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SIMULTANEOUS THERMOGRAVIMETRY–MASS SPECTROMETRY AND PYROLYSIS–GAS CHROMATOGRAPHY OF FLUOROCARBON POLYMERS*

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ABSTRACT

The thermal degradation of polytetrafluoroethylene (PTFE) and tetrafluoroethylene/hexafluoropropylene copolymer (FEP) has been investigated in different gas atmospheres by simultaneous thermogravimetry–mass spectrometry, pyrolysis–gas chromatography, combined gas chromatography–mass spectrometry, and IR analysis.

There are no significant differences in the decomposition products of the two polymers in helium or air at a temperature range of 450–790°C; C_1 to C_8 fluorocarbons and their oxidized products have been identified. The various fluorocarbons produced are plotted against the degradation temperature, and at temperatures of 450–550°C FEP evolves large amounts of tetrafluoroethylene formed by a decomposition reaction of perfluoropropylene.

From the traces of the TG–MS in an atmosphere of helium, the FEP clearly decomposes in two stages. The first stage degradation is mostly attributed to the evolution of perfluoropropylene with a small amount of perfluoro-1-butene or perfluoroisobutylene, and possibly traces of perfluorocyclobutane. Tetrafluoroethylene is evolved with these fluorocarbons at the second stage degradation, showing similar characteristics of the degradation mechanisms of FEP at the two stages. In the presence of air, the two polymers also decompose in two stages. Activation energies for the degradation products are calculated, and the decomposition mechanisms of the polymers are discussed with the results of IR analysis.

INTRODUCTION

Fluorine containing polymers have widespread utilization because of their chemical inertness, desirable plasticity and thermal stability. However, it is widely recognized that some of the degradation products of these polymers are very harmful

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to humans. A lot of work has been carried out on the degradation kinetics of polytetrafluoroethylene (PTFE), but the degradation products of fluorocarbon polymers have not been studied in detail.

The thermal degradation of PTFE was carried out[1] isothermally at pressures less than 760 mm Hg to find that the yield of C_2F_4 was decreased, and C_3F_6 and C_4F_8 were formed in increasing proportions as the pressure was increased. On the evolution mechanism of C_2F_4, Errede[2] suggested that the unzipping process might occur via elimination of CF_2 fragments to give C_2F_4 rather than via depolymerization of $CF_2{=}CF_2$ units. On the other hand, mass spectrometric thermal analysis of PTFE has been employed in vacuo by Schulman[3] by repeated scanning spectra, then plotting the peak heights as a function of temperature. The mass fragment ions of the decomposition products of PTFE and tetrafluoroethylene/hexafluoropropylene copolymer (FEP) have been identified[4] by an isothermal method with little differences between the two polymers. The toxic compounds in the pyrolysis gases from fluorine containing polymers have been reported in some literature[5-7]. However, the identification of degradation products from these polymers is not enough, and there appear to be few reports referring to the differences of the degradation mechanism of fluorocarbon polymers using a mass spectrometer.

In this study, the experimentation has been conducted for the identification of degradation products of PTFE and FEP, and for the determination of activation energies for some products at each degradation process in the atmosphere of helium or air. The degradation mechanisms will be discussed using simultaneous TG–MS, pyrolysis–GC, and IR analysis.

EXPERIMENTAL

Materials. The PTFE and FEP used in these experiments have molecular weights and particle sizes of 8.4 × 10^6, 3–5 μ, and 10^5–10^6, 1–2 μ, respectively.

Apparatus and procedure. A pyrolyzer used for the decomposition of the

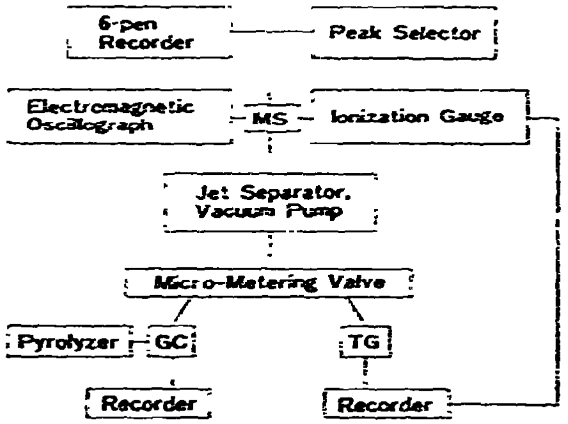


Fig. 1. Block diagram of GC–MS instrumentation.

polymers is the same as that used in the previous paper[8]. A quadrupole mass analyzer was combined with a gas chromatograph and with an IR ray thermobalance as shown in Fig. 1. The interface lines and the quadrupole were heated at around 100°C. For the identification of the degradation products a Shimadzu–LKB GC–MS was used.

For the pyrolysis–gas chromatography, samples weighing about 1 mg were placed for 30 sec in a quartz glass tube (~ 6 ml) heated at temperatures from 450 to 790°C for each increase of 20°C. The tube was coupled with the gas chromatograph (thermal conductivity detection or flame ionization detection) where Porapak Q (2 m × 3 mm i.d.) was used for the separation of the pyrolysis gases as the temperature was increased from 40 to 190°C. The amount of gas flowing into a jet gas-separator was controlled by a micro-metering valve, and then trace amounts of the gases were introduced into the quadrupole at pressures of around 10^{-4} torr. The mass spectra corresponding to each peak of the chromatographic traces were recorded using an electromagnetic oscillograph.

About 10 mg of the samples were used for the study of simultaneous TG–MS analysis. Gas atmospheres such as helium, air or oxygen were introduced from the thermobalance into the quadrupole through the micro-metering valve and the gas-separator at pressures of 1×10^{-4} torr (air or oxygen) and 1×10^{-5} torr (He). Emission currents of the analyzer were set to 0.3 mA for the experiments with air or oxygen and 1.0 mA with helium, and the electron energy was 70 V. The flow rate of these gases was 140–150 ml min^{-1}, so a volatile product took 3–5 seconds to reach the ion source from the furnace as the product passed through a glass tube 100 cm long (3 mm i.d.) and the gas separator. This dead time became slightly larger as the heating rate was increased.

The maximum ion current for a mass fragment ion was selected with a peak selector by watching the digital display of mass number and the corresponding ion current on the control console. Hence, the ion currents of any four peaks of mass spectra in a mass range 1–300 AMU were able to be recorded at constant time intervals on a multipen recorder. Variation of the voltage from an ionization gauge for the mass analyzer was also recorded as an evolved gas detection curve with a TG curve.

RESULTS

Pyrolysis–gas chromatography

Figure 2 shows a typical gas chromatogram of the decomposition of PTFE at 700°C in a helium gas atmosphere. The chromatographic trace was monitored by a total ion collector of the Shimadzu–LKB GC–MS. About 34 peaks appeared for C_1 to C_8 fluorinated compounds, corresponding mostly to perfluoroparaffins, perfluoro-olefines, and perfluorocyclic compounds as summarized in Table 1.

There seems to be no difference in the species of the degradation products of PTFE and FEP. Among the pyrolysis gases, tetrafluoroethylene, perfluoropropylene, and perfluorocyclobutane are the major products. The evolution of these three

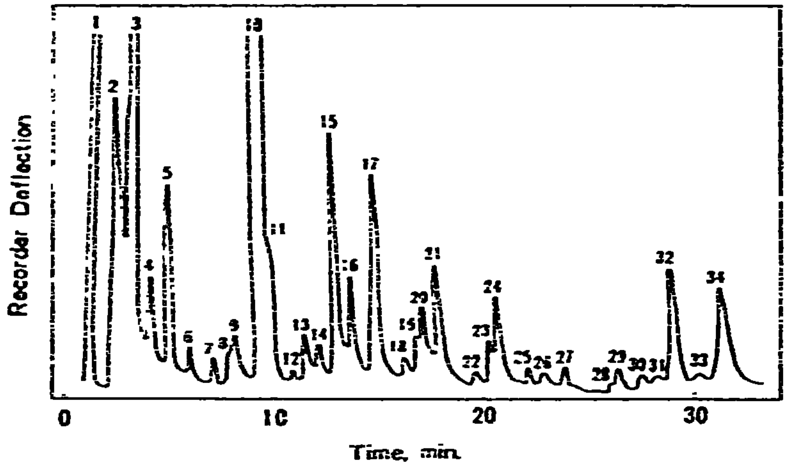


Fig. 2. Chromatographic trace of the degradation products of PTFE in helium at 700 °C monitored by total ion collector.

TABLE I

ANALYSIS OF DECOMPOSITION PRODUCTS OF POLYTETRAFLUOROETHYLENE AT 700 °C

Peak	*Decomposition products (molecular formula)*
1	Carbon monoxide (CO)
2	Silicon tetrafluoride (SiF_4)
3	Carbon dioxide (CO_2)
4	Hexafluoroethane (C_2F_6)
5	Tetrafluoroethylene (C_2F_4)
6	1,1- or 1,2-difluoroethylene ($C_2F_2H_2$)
7	Trifluoroethylene (C_2F_3H)
8	Not identified
9	Octafluoropropane (C_3F_8)
10	Hexafluoropropylene (C_3F_6)
11	Perfluorocyclobutene or (C_4F_6) Hexafluoro-2-butyne
12	Not identified
13	Pentafluoropropylene (C_3F_5H)
14	Perfluorocyclobutane (C_4F_8)
15	Decafluorobutane (C_4F_{10})
16	Perfluoro-1-butene (C_4F_8)
17	Perfluoroisobutylene (C_4F_8)
18	Perfluorocyclopentene or (C_5F_8) Octafluoro-2-pentyne
19	Perfluorocyclopentane (C_5F_{10})
20, 21	Perfluoropentene (C_5F_{10})
22	Not identified (C_5F_5H)
23, 24	Not identified (C_6F_{10}?)
25	Not identified
26, 27	Perfluoroheptene (C_7F_{12})
28–33	Not identified
34	Not identified (C_8F_{10}?)

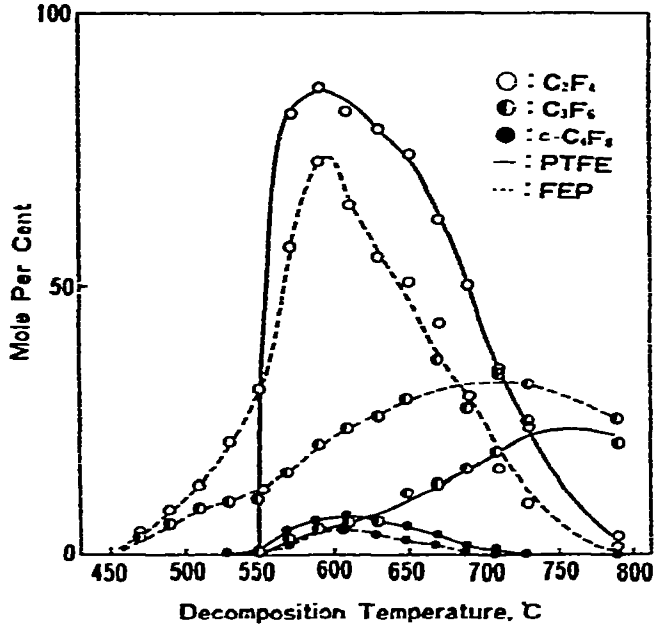


Fig. 3. C_2F_4, C_3F_6 and c-C_4F_8 produced by the pyrolysis in helium.

compounds are presented as a function of temperature in Fig. 3. They were calculated in mole per cent by considering the two polymers were completely decomposed into fluorocarbons at 600°C. Actually, silicontetrafluoride and oxidized products were not appreciably formed at this temperature.

C_2F_4 is the most abundant product for both polymers, and PTFE produces much more C_2F_4 and c-C_4F_8 than FEP at temperatures over 500°C. FEP begins to evolve C_2F_4 and C_3F_6 at relatively low temperatures, and C_3F_6 is produced in much larger quantities than by PTFE at all the degradation temperatures. When the degradation temperature is raised over 650°C, SiF_4, CO and CO_2 are produced abundantly by the reaction of fluorocarbons with silica (SiO_2) in quartz glass. The decrease of fluorocarbon products shown in Fig. 3 is due to this reaction.

When the samples are decomposed in the presence of air, carbonyl fluoride, carbontetrafluoride, SiF_4 and CO_2 are the main products. These gases are produced in quantity as the degradation temperature is increased. C_3F_6 is the most abundant product of all fluorocarbons, and fluoroalkanes such as C_2F_6, C_3F_8, and C_4F_{10} tend to be evolved in the oxidative degradation at 590–690°C. Perfluorocyclobutane and perfluoroisobutylene are also produced, but perfluoro-1-butene may not exist at any of the degradation temperatures in air.

Simultaneous TG–MS in helium

For the simultaneous TG–MS of the two fluorine containing polymers in helium, masses 50(CF_2^+), 69(CF_3^+), 81($C_2F_3^+$), 93($C_3F_3^+$), 100($C_2F_4^+$), 131($C_3F_5^+$), 150($C_3F_6^+$) and 181($C_4F_7^+$) were traced at one second intervals with the four channel peak selector, giving mass-spectrometric thermal analysis curves.

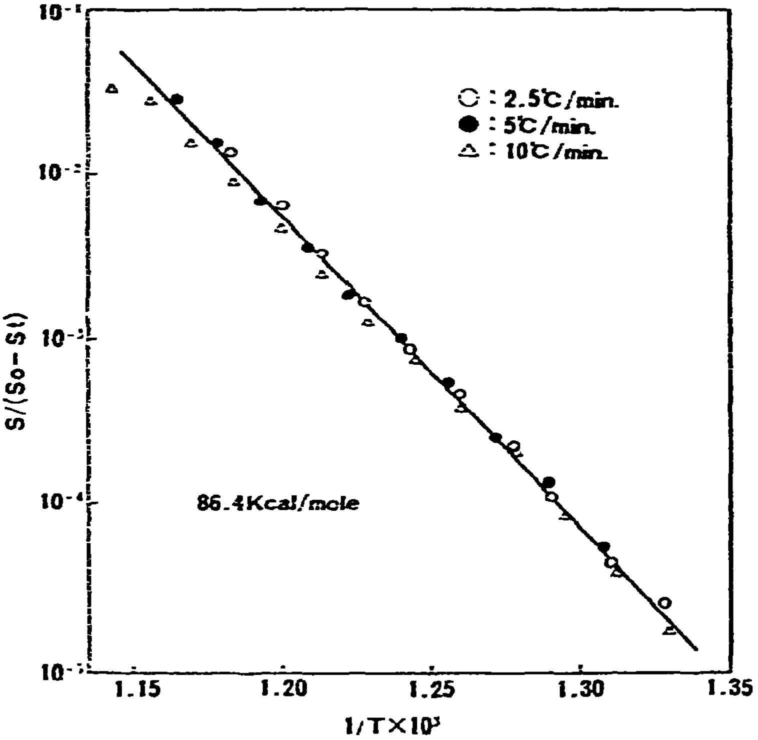


Fig. 4. Arrhenius plots of the reaction producing C_2F_4 (*m/e* 50) from PTFE in helium.

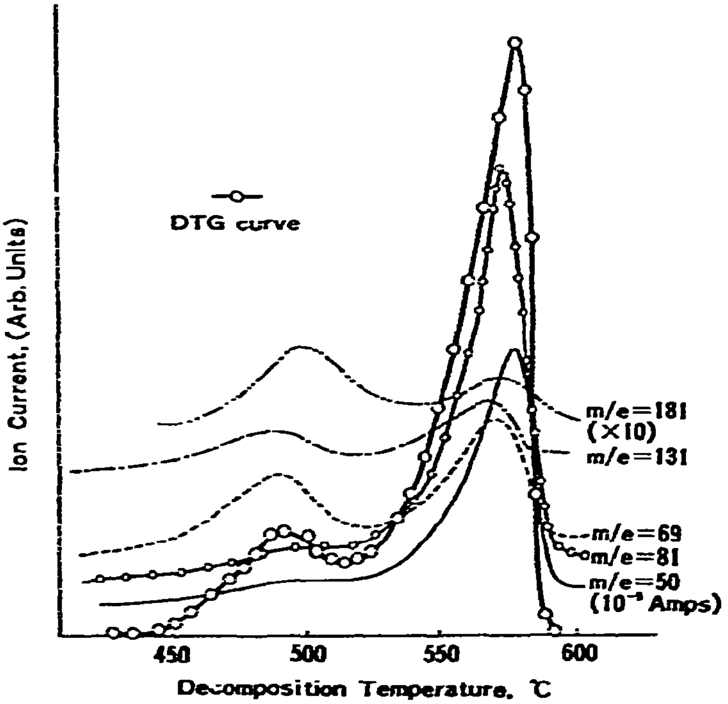


Fig. 5. DTG and MTA curves of FEP in helium at a heating rate of 5°C min^{-1}.

In the degradation process of PTFE, there are major peaks of masses 50, 81 and 100 which are assigned to tetrafluoroethylene with small peaks of masses 69, 131, and 150, assigned probably to perfluoropropylene. The evolution of C_2F_4 and C_3F_6 complete at one stage. Mass fragment ions of $C_3F_3^+$ and $C_4F_7^+$ are scarcely observed, so the formation of C_4F_6, C_4F_8 or the other high-molecular weight fluorocarbons appears to be negligible when decomposed at a certain heating rate.

An activation energy for the evolution of C_2F_4 from PTFE was calculated by taking an Arrhenius plot to be 86.4 kcal mol^{-1} (*m*/*e*: 50) or 86.1 kcal mol^{-1} (*m*/*e*: 81) as shown in Fig. 4. In this calculation it was assumed that the signal of a mass spectrometer(s) is proportional to the rate of formation of the product, and the remaining area under the MTA curve ($S_0 - S_t$) is proportional to the quantity of reactant at that time[9]. C_3F_6 evolves from PTFE with an activation energy of 89.7 kcal mol^{-1} (*m*/*e*: 131).

The copolymer clearly decomposes in two stages in a helium gas atmosphere as shown in Fig. 5. The quantity of the degradation products at the first stage gave almost the same value of about 16% in spite of the heating rates. The first degradation stage may be attributed to the evolution of perfluoropropylene with a small amount of perfluoro-1-butene or perfluoroisobutylene, which are identified by masses 69, 93, 131, 150 and 181. Perfluorocyclobutane is probably not formed as mass 181 hardly exists in the mass spectra of that compound. C_2F_4 is scarcely produced at the first stage

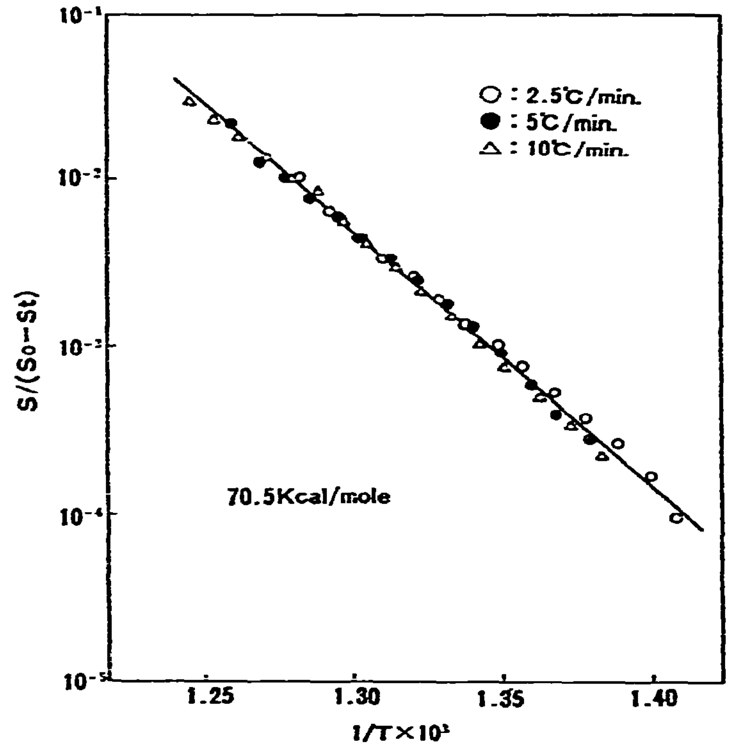


Fig. 6. Arrhenius plots of the reaction producing C_3F_6 (*m*/*e* 131) at the first stage degradation of FEP in helium.

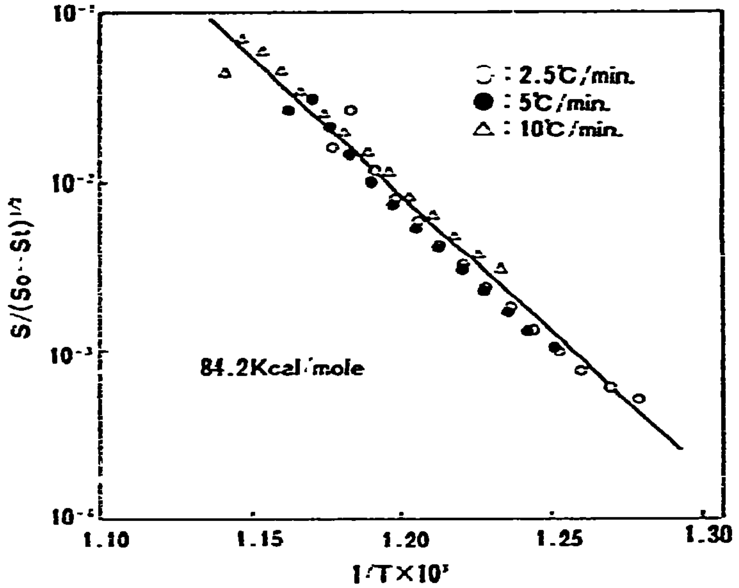


Fig. 7. Arrhenius plots of the reaction producing C_2F_4 (*m/e* 50) at the second stage degradation of FEP in helium.

due to the absence of masses 50 and 81. However, C_2F_4, C_3F_6 and C_4F_8 are evolved simultaneously at the high temperature degradation stage.

It is appreciated from the MTA that the shape of the curves of masses 69 and 131 becomes asymmetric at the second degradation stage as compared with that of the first stage. It suggests that the orders of the reactions producing C_3F_6 are different at each of the two stages, according to the method of Kissinger[10] in which DTA curves have been conducted. The MTA curves of mass 50 or 81 for the decomposition of FEP are also asymmetric as compared with those of PTFE.

The activation energy for the evolution of C_3F_6 (*m/e*: 131) at the first stage was evaluated by the Arrhenius equation giving a relatively low value of 70.5 kcal mol^{-1} as shown in Fig. 6. A first-order reaction was assumed in this calculation. However, for the production of C_3F_6 at the second stage, an order of reaction of 0.5 gave a good straight line giving an activation energy of 85.6 kcal mol^{-1}. From these results, the mechanism for producing C_3F_6 in the low temperature range is assumed to be different from that in the high temperature range. The order of the reaction for the production of C_2F_4 (*m/e*: 50) from FEP is also assumed to be 0.5 and the activation energy is equal to 84.2 kcal mol^{-1} as shown in Fig. 7.

Simultaneous TG–MS in air or oxygen

Masses 44(CO_2^+), 47(OCF^+), 66(OCF_2^+), 69, 81, 85(SiF_3^+ or OCF_3^+), 131, and 181 were selected for the decomposition of the two samples in an atmosphere of air or oxygen. As the fragment ions of SiF_3^+ and $C_4F_7^+$ are not observed in the degradation products, the formation of SiF_4 or C_4F_8 are hardly feasible. The formation of CO_2 and COF_2 is the dominant reaction during pyrolysis, whereas small quantities of

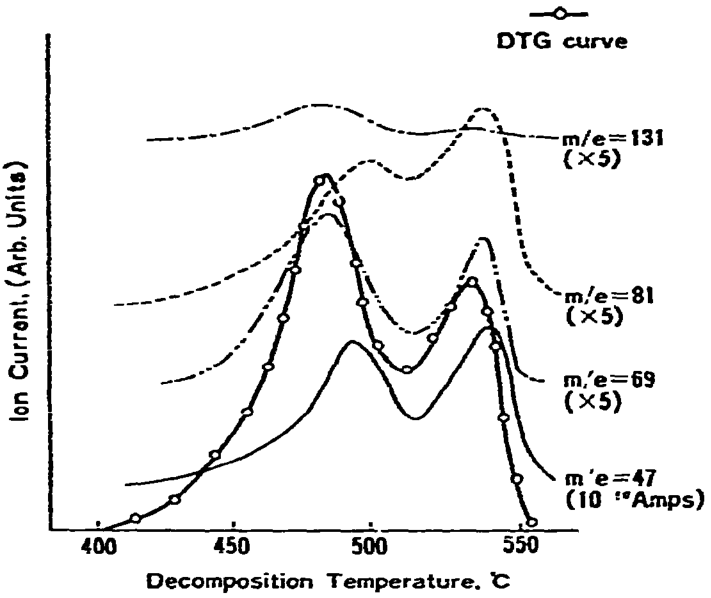


Fig. 8. DTG and MTA curves of FEP in air at a heating rate of 5°C $\min^{-1}$.

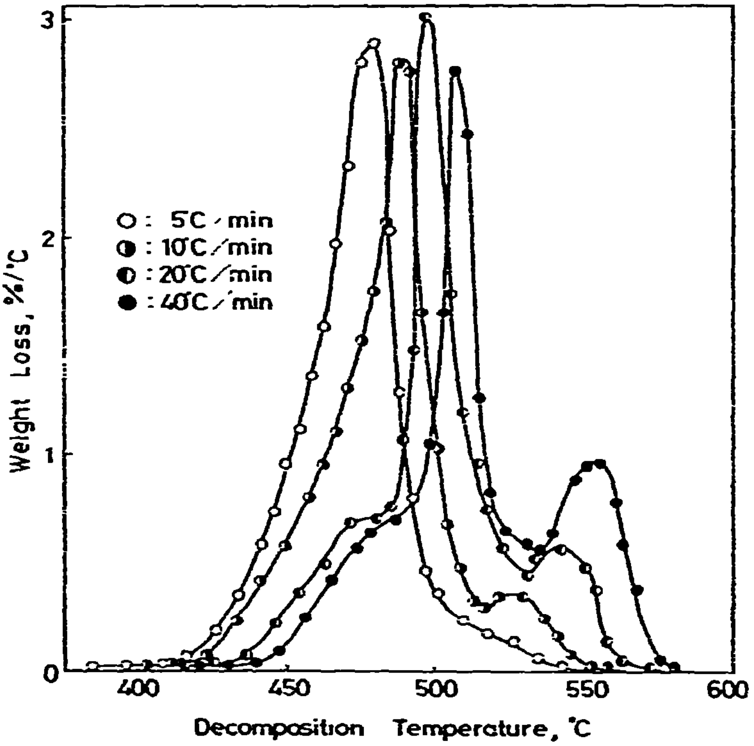


Fig. 9. DTG curves of FEP in an atmosphere of oxygen.

CF_4, C_2F_4 and C_3F_6 are also confirmed. As is shown in Fig. 8, the degradation of PTFE or FEP in air is characterized by separation of the reaction into two stages, and no sharp boundary exists as the heating rate is increased.

Figure 9 shows the DTG curves of FEP in an atmosphere of oxygen. The degradation rate of FEP at the second stage increases as the heating rate is increased. This tendency is not noticed for the oxidation of PTFE which results in a violent ignition at the first stage oxidation.

Activation energies for the evolution of COF_2 (*m/e*: 47) in air were calculated from a linear relation between peak temperature and heating rate. The values thus determined for PTFE are 48.9 kcal mol^{-1} for the reaction at the low temperature range and 43.6 kcal mol^{-1} at the high temperature range. Activation energies at the two stages for FEP were determined as 47.9 and 48.1 kcal mol^{-1}, respectively. The measurements of activation energies for producing CF_4 (*m/e*: 69) at the stages in air were carried out for PTFE and FEP in varying the values from 35.7 to 45.7 kcal mol^{-1}.

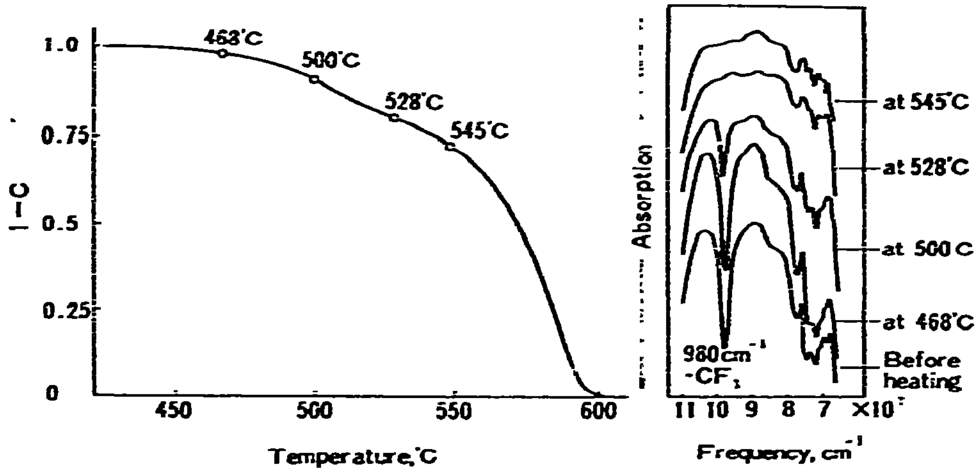


Fig. 10. TG curve and IR spectra of the decomposing FEP at a heating rate of 10°C min^{-1}.

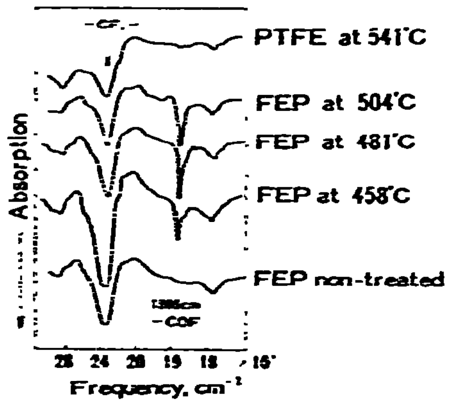


Fig. 11. IR spectra of the decomposing FEP and PTFE in air or oxygen at a heating rate of 10°C min^{-1}.

IR analysis

Figure 10 shows a TG curve and IR spectra of residual substances of FEP, which were taken out of the furnace at desired temperatures. The absorption of trifluoromethyl radical exists in the frequency of 980 cm^{-1}. The number of these radicals decreases as the decomposition temperature is increased, and they do not exist after the first stage degradation at around 530°C. When the IR spectra of FEP heated at 545°C in a helium gas atmosphere was compared with that of non-treated PTFE, there seemed to be little difference in the spectra.

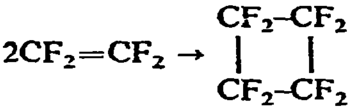
In the presence of air or oxygen, $-CFO$ radicals are observed in the decomposition of FEP, but the existence of the radicals is not observed in the decomposition of PTFE as shown in Fig. 11.

DISCUSSION

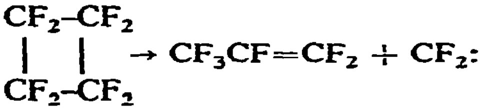
From the results of the pyrolysis–GC, the formation of fluorocarbons (C_1 to C_5) from PTFE may be represented in the following reaction scheme considering difluorocarbene radicals[2]

$$R_f\text{–}CF_2\text{–}CF_2\text{–}CF_2 \ldots \rightarrow R_f\text{–}CF_2\cdot + nCF_2: \qquad (1)$$

$$CF_2: + CF_2: \rightarrow CF_2{=}CF_2 \qquad (2)$$



(3)

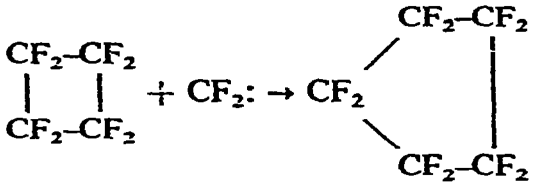


(4)

$$CF_2{=}CF_2 + CF_2: \rightarrow CF_3CF{=}CF_2 \qquad (5)$$

$$CF_3CF{=}CF_2 + CF_2: \rightarrow CF_3CF_2CF{=}CF_2 \text{ or } (CF_3)_2C{=}CF_2 \qquad (6)$$

$$\begin{array}{l} CF_3CF_2CF{=}CF_2 \\ \text{or } (CF_3)_2C{=}CF_2 \end{array} + CF_2: \rightarrow CF_3CF_2CF_2CF{=}CF_2 \text{ and isomers} \qquad (7)$$



(8)

All the products described above have the formula $(CF_2)_n$. However, the explanation based on CF_2 radicals does not account for the production of fluoroalkane compounds such as C_2F_6, C_3F_8 and C_4F_{10} which are evolved at temperatures over 610°C. A reaction scheme based on trifluoromethyl radicals has been suggested by Atkinson[11] for the decomposition of perfluoroisobutylene to give perfluoroethane at temperatures over 700°C. The formation of C_3F_8 or C_4F_{10} cannot be explained by this reaction scheme; these fluoroalkanes and unsaturated cyclic compounds or fluoroalkines (C_4F_6, C_5F_8 and C_6F_{10}) may be formed by the decomposition of high-molecular weight fluorocarbons.

The formation of fluorinated hydrocarbons such as $C_2F_2H_2$ or C_3F_5H may be due to the reaction of fluorocarbons near the ion source with water which may exist in the polymers or in the mass analyzer. In the presence of oxygen, CF_2 radicals react mainly with O_2 to produce COF_2 in the cases of both TG–MS and pyrolysis–GC, followed by a decomposition reaction

$$2CF_2: + O_2 \rightarrow 2COF_2 \qquad (9)$$

$$2COF_2 \rightarrow CO_2 + CF_4 \qquad (10)$$

Though the carbon–fluorine bond strength involves a great energy of about 116 kcal mol^{-1}, the C–F bond is assumed to be broken to produce fluorine radicals in the presence of O_2 at high temperatures. Hence, fluoroalkenes may react with fluorine radicals to produce more fluoroalkanes in air than in a helium gas atmosphere.

According to TG–MS analysis for PTFE in helium, C_2F_4 and C_3F_6 are formed mainly via reactions (1), (2) and (5), and reactions (3) and (4) relating to c-C_4F_8 may not occur in an inert gas atmospheres.

For TG–MS of FEP in helium, the first stage degradation is mainly due to evolution of perfluoropropylene. This evolution mechanism is distinct from that at the second stage as shown by IR analysis and DTG owing to the relatively low value of the activation energy (70.5 kcal mol^{-1}). At the first stage degradation of FEP, $CF_3CF{=}CF_2$ may be directly liberated or evolved via the reaction of CF_3CF: and CF_2:. The evolution of C_2F_4 and C_3F_6 at the second stage seems to be identical with the reactions of PTFE, and C_4F_8 may be formed at the two stages via the reaction (6).

In the decomposition process of FEP with pyrolysis–GC, most of the C_2F_4 can be regarded as being produced at a temperature range of 450–550°C (Fig. 3) by the reverse reaction of (5)

$$CF_3CF{=}CF_2 \rightarrow CF_2{=}CF_2 + CF_2:$$

The reaction scheme for FEP in air or oxygen seems to be the same as (9) and (10), but end groups of the polymer may react with O_2 to form –CFO radicals in the decomposing FEP as shown in the IR spectra. This may be caused by a reaction with oxygen incorporated into the polymer which is liable to melt as compared with PTFE.

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