Development of A High-performance Amorphous Fluorinated Polymer Electret Based on Quantum Chemical Analysis

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Abstract. In the present study, for the first time, a novel high-performance amorphous fluorinated polymer electret based on quantum chemical analysis is proposed. Density functional theory is adopted to analyse the electron affinity of CYTOP polymers with different end groups. In analysis of CYTOP series with different end groups, it is found that the amide bond at the end of CYTOP chain attract electron, leading to high electron affinity of the molecule. Based on the DFT results, a new electret material has been developed by adding Tris(2-aminoethyl)amine (TAA) into CYTOP CTX-A. With a 15 µm-thick film, a record-high surface charge density of -4 mC/m² has been obtained. It is also found from the thermally stimulated discharge experiment that the electron trapped in the CTX-A/TAA have higher thermal stability than CYTOP EGG, which is known as the best fluorinated polymer electret.

1. Introduction
An electret is a dielectric material with quasi-permanent charge. The charges trapped in proper electret materials can be stably maintained for tens of years [1]. Electret energy harvesters convert kinetic energy into electricity by electrostatic induction, and have higher output power than electromagnetic or piezoelectric counterparts in the low-frequency range [2]. Thus, the electret energy harvesters attract much attention as a power supply for low-power-consumption electronics. Because their power output is proportional to the square of surface potential of the electret, it is necessary to develop a high-performance electret with long-term stability of trapped charges.

In the last few decades, electrets have been improved for high-output-power electret generators. Boland et al. [3] employed Teflon AF, and prototyped a MEMS rotational electret generator. They obtained the surface charge density of 0.5 mC/m² for a 9 µm-thick film. Lo and Tai [4] utilized parylene HT for their MEMS electret energy harvester (EH), and achieved high surface charge density as high as -3.69 mC/m² for a 7.32 µm-thick film. Tao et al. [5] employed low-density polyethylene (LDPE) electret and obtained -0.43 mC/m² initial surface charge density with a 50 µm-thick sample for their electret EH. Tsutsumino et al. [6] firstly investigated an amorphous perfluoro polymer CYTOP as electret, and found that 15 µm-thick CTL-M film with the alkoxysilane/amide end group sustains high surface charge density of 1.37 mC/m² over more than 100 days. Sakane et al. [7] and Kashiwagi et al. [8] examined the effect of excessive aminosilane additives into CYTOP CTL-A and found that nanoclusters bonded to the CYTOP chain are formed during the thermal curing process at 280 °C. The surface charge density of this material (CYTOP EGG) is as high as -2.0 mC/m² for a 15 µm-thick film. In addition, high thermal stability of the implanted charges is obtained.
Recently, we have adopted quantum chemical analysis for evaluating charge trap of polymer electrets [9]. CYTOP with different end groups, i.e., CTL-S with trifluoromethyl (-CF₃) end group, CTL-A with carboxyl (-COOH) end group, and CTL-M with alkoxysilane/amide (-CONH~Si(OR)₃) end group are analyzed. Electron affinities obtained with the DFT are in qualitative agreement with the data taken with the thermally stimulated discharge (TSD) experiments and with the low energy photoelectron spectroscopy (LEIPS) measurement, indicating that the performance of amorphous polymer electret can be predicted by the present analysis.

In this paper, we aim to develop a novel high-performance electret based on quantum chemical analysis. Electron affinity of CYTOP series are analyzed. A new electret is proposed by the analysis and evaluated with a series of measurements.

2. Quantum Chemical Analysis on Electron-trapped CYTOP Series

Figure 1 shows chemical structures of CYTOP (AGC Co. Ltd.). A single polymer chain consists of about 540 repeat units (for CTL type) or 1080 repeat units (CTX type) and two functional groups at both ends; CTX-A has carboxyl end groups and CTX-M has alkoxysilane/amide end groups. In our recent quantum chemical analysis on CYTOP series with different end groups, we have found the amino bond in CTL-M serves as a strong charge trapping site [9]. Considering that, we have chosen Tris(2-aminoethyl)amine (TAA) with three free amine functional group as the candidate additive to CTX-A. Figure 2 shows chemical structure of TAA and CTX-A reacted with TAA (CTX-A/TAA) monomer.

In order to analyze electronic state of electron-trapped molecules, we perform density functional theory (DFT) calculation using the software package NWChem [10]. The Kohn-Sham equation of single molecular system is solved with the CAM-B3LYP functional and the 6-31+G(d,p) basis set. Molecular orbital energies are acquired from the self-consistent field (SCF) procedure; the sum of them is the energy of system. Since calculation cost of DFT calculation exponentially increases with the number of electrons in the system, it is necessary to simplify the molecular system. In our previous work, we found that the trapped electron in CYTOP is localized near the end group of the molecule [9]. Therefore, we build a simple chain with 6 repeat units and connect one end to the functional group of interest (carboxyl, alkoxysilane/amide, TAA with amide bond) and attach trifluoromethyl group to the other end. Prepared structures are transformed into the ground state structure by quantum mechanical geometry optimization algorithm in NWChem. In this process, we set the electronic state of the molecule to be negatively charged (-1) to reproduce the electron-trapped electret, and obtain the anionic ground state structures. Figure 3 displays distribution of trapped electron in the CTX-A/TAA hexamer; the electron is located near the amide bond, showing that amide bond connected to CYTOP is acting as the electron trap site as we expected. In Fig. 4, calculated orbital energies are sorted in order and plotted. The bar with arrow...
represents the energy of orbital where the additional electron is trapped. For CTX-A, CTX-M, and CTX-
A/TAA, the trapped electron has negative energy, indicating that the electrons are trapped stably.

Molecular electron affinity (EA) is used to estimate electron-trapping energy of electret molecules.
If a molecule is placed in vacuum, it can freely deform to other ground-state structures when its
electronic state is changed. However, in real solid-state polymer systems, surrounding molecules are
acting as physical obstacle, suppressing its deformation. Therefore, the molecule cannot relax to the
ground state when the electronic state is changed. Accordingly, for the present analysis, we use the
vertical electron affinity defined by,

\[ E_{A_{\text{vert}}} = U(g(e), s(n)) - U(g(e), s(e)) \]

(1)

where \( U(g(x), s(x)) \) is the total energy of system at the geometry \( g(x) \) and the electronic state \( s(x) \), while
\( n \) and \( e \) represent the neutral/negatively-charged electronic states. The electron affinities obtained with
Eq. (1) are 3.5 eV (CTX-A), 4.13 eV (CTX-M), and 4.45 eV (CTX-A/TAA). Therefore, CTX-A/TAA
should have higher electron affinity and thus better stability of implanted charges than CTX-A and CTX-
M.

3. Experimental Evaluation of Trapped Charge Stability in Electret

Based on the quantum chemical analysis, the CTX-A/TAA electret is prepared by adding TAA
solution (1 wt% in 2-(Perfluorohexyl)ethanol) to 9% CTX-A solution. The ratio between amine of TAA
and carboxylic group of CTX-A is 3:1. After that, the solution is mixed for 24 hours by the low-speed
rotational mixer. Then, the solution is spin-coated on the copper plate (30 × 30 × 0.3 mm\(^3\)) and baked at
230 °C for 1 hour to evaporate the solvent. In addition to CTX-A, CTX-M and CYTOP EGG samples
are also prepared for comparison. CTX-A and CTX-M are cured at 200 °C, while CYTOP EGG is cured

Fig. 5. IR absorption spectra of samples, measured by JASCO FT/IR-6600. Numbers in the
bracket stand for the baking temperature.
at 280 °C. The thickness of prepared samples is 15 µm. Note that the curing temperatures of CTX-A, CTX-M and CYTOP EGG are determined based on our previous studies [7, 8].

IR absorption spectra of the present samples are measured in order to trace chemical species in the system. As shown in Fig. 5, the C-F overtone spectra corresponding to repeat units shows broad peak around 2350 cm⁻¹ for every samples. In CTX-A, the carboxylic group is found from the O-H peaks at 3555 cm⁻¹ and 3100 cm⁻¹, and divided C=O peaks at 1812 cm⁻¹ and 1773 cm⁻¹. In CTX-M, the C=O peak from amide bond is found at 1725 cm⁻¹, while a peak at 1790 cm⁻¹ is originated from the methylester group (-COOCH₃), implying that two kind of end groups are coexisting in the system. In CTX-A/TAA and CYTOP EGG, the C=O peaks of carboxylic group are disappeared, while the C=O peak of amide bond is emerged, showing that TAA has made reaction with the carboxylic end of CTX-A during the curing process.

Samples are then negatively charged with soft X-ray charging [11]. Figure 6 displays charging setup. Soft X-rays penetrate aluminum foil and photoionize air molecules. 3.5 kV bias voltage is applied between the aluminum foil and the copper substrate for attracting generated electrons to the electret film. The X-ray source is placed 35 mm above the aluminum foil to ensure uniform irradiation on all around the sample, and the distance between aluminum foil and bottom of copper plate is 10 mm. Surface potential of the electret increases with the irradiation time. The charging process stops when the surface potential become almost the same as the bias voltage; the irradiation time is 25 minutes for all the samples. After charging, surface potentials of CTX-A, CYTOP EGG and CTX-A/TAA are measured. For CTX-A, the initial surface potential is only -1887 V and decreases rapidly to -1310 V within several days. For CYTOP EGG and CTX-A/TAA, the initial surface potential is as high as -3200 V, which corresponds to the surface charge density of -4.0 mC/m². The surface potential of CTX-A/TAA is stably sustained even after 400 hours, while that of CYTOP EGG is decreased to -2680 V.

In order to evaluate thermal stability of trapped electrons, samples are examined with thermally stimulated discharge (TSD) measurement shown in Figure 8a. The sample is secured in a metal measurement setup and heated from 40 °C to 300 °C at a ramping rate of 1 °C/min. Change of the induced charge on the upper probe is measured by the sub-femtoampere meter (Keithley 6430). Figure 8b displays measured current versus temperature. The peak temperature, which represents the index of thermal stability of trapped charge, is in the order of CTX-A (144 °C), CTX-M (169 °C), CYTOP EGG (232 °C), and CTX-A/TAA (258 °C). The present result clearly shows strong thermal stability of trapped electrons in CTX-A/TAA, even more than that of CYTOP EGG.

Note that, we have also examined samples having different ratios of CTX-A and TAA. The TSD peak is unchanged if the number of carboxylic groups is more than 3 times of that of amine. Also, the samples cured at higher temperatures than 230 °C show the same TSD peak temperature as the sample cured at 230 °C, showing that the curing temperature of CTX-A/TAA can be lower than CYTOP EGG.
4. Conclusion

In the present study, we have developed a novel amorphous fluorinated polymer electret based on quantum chemical analysis. Electron affinity of CYTOP polymers with different end groups is analysed to evaluate the electret performance. Based on the analysis, CTX-A/TAA has been proposed as a new high-performance electret material. It has been shown that CTX-A/TAA gives surface potential as high as -4.0 mC/m² for more than 400 hours. In the TSD measurement, it is also shown that electron trapped in CTX-A/TAA have excellent thermal stability, even better than the high-performance electret, CYTOP EGG.

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