (a)アントラセン分子、(b)テトラセン分子

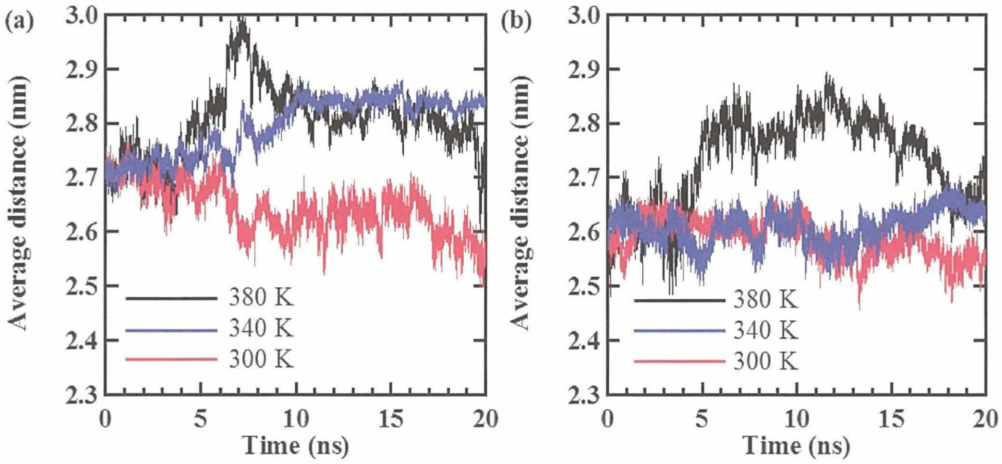


Fig. 4 Temperature dependence of averaged-intermolecular distance in PE chains: (a) anthracene molecules and (b) tetracene molecules

図 4 各温度における分子間距離の推移: (a)アントラセン分子、(b)テトラセン分子

tree is affected by the voids inside the polymeric material. The charges that were injected from the needle electrode because of the high electric field are accelerated at the vicinity of the tip of the electrode. When the charges have a large kinetic energy, the chemical bonds of the insulating molecule are broken. Therefore, the decrease of the energy of charges is important to prevent the degradation of polymeric materials. The aggregation of additive molecules at the interface between the electrode and polymeric materials has a blocking effect by reducing the void (or space) where charges are accelerated [7].

Second, the UV ray generated in the bond session is another factor that promotes degradation. Past studies have shown that anthracene has more of a suppressing effect on the electrical tree than tetracene. From the results of the present study, both anthracene and tetracene have the effect of UV ray absorbers and aggregation properties. However, experiments have shown that anthracene is more effective than tetracene for the suppression of electrical trees. This difference is related to the dimerization of molecules. When two anthracene molecules are irradiated with UV rays, an anthracene dimer is formed[8].

4. Conclusions

In this study, the electrical tree suppression effect of a UV-ray absorber was verified by computer simulation. The molecular properties of anthracene and tetracene molecules and their dynamic behavior in PE chains were evaluated by DFT and MD simulation, respectively. It is clear that the intermolecular distance of the additive molecules depends on the temperature of the system. The electrical tree suppression mechanism was discussed, and it was pointed out that the aggregation of anthracene and tetracene molecules and the dimerization of anthracene are important.

Acknowledgments

This work was supported by the Japan Society for the Promotion of Science KAKENHI Grant Number JP18K13751. The DFT calculations were performed using the large-scale supercomputer system at the Institute for Information Management and Communication at Kyoto University.

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(May 13, 2019 Accepted)

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Yasuo Sekii was born on September 8, 1936. He received his Ph.D. degree from The University of Tokyo in 1976. In 1965, he joined Hitachi Cable, Ltd., where he was engaged in R&D work on medium- and high-voltage AC and DC XLPE cable systems. In 1994, he moved to Chiba Institute of Technology. During 1994-2007, he was engaged in educational work while undertaking material studies on electrical and thermal degradation and on space charge generation in polymeric dielectrics. In June 2007, he was nominated to be the chairman of Japan Electric Cable Technology Center (JECTEC). He is now an advisor of the Institute Electrostatics Japan (IEJ) and a member of the Institute of Professional Engineers Japan (IPEJ).

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