THERMAL DEGRADATION PRODUCTS OF POLYTETRAFLUOROETHYLENE (PTFE) UNDER ATMOSPHERIC CONDITION

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Introduction

Increasing number and amount of organofluorine chemicals were produced and used, and recently identified toxicities of these chemicals have been attracted scientific concerns. Perfluorinated compounds (PFCs) such as perfluorooctanoate (PFOA) are environmental contaminants posing special public health concerns because of their long-term persistency in the environment and bioaccumulation in organisms [1]. PFOA and perfluorinated carboxylic acids (PFCAs) with various chain lengths have been detected in a variety of environmental compartment [2]. The sources of PFCAs in the environment remain unclear, however thermal degradation and combustion of fluoro-resins, particularly such as polytetrafluoroethylene (PTFE), may be one of the indirect sources of PFCAs.

Fluoro-resins are one of important industrial and domestic materials based on their unique characteristics. These characteristics give fluoro-resins specific applications such as good electric insulator and good fire resistant. In 2004, annual world consumption of fluoro-resins reached almost 133,000 metric tonnes [3], PTFE being the dominant fluoro-resin, accounting for 59 wt. % of global amount [3]. In spite of the thermal stability of the PTFE, the study of the products resulting from its thermal degradation has been always considered a matter of interest. Early research work indicates that PTFE decomposition involves random chain cleavage followed by depolymerization and termination by disproportion [4]. Degradation of PTFE begins slowly at 260℃; however, for a significant degradation to occur, temperatures above 400℃ are needed [5].

According to the tests commissioned by Environmental Working Group (EWG, USA), within two to five minutes on a conventional stovetop, cookware coated with PTFE (known to Teflon®) and other non-stick surfaces can exceed temperatures at which the coating breaks apart and emits toxic particles and gases. There are information that pet bird died and may cause unknown number of human illnesses [6].

The aim of the present study was to determine the thermal degradation products of PTFE under atmospheric condition. We have developed a method to collect degradation products and to determine several different perfluorinated compounds including perfluoroisobutylene (PFIB), hexafluoropropene (HFP), tetrafluoroethylene (TFE), hexafluoroethane (HFE), perfluorocyclobutane (PFCB) and perfluorinated calboxylic acids (PFCAs).

Materials & Methods

PTFE

The thermal degradation experiments were carried out with commercial PTFE tubes (8 mm i.d. obtained from Sanplatec Co., Japan). These tubes were cut to a small piece (about 1.5g) and put on a quartz boat (77 mm × 20 mm) for the thermal degradation experiments.

A thermogravimetry-differential thermal analysis (TG-DTA: Thermo Plus TG8120, Rigaku Co., Japan) for PTFE was performed prior to the thermal degradation experiments of these tubes in order to determine the critical temperature for the thermal degradation. Result of a TG-DTA which was shown in Fig.1, indicated that significant thermal degradation of PTFE occurred between 540℃ to 590℃. Based on the result of a TG-DTA, thermal degradation temperature of the tubes was set up at 550℃.
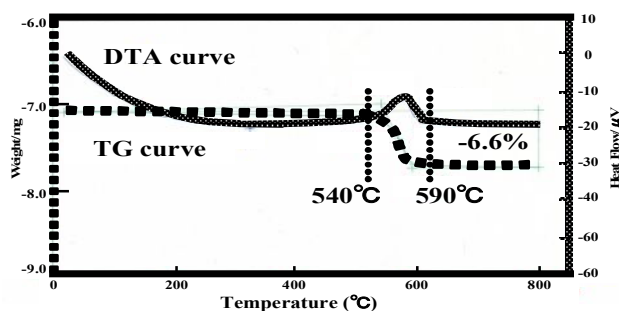

Fig. 1. Results of TG-DTA for PTFE

Standard materials

The standard materials, hexafluoropropene (HFP; purity > 98.5 %), for qualitative analysis were purchased from SynQuest Laboratories Inc. (FL, USA). Hexafluoroethane (HFE; purity > 99.9 %) and perfluorocyclobutane (PFCB; purity > 99.9 %) were purchased from Japan Fine Products Co. (Kanagawa, Japan).

Experimental procedures

The apparatus devised for PTFE degradation and trap of its products was shown in Fig.2. This was constructed of a horizontal reactor tube (40 mm diameter; 470 mm length, connected 18 mm diameter; 130 mm length) with a ball joint (28/15 male) ([A] in Fig.2). The trap part for the products generated from PTFE was consisted of a cold trap tube (60 mm diameter: 300 mm length) with a ball joint (28/15 female) [B]. All parts of the apparatus were made from quartz glass. An electric furnace (FUT040MA, ADVANTEC Co., Japan) was placed by the reactor tube [C]. The procedure used was as follows: firstly, the furnace was switched on and the reactor tube was heated. The temperature of the reactor tube was raised to the desired value by an electric furnace. The tem-
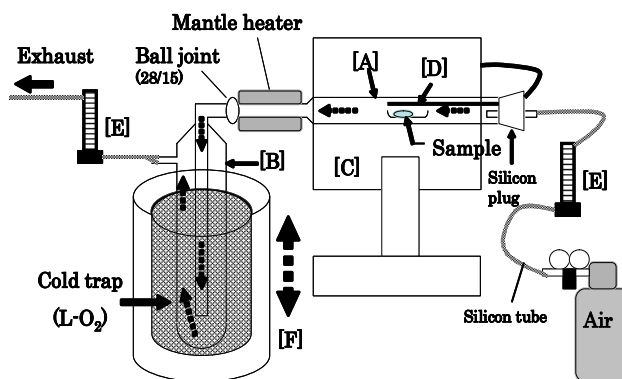

Fig. 2. The construction of the apparatus for degradation of PTFE and trap for its products : [A] quartz reactor tube : [B] quartz cold trap tube : [C] electric furnace : [D] thermocouple: [E] flowmeter: [F] Dewar vessel

-perature of the reactor was measured by the thermocouple [D]. When the reactor was heated up to the temperature set on and stable, immediately the apparatus was purged for a few minutes with purified air, and PTFE tube sample was introduced to inside of the reactor. The flow rate of air was set at 100 mL/min (measured at 1 atm and 20°C, [E]). At the outlet of the reactor tube, the gas stream from PTFE was made to pass through into a cold trap tube cooled with liquid oxygen (L-O_2), in order to collect volatile degradation products. The thermal degradation of PTFE tube and cold trapping of its products were performed for 30 min each other.

After the thermal degradation, the cold trap tube was sealed up, and a Tedlar bag (5 L capacity with faucets) was connected to the outlet of the cold trap tube. Dewar vessel, which was filled with L-O_2 [F], took down to the bottom. The volatile constituents were collected in a Tedlar bag, which were gradually vaporized according to rising temperature from cold one to room one for around 20 min. The degradation products collected in a Tedlar bag as gas phase (gas samples) were analyzed immediately by gas chromatograph-mass spectrometer (GC/MS).

The constituents which were trapped on the internal surface of the apparatus, in other words, non-volatiles at room temperature, were extracted with dichloromethane (DCM).The extracts (DCM samples) were concentrated under a gentle stream of high-purified nitrogen gas and injected to GC/MS for analysis.

Analysis of thermal degradation products

Both gas and DCM samples were analyzed by GC/MS (HP6890series Agilent Co., USA /JMS AM SUN200 JEOL Co, Japan) with electron impact ionization (EI$^+$) mode using total ion monitoring from 40 to 450(m/z). EI/MS analysis was performed at 70 eV with the ion source temperature at 250°C and transfer line was heated at 250°C. Gas samples were separated on an CP pora BOND Q capillary column [25 m (length) ×0.53 mm (i.d.) × 10 μm (film thickness),Varian Co. USA] with a cryogenic GC oven (L-CO_2) temperature program of -30°C (2 min)–at 2°C/min–10°C(0min)–at 10°C/min–200°C (0 min) using helium as carrier gas at a flow rate of 1.2 mL/min. Pulsed splitless injection (50 μL) was performed with the injector set at 100°C. DCM samples were separated on an BPX-5 capillary column [60 m (length) ×0.25 mm (i.d.) × 1 μm (film thickness), SGE Co. USA] with a temperature program of 70°C (1 min)–at 10°C/min–150°C (1min)–at 5°C/min–260°C (0 min) using helium as carrier gas at a flow rate of 1.0 mL/min. Pulsed splitless injections (2 μL) were performed with the injector set at 200°C.

Qualitative analysis of the degradation products of PTFE was carried out considering and comparing the data obtained from the standard material, and using library search software (NIST MAS search Ver 2.0 1998).

Results & Discussion

<u>Gas samples</u>

Components in a gas sample were well separated by using the cryogenic GC oven system with CP pora BOND Q capillary column. Total ion chromatogram (TIC) obtained from the gas samples was shown in Fig.3. Qualitative analysis of all peaks shown in Fig.3 was performed using library search software. Results of qualitative analysis were shown in Table 1.

According to Table 1, All peaks have mass fragment ions derived from perfluorinated compounds, for instance, 69 denotes $[CF_3^+]$ mass fragment ion, and almost peaks indicated a highly matched rate (%) to the data compiled in the NIST library as some perfluorinated compounds. Compounds of peaks [1], [2], [4], [5], [8], had quite similar mass fragment pattern of Freon 23, Freon 116, Freon 14, Freon 218, and Freon 318, respectively. Therefore, we may be aware of influence on global warming by the degradation products of PTFE in the environment. Compounds of peaks [2], [7], [8], denoted by asterisks were identified with the data obtained from standard materials. The compound of peak [10], whose mass spectrum was shown in Fig.4, is known as one of highly toxic products of PTFE degradation. Compared mass spectrum of PFIB (shown in Fig.5) with mass spectrum of peak [10] (Fig.4), both spectra are found to be similar closely. It is thought that exposure of PFIB from PTFE degradation may be caused toxic influences not only on pet birds but also on human health. The compound of peak [12], needs more effort for identification although mass fragment pattern is similar.

HFP, HFE, and PFCB in the gas samples from PTFE degradation at the temperature 550℃ were identified. Moreover, the possibility was suggested the presence of perfluorinated compounds such as PFIB which is highly toxic.
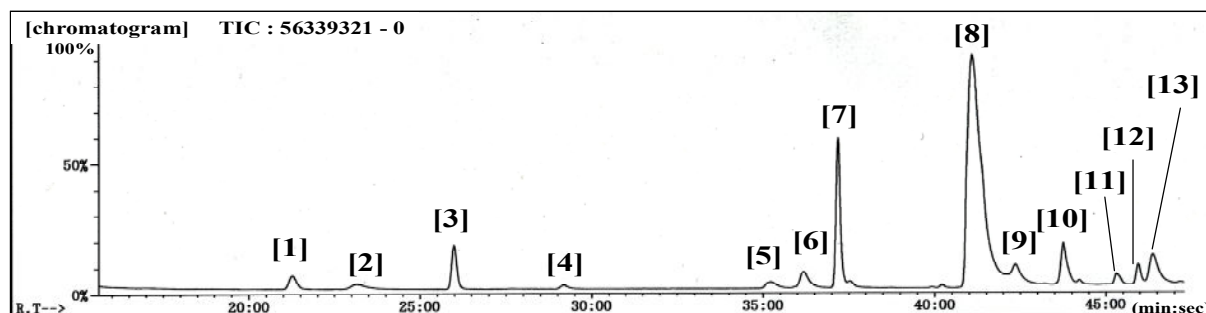

Fig. 3. TIC obtained from gas samples

Table 1. Results of qualitative analysis for gas samples

| Peak	Retention time(min:sec)	Compound	Match of library (%)	Mass fragment ions (m/z)
[1]	21:15	trifluoro-ethane(CHF_3)	90.3	51, 69
[2]	23:09	hexafluoro-ethane(C_2F_6)*	90.0	69, 119
[3]	25:59	tetrafluoro-ethylene(C_2F_4)	93.2	50, 81, 100
[4]	29:10	tetrafluoro-methane(CF_4)	87.6	50, 69
[5]	35:12	octafluoro-propene(C_3F_8)	97.2	69, 169
[6]	36:10	—	—	50, 69, 100, 119
[7]	37:11	hexafluoro-propene(C_3F_6)*	98.9	69, 100, 131, 150
[8]	41:04	perfluoro-cyclobutane(c-C_4F_8)*	90.5	50, 69, 100, 131
[9]	42:20	decafluoro-butane(C_4F_{10})	85.8	69, 100, 119, 219
[10]	43:45	perfluoro-isobuthylene(C_4F_8)	92.7	69, 93, 181, 200
[11]	45:19	—	—	69, 119, 216
[12]	45:57	difluorodimethyl-silane($C_2H_6F_2Si$)	89.5	47, 81
[13]	46:22	perfluoro-cyclopentane(c-C_5F_{10})	78.8	69, 100, 131, 181, 231
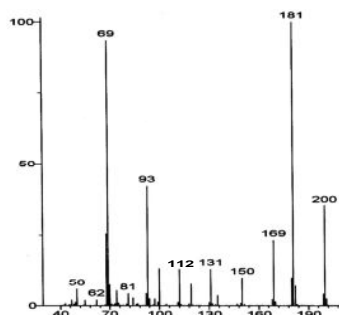
Fig. 4. Spectrum of peak [10]
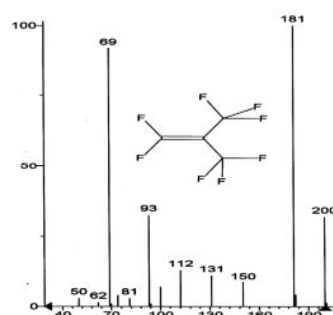

Fig. 5. Spectrum of PFIB

DCM samples

TIC obtained from DCM samples was shown in Fig.6. The mass spectra of peaks are categorized into 5 patterns (**a**, **b**, **c**, **d**, **e**). The peaks of pattern **[a]** showed similar mass spectra to those of PFCAs such as PFOA. These peaks indicated about 80% match of NIST library for PFCAs such as PFOA, PFNA, and PFDoA. The peak of pattern **[b]** indicated perfluro (methyl) cyclohexane (C_7F_{14}) with 81.5% match of library search. The peaks of pattern **[c]** were unknown although including mass fragment ions derived from PFCs. The peaks of pattern **[d]** were non-fluorine compounds such as aldehydes, and phenols, and also detected in the blank sample. The peaks of pattern **[e]** indicated perfluroro-1-heptene (C_7F_{14}) with about 80% match of NIST library.

The possibility was suggested that the PFCAs such as PFOA may be produced from PTFE degradation at the temperature 550℃, although further research is necessary for confirmation.
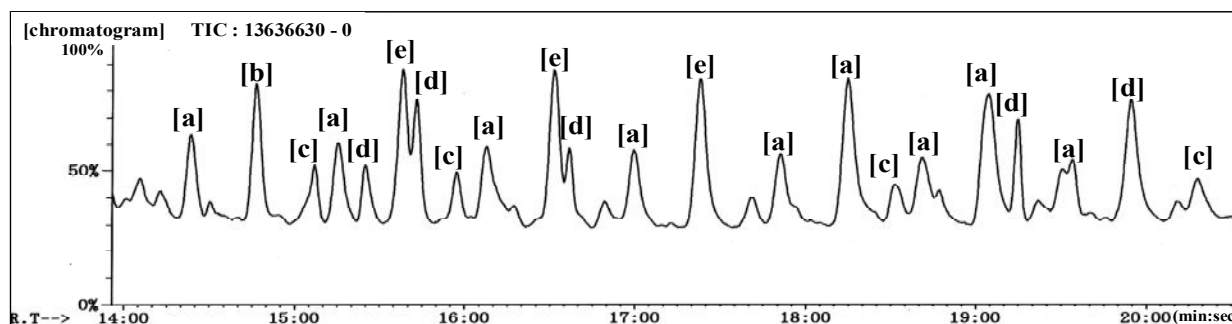

Fig. 6. TIC obtained from DCM samples

Conclusions

As a part of our continued organofluorine projects, we have developed a practical method for the collection of perfluorinated compounds obtained from PTFE degradation using specially designed apparatus and an optimal analysis technique by GC/MS.

From the results of PTFE degradation at the temperature 550℃, many perfluorinated compounds were confirmed from both volatile and less volatile fractions. HFP, HFE, PFCB were identified in volatile fractions. PFIB which is known to be a highly toxic compound and other several Freon gases were confirmed with the spectral data in volatile fractions. Generation of PFCAs such as PFOA was suspected in less volatile fractions. Unintentional sources of these compounds seem very important in the environment.

References

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