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**Hydroxide-Ion Induced Complete Mineralization of
Poly(tetrafluoroethylene-*co*-hexafluoropropylene) Copolymer (FEP) in
Subcritical Water**

Hisao Hori,^{a*} Hisashi Saito,^a Abdelatif Manseri,^b Bruno Ameduri^b

^a *Faculty of Science, Kanagawa University, 3-27-1 Rokkakubashi, Kanagawa-ku, Yokohama
221-8686, Japan*

^b *Institut Charles Gerhardt, Univ Montpellier, CNRS, ENSCM, Montpellier, France*

*Corresponding author.

E-mail address: h-hori@kanagawa-u.ac.jp

ABSTRACT

Decomposition of poly(tetrafluoroethylene-*co*-hexafluoropropylene) copolymer (FEP) in supercritical and subcritical water was investigated with the aim of waste treatment. The efficiency of such decomposition was examined by using either oxidizing agents (O_2 , H_2O_2) or an alkaline reagent (KOH). When O_2 was chosen, the highest F^- and CO_2 yields, 75% and 64%, respectively, were obtained from a reaction of FEP in supercritical water at 384 °C for 24 h. Under these conditions, traces of CHF_3 were detected in the gas phase, the amount of which decreased with increasing the reaction time. H_2O_2 gave slightly higher reactivity than O_2 . In contrast, reactions with KOH induced efficient fluorine mineralization. When FEP reacted in 3.0 M KOH solution at 360 °C for 18 h, the F^- yield reached 98%. Hence, complete fluorine mineralization was achieved, where very little CO_2 (~0% yield) and no CHF_3 were generated in the gas phase. Furthermore, ^{19}F -NMR spectroscopy and combustion-ion chromatography revealed that the reaction solutions did not contain any organofluorine compounds during the reactions. FEP decomposed, releasing F^- into the reaction solution, resulting in the formation of amorphous carbon in the residue.

Keywords: Decomposition; Fluoropolymer; Mineralization; PFAS; Subcritical water

1. Introduction

Fluoropolymers are specialty polymers where all or partial hydrogen atoms in polyolefins are substituted by fluorine atoms. The small size (similar to hydrogen atom) and high electronegativity of the fluorine atom make the carbon-fluorine bond exceptionally strong. Hence, fluoropolymers offer high stabilities against chemicals, heat, and UV-light irradiation that cannot be achieved with other materials. Furthermore, they show high insulation and low refractive index. Owing to these unique properties, fluoropolymers are used in many sectors as in common industrial equipment (for example, sinks, tubes, valves, O-rings, cable and wire insulations) and in high-tech applications such as proton-exchange fuel cell membranes, cores and claddings of optical fibers, backsheets for solar cell panels, piezoelectric devices, cathode binders for lithium-ion batteries, specific UV- and aging-resistant coatings, and so forth [1–8].

Fluoropolymers are niche materials: the global market of fluoropolymers **in recent years was estimated at 330,300 tons in 2021 [9] and 346,970 tons in 2023 [10], although the exact figures vary on the source. These volumes are much lower than the global plastics production, which** were about **390.7 million** tons in 2021 [11]. Nevertheless, the consumption of fluoropolymers has been increasing [12], because they are crucial components in chemical, electronics, automobile, petroleum, building, textile, aerospace, and other manufacturing industries. While usages of fluoropolymers have spread, development of waste treatment techniques should meet their increasing volumes. During the treatment process, emission of low-molar mass per- and polyfluoroalkyl substances (PFASs), such as perfluorooctanoic acid and other analogues, to the environment must be avoided [13]. Fluoropolymer waste can be decomposed by incineration at high temperature (~1000 °C) [14]. However, incineration releases hydrogen fluoride gas that damages firebricks of incinerators. If such wastes are destructed to fluoride ions (F^-) (i.e., mineralization), by use of environmentally benign techniques, combination of the F^- ions and calcium cations can produce calcium fluoride.

Because calcium fluoride is the source for all fluorinated compounds, the chemical system that transforms fluoropolymers into F^- ions would contribute to recycling of a relevant fluorine resource.

Among fluoropolymers, poly(tetrafluoroethylene-*co*-hexafluoropropylene) copolymer ($-\text{[(CF}_2\text{CF}_2)_n\{\text{CF}_2\text{CF}(\text{CF}_3)\}]_p-$, FEP) which consists of only carbon and fluorine atoms, has the third largest market share for fluoropolymers [12], after poly(tetrafluoroethylene), $-\text{(CF}_2\text{CF}_2)_n-$, PTFE [15] and poly(vinylidene fluoride), $-\text{(CF}_2\text{CH}_2)_n-$, PVDF. Because FEP has not only outstanding resistance to chemicals and heating but also has melt-processability which PTFE does not have [16], it is widely used in electrical applications as electric wire covering and chemical applications including lined tanks, lined pipes, gaskets, hoses, etc [1,3,6,16–18].

Many reports described the decomposition of FEP [19–39]. However, all these studies investigated the radiation or thermal damage of FEP surface to evaluate the degradation at the usage environment of FEP products. It can be expected that the level of the surface degradation is much lower than that required for waste treatment because the latter requires the whole destruction.

Supercritical water is a water state at temperatures and pressures higher than the critical point (374 °C, 22.1 MPa) while subcritical water (superheated water) is liquid water under high pressure at temperatures ranging from 100 °C to 374 °C. These waters are attractive in waste management because the implementation can produce useful compounds (biofuels, etc.) or convert hazardous compounds into harmless, as summarized by several books or review articles [40–51].

Herein, we focus on the decomposition behavior of FEP in supercritical water and subcritical water, with the aim of the waste treatment, for the first time. The effect of oxidizing agents (O_2 or H_2O_2) and an alkaline reagent (KOH) on the mineralization of the

copolymer is described. We hope that our findings will contribute to the development of environmentally benign industrial processes for the waste treatment of FEP.

2. Experimental section

2.1. Materials and reagents.

FEP powder (the molar ratio of tetrafluoroethylene/hexafluoropropylene was 95/5 and the weight-average molar mass was ca. 400,000) was obtained from Daikin Chemical Europe (Düsseldorf, Germany). The fluorine weight percentage quantified by combustion ion chromatography was 75.8 wt %, which was almost identical with the ideal value (76.0%). The F⁻ yields of the reactions were calculated based on the analytical value. PTFE powder was obtained from Sigma-Aldrich Japan (Tokyo, Japan). Other reagents were purchased from Fujifilm Wako Pure Chemical (Osaka, Japan) or Sigma-Aldrich. High purity argon (99.99%) and O₂ (99.999%) used for the reactions and two standard gas mixtures, carbon dioxide (1.00% or 1.01%)/nitrogen and fluoroform (CHF₃, 0.971%)/nitrogen for analysis, were provided by Nissan Tanaka (Saitama, Japan).

2.2. Autoclave.

The reaction was carried out in a stainless-steel autoclave (internal space, 96 mL) and a stainless-steel cap was attached on the top. The cap was connected to a pressure gauge and to two valves connected to gas supply and sampling units, respectively. A gold vessel was placed into the autoclave to suppress contamination from the autoclave wall. The reaction mixture in the gold vessel was stirred by an impeller. **A flowchart of the experimental procedure of this study is shown in Fig. S-1 in the Electronic Supplementary material.**

2.3. Procedure for subcritical and supercritical water treatment in the presence of oxidizing

agent.

2.3.1. Reactions in the presence of O₂.

In a typical reaction, the FEP powder (30.0 mg) and ultrapure milli-Q water (30 mL) were introduced into the gold vessel in the autoclave under O₂ atmosphere. Then, the autoclave was filled with O₂ up to 1.1 MPa. This O₂ pressure corresponded to 26.8 mmol. Then, the autoclave was heated to the planned reaction temperature (300–384 °C) with a rate of 10 °C min⁻¹. After holding for a specified reaction time, the autoclave was quickly cooled to room temperature. The gas in the headspace of the autoclave was transferred into a gas bag through the gas sampling unit and the recovered gas was subjected to gas measurement. After the gas collection, the cap of the autoclave was opened. The content was transferred into a polypropylene tube and centrifuged if solid was present, while the liquid and solid (residue) were subjected to analysis.

2.3.2. Reactions in the presence of H₂O₂.

The FEP powder (30.0 mg) and aqueous H₂O₂ (2.0 M, 30 mL) were transferred into the gold vessel in the autoclave under argon atmosphere. After the autoclave was sealed, the autoclave was filled with argon up to 0.6 MPa. The procedure after that was the same as that described in section 2.3.1.

2.4. Procedure for subcritical water treatment in the presence of alkaline reagent.

In a typical reaction, the FEP powder (30.0 mg) and aqueous solution of KOH (3.0 M, 30 mL) were transferred into the gold vessel in the autoclave under argon atmosphere. After being sealed, the autoclave was filled with argon up to 0.6 MPa. After that, the procedure was similar to that reported in section 2.3, except that the reactions were performed at subcritical water state (300–360 °C).

2.5. Instrumental analysis.

The recovered gas was analyzed by gas chromatography-mass spectrometry (GC/MS) using a QP2010 SE instrument (Shimadzu, Kyoto, Japan) attached by a Rt-Q-BOND porous polymer column (Restek, Bellefonte, PA, USA). The carrier gas was helium, and the injection port temperature was kept at 120 °C. The split ratio (ratio of the flow rate of gas through the split vent to the flow rate through the column) was 20/1 and the MS spectrometer was operated in full-scan mode with m/z ranging from 2.0 to 200. The temperature program of the column oven after gas injection was as follows: keeping at 30 °C (for 5 min), raising to 200 °C at 20 °C min⁻¹, keeping at 200 °C (for 20 min), then cooling to 30 °C.

The F⁻ ions released into the reaction solution were quantified by ion chromatography using an IC-8100 instrument (Tosoh, Tokyo, Japan) with a TSKgel Super IC-A HS column (Tosoh). The eluent was an aqueous solution consisting of 7.5 mM sodium hydrogen carbonate and 0.8 mM sodium carbonate, and flowed at 1.5 mL min⁻¹. The total organic carbon (TOC) amount in the reaction solution was determined by a N/C 3100 BU TOC instrument (Analytik Jena, Jena, Germany). Several reaction solutions were also analyzed by combustion-ion chromatography to quantify total fluorine (TF) amount. The sample was delivered into a combustion instrument (AQF-2100H, Nittoseiko Analytech, Yamato, Japan; combustion temperature, 900–1000 °C), where all fluorine content in the reaction solution was destructed to HF gas, which was recovered in an absorbing liquid (H₂O₂ solution). Then the solution was delivered into an ion chromatograph (Dionex ICS-1100, Thermo Fisher Scientific, Waltham, MA) to quantify the F⁻ amount. TF is the sum of total organic fluorine (TOF: fluorine atoms that compose **organofluorine** compounds) and inorganic fluorine (fluorine atoms that compose F⁻) amounts in the reaction solution. Therefore, the relation of TF, TOF and F⁻ can be expressed by Eq. (1).

$$\text{Moles of TF} = \text{moles of TOF} + \text{moles of F}^- \quad (1)$$

^{19}F NMR spectra (565 MHz) of several resulting reaction solutions from subcritical water treatment with potassium hydroxide were measured by means of an NMR spectrometer (ECZ600, JEOL, Tokyo, Japan). D_2O was added to the reaction solution, and subjected to measurement. The chemical shifts are relative to an external standard of trifluoroacetic acid in D_2O . Raman spectra of solid residues and FEP before the treatment were measured at 532 nm excitation using a Raman imaging microscope (SENTERRA, Bruker, Billerica, MA, USA).

The yields of F^- in the reaction solution and of CO_2 in the gas phase and the remaining ratio of TOC in the reaction solution were calculated by Eq. (2–4), respectively.

$$\text{F}^- \text{ yield} = [(\text{moles of F}^- \text{ formed}) / (\text{moles of fluorine atoms in the initial FEP})] \quad (2)$$

$$\text{CO}_2 \text{ yield} = [(\text{moles of CO}_2 \text{ formed}) / (\text{moles of carbon atoms in the initial FEP})] \quad (3)$$

$$\text{TOC ratio} = [(\text{moles of TOC formed}) / (\text{moles of carbon atoms in the initial FEP})] \quad (4)$$

3. Results and discussion

3.1. Reactions in supercritical water with oxidizing agent.

First, the reactivity of FEP in supercritical water in the presence of O_2 was carried out because we previously reported that a partially fluorinated polymer, PVDF, was almost completely transformed into F^- and CO_2 in supercritical water at 384 °C in the presence of 5.8-fold molar excess of O_2 , relative to the fluorine or carbon content in PVDF [52]. Fig. 1 displays the effect of initial O_2 amount on the FEP decomposition induced by reactions at 384 °C for 6 h, where the initial FEP amount was 30.0 mg (the amounts of the fluorine and carbon atoms were 1.20 mmol and 0.60 mmol, respectively) and the initial O_2 amount varied

from 0 to 26.8 mmol. In the absence of O₂ (i.e., in an argon atmosphere), the F⁻ amount in the reaction solution was 118 μmol, which corresponded to 10% yield (Table 1, entry 1). In the gas phase, 40.8 μmol of CO₂ was detected, leading to 7% yield (Table 1, entry 1). These results indicated that FEP was only slightly mineralized in the absence of O₂. In the gas phase, trace amount of CHF₃ (1.7 μmol) was also detected (Fig. 1b and Table 1, entry 1). Increasing initial O₂ amount enhanced the F⁻ and CO₂ formations (Fig. 1a). For a reaction performed with 26.8 mmol of O₂, which corresponded to a 22-fold molar excess of the initial fluorine atoms and a 45-fold molar excess of the initial carbon atoms in HFP, the F⁻ amount reached 367 μmol (31% yield) while the CO₂ amount reached 182 μmol (30% yield) (Table 1, entry 2). When the reactions were performed with O₂ (6.7–26.8 mmol), the CHF₃ amounts (0.5–0.9 mol, Fig. 1b) were smaller than that (1.7 μmol) generated in the absence of O₂, suggesting that CHF₃ reacted with O₂. Reactions at lower temperatures, that is, at subcritical water states (<374 °C), were also carried out. Fig. 2 displays temperature dependences of the amounts of (a) F⁻, CO₂ and (b) CHF₃ generated from reactions at 300–384 °C for 6 h with 26.8 mmol of O₂. When FEP was reacted at 300 °C, almost no mineralization occurred: the F⁻ and CO₂ amounts (Fig. 2a) were 11.9 μmol (1% yield) and 13.7 μmol (2% yield), respectively, reflecting high durability of FEP against heating and oxidation. Consistently, the CHF₃ amount was produced in trace only (0.4 μmol) (Fig. 2b). Elevating temperature up to 350 °C somewhat increased the reactivity, but the F⁻ and CO₂ yields remained in few percentages (F⁻, 80.4 μmol, 7% yield; CO₂, 32.4 μmol, 5% yield). Significant increase of these amounts was observed when the temperature increased to supercritical water state (384 °C), where the F⁻ and CO₂ amounts reached 367 μmol (31 % yield) and 182 μmol (30% yield), respectively. The CHF₃ amount showed different tendency upon heating. The amount became maximum at 350 °C and then decreased at higher temperature, 384 °C (Fig. 2b). This phenomenon suggests that the release of CF₃ side group of FEP began at around 350 °C and

the formed CHF_3 can decompose at $384\text{ }^\circ\text{C}$.

Because FEP was mineralized by O_2 at supercritical water state ($384\text{ }^\circ\text{C}$), the reaction time was extended at this temperature (Fig. 3). Both F^- and CO_2 amounts clearly increased with increasing reaction time (Fig. 3a). When the reaction was performed for 24 h (i.e., the maximum reaction time in this study), the F^- and CO_2 amounts were $904\text{ }\mu\text{mol}$ (75% yield) and $385\text{ }\mu\text{mol}$ (64% yield), respectively (Table 1, entry 3). Fig. 3b displays the evolution of CHF_3 versus time. The amount clearly reduced with increasing reaction time, indicating that CHF_3 can be decomposed in the presence of O_2 . A reaction performed for 24 h induced a minimum amount ($0.1\text{ }\mu\text{mol}$) (Table 1, entry 3).

As described above, FEP can be clearly decomposed to F^- and CO_2 by use of supercritical water with O_2 and a minor gaseous product, CHF_3 , also decomposed by prolonged reaction time. However, the highest F^- yield did not reach 100% within 24 h treatment. Then H_2O_2 was used since it has a higher reactivity than O_2 in the decomposition of PVDF and related copolymers [53]. Fig. 4 displays temperature dependences of the amounts of (a) F^- , CO_2 and (b) CHF_3 formed from reactions at $300\text{--}384\text{ }^\circ\text{C}$ for 6 h, involving 60.0 mmol of H_2O_2 (2.0 M as the concentration). Similar to reactions using O_2 , almost no reaction occurred at $300\text{ }^\circ\text{C}$: the F^- and CO_2 amounts were $21.1\text{ }\mu\text{mol}$ (2% yield) and $21.4\text{ }\mu\text{mol}$ (4% yield), respectively. Higher temperature enhanced the F^- and CO_2 amounts (Fig. 4a). At $384\text{ }^\circ\text{C}$, the F^- amount reached $429\text{ }\mu\text{mol}$ (36% yield) whereas that of CO_2 reached $212\text{ }\mu\text{mol}$ (35% yield) (Table 1, entry 4). These values were slightly higher than the corresponding ones obtained from reactions with O_2 :

31% and 30% yields for F^- and CO_2 , respectively (Table 1, entry 2). As for the CHF_3 amount, the value became a maximum at $350\text{ }^\circ\text{C}$ (Fig. 4b) while $0.6\text{ }\mu\text{mol}$ was detected at $384\text{ }^\circ\text{C}$ (Table 1, entry 4). This tendency was similar to that observed for reactions using O_2 (Fig. 2b).

Compared to O_2 , H_2O_2 somewhat enhanced the mineralization of FEP in supercritical

water. However, high pressure (26.5 MPa, Table 1, entry 4) was required, which is not suitable for safety. To achieve the mineralization of FEP at lower temperature and pressure, we examined reactions in the presence of an alkaline reagent as in the following section.

3.2. Reactions in subcritical water in the presence of alkaline reagent.

3.2.1. Effect of potassium hydroxide concentration, temperature, and reaction time.

Fluoropolymers such as PVDF and related materials were degraded by alkaline reagent and such phenomenon was applied to their surface modification [54–59]. Brewis et al. reported that heating PVDF in aqueous KOH (15 M) at 80 °C caused C=O and C=C bonds on the surface, resulting in large increase in adhesion [54]. Similarly, Ross et al. reported that treatment of PVDF with aqueous NaOH (12 M) at 80 °C for 256 h generated hydroxyl and carbonyl groups on the PVDF surface [55]. Bottino et al. also modified PVDF by 5 wt% KOH solution in methanol, after this treatment the hydrophilicity and fouling resistance of the membranes were improved [56]. However, the majority of these reports were limited for PVDF and VDF- containing copolymers. Furthermore, even if such (co)polymers were used, the decomposition that favored a total mineralization, aimed at waste treatment, was rare [60,61].

Fig. 5 displays effect of KOH concentration on the FEP decomposition upon reactions at 350 °C for 6 h. When FEP was reacted without KOH, almost no FEP was decomposed: the F⁻ amount was 4.9 μmol (~0% yield) (Table 2, entry 1). We measured TOC in the resulting reaction solutions to evaluate the carbon mineralization because when the reactions were achieved with an alkaline reagent, the pH of the resulting reaction solutions was high. In such a case, even if CO₂ was generated, most of the molecules transformed into carbonate (CO₃²⁻) in the reaction solution. Therefore, the CO₂ amount in the gas phase did not reflect the mineralization extent of the carbon content. When the reaction was performed in the absence

of KOH, the TOC and CO₂ amounts were 8.9 μmol and 11.6 μmol, assigned to 1% and 2% of the amount of carbon atoms in the initial FEP, respectively (Table 2, entry 1). As described above, when the reaction was carried out in supercritical water at 384 °C with argon, trace of CHF₃ (1.7 μmol) was detected (Table 1, entry 1). In contrast, no CHF₃ was observed after the reaction at 350 °C, indicating high stability of FEP at 350 °C.

While FEP was poorly reacted in the absence of KOH at 350 °C, the F⁻ and TOC amounts increased with elevating [KOH] (Fig. 5a). When FEP was mixed with 3.0 M of [KOH] (the KOH amount was 90 mmol, i.e., 75-fold molar excess of the fluorine atoms in initial FEP), the F⁻ amount reached 325 μmol (27% yield) (Table 2, entry 2). Likewise, the TOC amount raised to 159 μmol (27% of the carbon content in the initial FEP) (Table 2, entry 2). These results demonstrate that FEP clearly reacted with KOH. For reactions using KOH, the CO₂ amounts became two orders of magnitude lower (0.1 μmol level) than that generated from the experiment without KOH (Fig. 5b). For a reaction with 3.0 M of [KOH], the CO₂ amount was reduced to 0.3 μmol (Table 2, entry 2). This is not surprising because the pH of the resulting reaction solution was high (13.3) as mentioned above. Besides trace CO₂, no species such as CHF₃ were detected in the gas phase. One advantage of the present method deals with the absence of CHF₃, as it has a high global warming potential [62].

Temperature dependences of FEP decomposition upon reactions with 3.0 M of [KOH] are shown in Fig. 6. For a reaction achieved at 300 °C, FEP slightly reacted: the F⁻ amount was 56 μmol (5% yield) while the TOC amount was 3.5 μmol (1% of the carbon content in the initial FEP). The defluorination became obvious above 340 °C (Fig. 6a). At 360 °C, as the maximum temperature among reactions in subcritical water we tested, the F⁻ amount reached 506 μmol (42% yield) (Table 2, entry 3, average of two reactions). On the other hand, the TOC amount markedly increased at 340 °C, and almost saturated above 350 °C, suggesting that organic compounds that compose TOC began to decompose around 360 °C. At 360 °C,

the TOC amount was 139 μmol , or 23% of the carbon content in the initial FEP (Table 2, entry 3, average of two reactions). In contrast to the formation of F^- and TOC, only trace amount of CO_2 was detected in the gas phase (Fig. 6b). After the reaction at 360 $^\circ\text{C}$, the CO_2 amount was 0.3 μmol (0% yield, Table 2, entry 3, average of two reactions).

Because FEP was efficiently mineralized in subcritical water with 3.0 M of $[\text{KOH}]$ at 360 $^\circ\text{C}$, the reaction time varied at this temperature (Fig. 7). The F^- amount further increased with increasing reaction time (Fig. 7a). At 18 h, that amount reached 1170 μmol (98% yield, Table 2, entry 4). Therefore, quasi-complete fluorine mineralization of FEP was achieved. The TOC amount ranged from ca. 100 to 200 μmol , and finally reached 98.1 μmol after 18 h, which corresponded to 16% of the carbon content in the initial FEP (Table 2, entry 4). Throughout the time, the CO_2 amount in the gas phase was negligible. At 18 h, the value was 0.8 μmol (0% yield, Table 2, entry 4). In contrast to little CO_2 formation, black colored solid residue formed, which was subjected to Raman spectroscopy as shown in the next section.

In addition, effect of initial FEP amount was examined on reactions at 360 $^\circ\text{C}$ for 6 h with 3.0 M of $[\text{KOH}]$. Reducing initial FEP amount to 15.3 mg increased the F^- yield (86%, Table S-1 in Supplementary material, entry 1, average of two reactions). This yield was clearly higher than that obtained from reaction with 30.0 mg (42%, Table S-1, entry 2, average of two reactions). On the other hand, when the initial FEP amount was increased to 60.0 mg, the F^- yield was 44% (Table S-1, entry 3), which was almost identical to that obtained from 30.0 mg FEP (42%). Hence, the F^- yield was significantly increased when the initial FEP amount was reduced to 15.3 mg.

3.2.2 Reaction intermediates.

As described above, when the reaction was performed in subcritical water (360 $^\circ\text{C}$) with excess KOH (3.0 M), the fluorine atoms in the initial FEP showed a quasi-complete

mineralization, releasing F^- ions into the reaction solution after 18 h treatment. Advantageously, under such conditions, no environmentally harmful gases, such as CHF_3 , were detected in the gas phase. To estimate whether any organofluorine compounds remained in the resulting reaction solutions, the solutions obtained from the reactions with 3.0 M of $[KOH]$ at $360\text{ }^\circ\text{C}$ were characterized by ^{19}F -NMR spectroscopy (Fig. 8). When a reaction was performed for 6 h, which led to 44% F^- yield, the spectrum of the resulting reaction solution exhibited only one peak at -122 ppm , assigned to F^- (Fig. 8a). The ^{19}F -NMR spectra of reaction solutions after different times (12 h to 18 h) also showed this peak only (Fig. 8b to 8d). The absence of any peaks other than F^- indicates that no organofluorine compounds were present in the resulting reaction solutions. The resulting reaction solutions were analyzed by combustion-ion chromatography to quantify TF. The TF amount obtained for each reaction time was in good agreement with the F^- amount in the reaction solution, that is, virtually no presence of TOF (Fig. 9, detailed data are shown in Table S-2 in Supplementary material). This result also demonstrates the absence of organofluorine compounds in the reaction solutions.

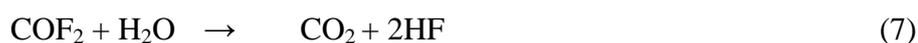
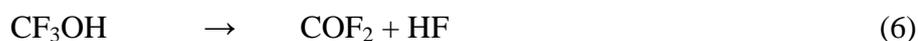
As described above, after reactions that gave insufficient fluorine mineralization, black colored residues were formed. Fig. 10a displays Raman spectrum of the residue obtained from a reaction with 3.0 M of $[KOH]$ at $360\text{ }^\circ\text{C}$ for 6 h, which conditions resulted in 44% F^- yield. The spectrum exhibits peaks at $1596, 1376, 1298$ (shoulder), 1215 (shoulder), $728, 595, 380,$ and 286 cm^{-1} . On the other hand, the spectrum of virgin FEP powder (before reaction) showed peaks at $1378, 1297, 1214, 729, 594, 379,$ and 286 cm^{-1} (Fig. 10b: the assignments of these peaks are described in Table S-3 in Supplementary material, based on literature [63,64]. Actually, the spectrum of the residue (Fig. 10a) includes peaks corresponding to FEP. When the intensity due to FEP was subtracted from the spectrum of the residue (Fig. 10a), it showed two broad intense peaks at 1595 and 1371 cm^{-1} (Fig. 10c). This pattern matches with

amorphous carbon [65–68], where both peaks are assigned to the C=C bond stretching. Therefore, this residue consisted of FEP and amorphous carbon. Measurements for both reaction solution and residue indicate that FEP was decomposed, releasing F⁻ into the reaction solution, while generating residue containing amorphous carbon.

Based on these results, we propose a mechanism for the initial step of the FEP decomposition. First, the OH⁻ ion reacts with the quaternary carbon atom bearing the CF₃ group in the HFP unit, resulting in the release of CF₃OH from the main chain [Eq. (5)].



The formed CF₃OH is unstable, which transforms into COF₂ and HF [69] [Eq. (6)], and COF₂ is easily hydrolyzed into CO₂ and HF [70] [Eq. (7)], because the resulting reaction solution was basic, most of the HF molecules are dissociated but here we describe non-dissociated form for convenience).



Therefore, CHF₃ cannot be produced in the reactions in subcritical water using KOH.

On the other hand, on the main chain, a C=C bond is formed, which can further release F⁻ [Eq. (8)].



Once C=C bond is generated in the polymer chain, the bond could react onto OH⁻ ions and/or water, which induces defluorination of the chain, forming amorphous carbon as a final product.

To make clear whether the quaternary carbon atom bearing CF₃ group in FEP can act as the initial reactive point as described above, a control reaction using PTFE was performed at

360 °C for 18 h using 3.0 M of [KOH]. These conditions were the same as those where FEP underwent a complete fluorine mineralization (F^- yield = 98%, Table 2, entry 4). After the reaction, the F^- yield from PTFE was rather low, 21% (Table 2, entry 5), indicating that FEP was more reactive than PTFE and the decomposition of FEP initiates at the quaternary carbon atom bearing CF_3 group. This result is consistent with FEP being less thermally stable than FEP [20].

4. Conclusions

The mineralization of FEP was investigated by use of super- and subcritical water with an oxidizing agent (O_2 , H_2O_2) and of subcritical water with KOH. When O_2 was used, the highest yields of F^- and CO_2 reached 75% and 64%, respectively, by the treatment of FEP in supercritical water at 384 °C for 24 h. Under these conditions, trace of CHF_3 was detected in the gas phase and the amount decreased with increasing the reaction time. H_2O_2 gave a slightly higher reactivity than O_2 . In contrast, an alkaline reagent, KOH induced almost complete fluorine mineralization under milder conditions: the F^- yield reached 98% after the treatment in subcritical water at 360 °C for 18 h. This treatment simultaneously produced very little CO_2 and no CHF_3 in the gas phase. **The decomposition of FEP proceeded by releasing F^- into the reaction solution and forming amorphous carbon in the residue, while no organofluorine compounds were present in the resulting reaction solution.**

Further work to mineralize other perfluorinated polymers is being investigated in our laboratories.

CRedit authorship contribution statement

Hisao Hori: Conceptualization, Investigation, Project administration, Supervision, Validation, Writing – original draft. **Hisashi Saito:** Investigation, Validation. **Abdelatif Manseri:**

Writing – review & editing. **Bruno Ameduri**: Conceptualization, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

The raw/processed data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.eurpolymj>.

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Table 1

Products from reactions of FEP in supercritical water (384 °C) in the presence of O₂ or H₂O₂^a

Entry	Oxidizing agent	Initial amount of oxidizing agent (mmol)	Reaction time (h)	Reaction pressure (MPa)	F ⁻ (μmol) [yield (%)]	CO ₂ (μmol) [yield (%)]	CHF ₃ (μmol)
1	none	none	6	24.7	118 [10]	40.8 [7]	1.7
2	O ₂	26.8	6	25.2	367 [31]	182 [30]	0.7
3	O ₂	26.8	24	25.4	904 [75]	385 [64]	0.1
4	H ₂ O ₂	60.0 ^b	6	26.5	429 [36]	212 [35]	0.6

^a Charged FEP, 30.0 mg; amount of fluorine atoms, 1.20 mmol; amount of carbon atoms, 0.60 mmol.^b Concentration, 2.0 M (60.0 mmol in 30 mL).

Table 2

Products generated from reactions of FEP and PTFE in subcritical water in the presence of KOH^a

Entry	(Co)polymer	Initial [KOH] (M)	Reaction time (h)	Reaction temperature (°C)	Reaction pressure (MPa)	F ⁻ (μmol) [yield (%)]	TOC (μmol) [ratio (%)]	CO ₂ (μmol) [yield (%)]
1	FEP	none	6	350	16.5	4.9 [0]	8.9 [1]	11.6 [2]
2	FEP	3.0	6	350	16.8	325 [27]	159 [27]	0.3 [0]
3	FEP	3.0	6	360	18.2	506±24 ^b [42±2]	139±34 ^b [23±6]	0.3±0.1 ^b [0]
4	FEP	3.0	18	360	19.6	1170 [98]	98.1 [16]	0.8 [0]
5	PTFE	3.0	18	360	17.9	253 [21]	— ^c	0.6 [0]

^a Charged (co)polymer, 30.0 mg; ^b Obtained from two replicate experiments under the same reaction conditions; ^c not measured.

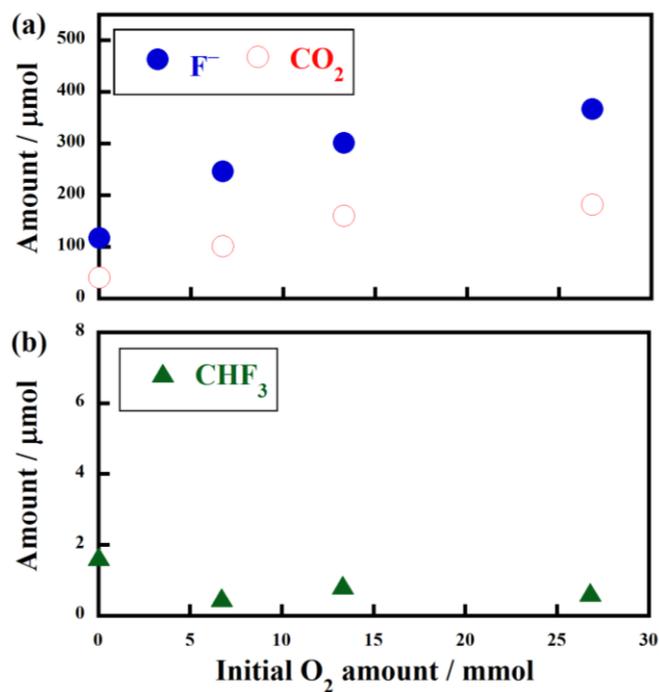


Fig. 1. Effect of initial O₂ amount on: (a) the F⁻ amount in the reaction solution and CO₂ amount in the gas phase and (b) the CHF₃ amount in the gas phase. FEP (30.0 mg; fluorine content, 1.20 mmol; carbon content, 0.60 mmol) was heated with O₂ in supercritical water at 384 °C for 6 h.

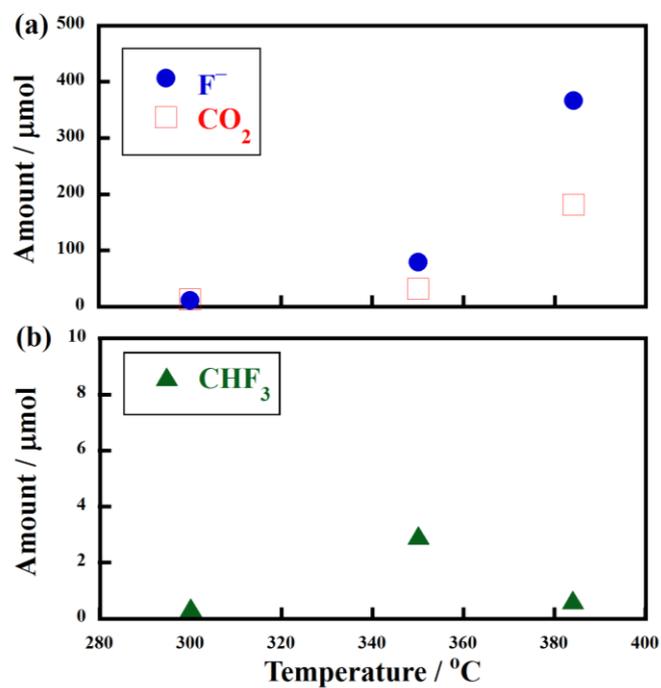


Fig. 2. Temperature dependences of FEP decomposition in the presence of O₂: the amounts of (a) F⁻ in the reaction solution and CO₂ in the gas phase and (b) CHF₃ in the gas phase. FEP (30.0 mg) was heated with O₂ (26.8 mmol) in subcritical or supercritical water for 6 h.

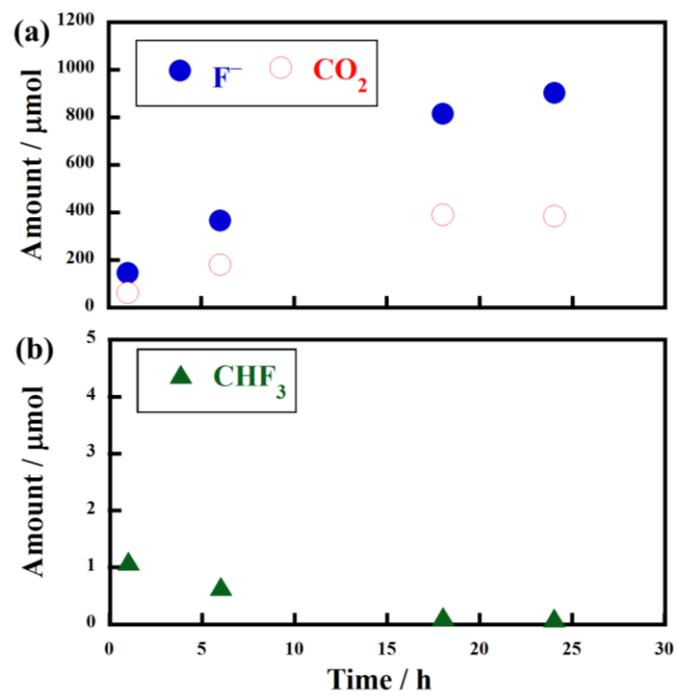


Fig. 3. Reaction-time dependences of the amounts of (a) F^- in the reaction solution and CO_2 in the gas phase and (b) CHF_3 in the gas phase. FEP (30.0 mg) was heated with O_2 (26.8 mmol) in supercritical water at 384 °C.

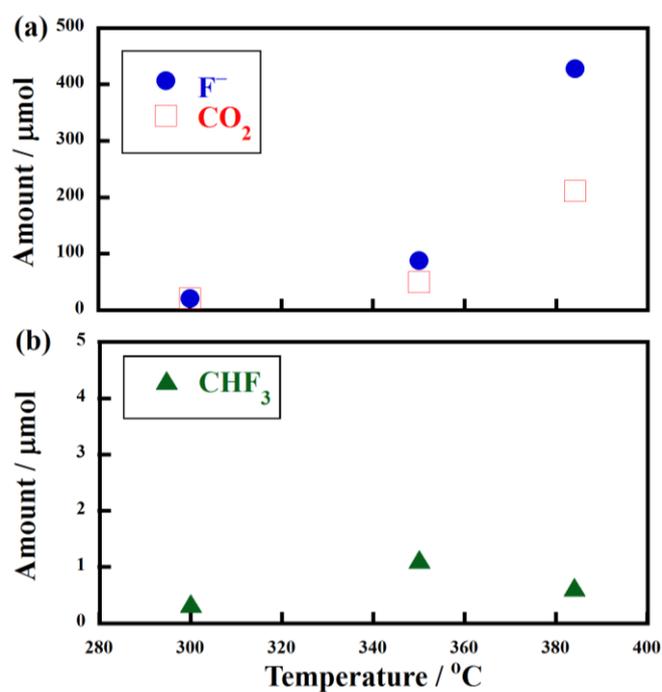


Fig. 4. Temperature dependences of FEP decomposition in the presence of H_2O_2 : the amounts of (a) F^- in the reaction solution and CO_2 in the gas phase and (b) CHF_3 in the gas phase. FEP (30.0 mg) was heated with 2.0 M of initial $[H_2O_2]$; 60 mmol in 30 mL) in subcritical or supercritical water for 6 h.

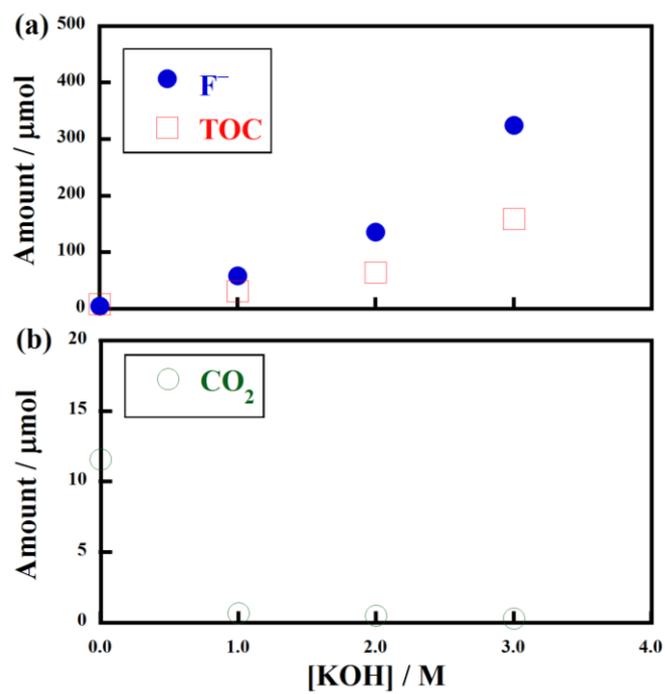


Fig. 5. Effect of initial [KOH] on (a) the F⁻ and TOC amounts in the reaction solution and (b) CO₂ amount in the gas phase. FEP (30.0 mg) was heated with KOH in subcritical water at 350 °C for 6 h.

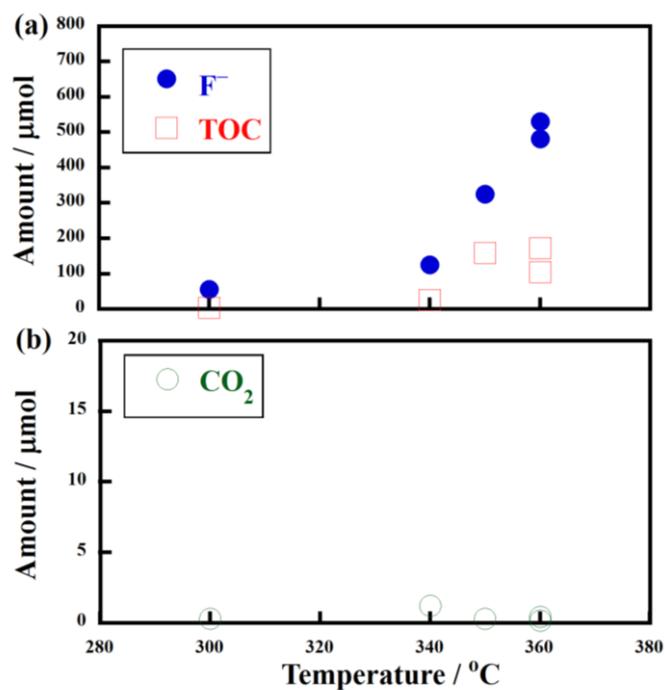


Fig. 6. Temperature dependences of FEP decomposition in the presence of KOH: (a) the F⁻ and TOC amounts in the reaction solution and (b) CO₂ amount in the gas phase. FEP (30.0 mg) was heated with 3.0 M of initial [KOH] in subcritical water for 6 h. For 360 °C, two replicate experiments were performed.

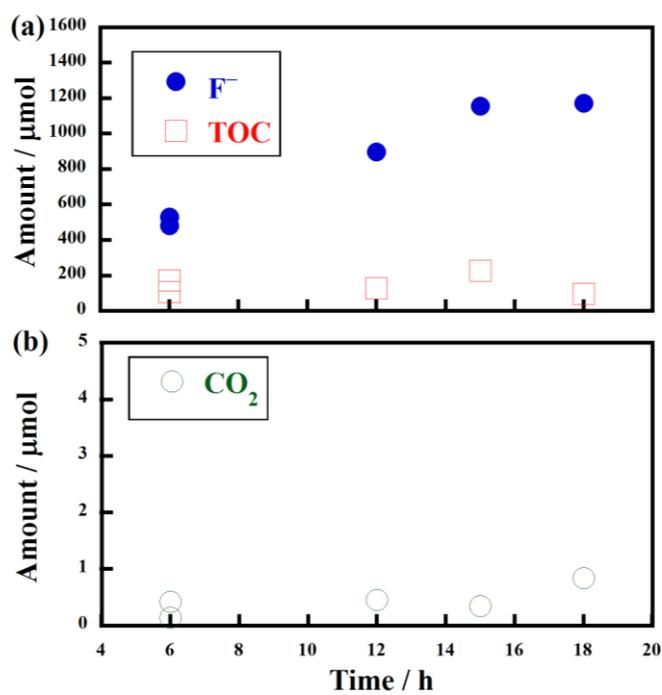


Fig. 7. Reaction-time dependences of the amounts of (a) F^- and TOC in the reaction solution and (b) CO_2 in the gas phase. FEP (30.0 mg) was heated with 3.0 M of initial [KOH] in subcritical water at 360 °C for 6–18 h. For 6 h, two replicate experiments were performed.

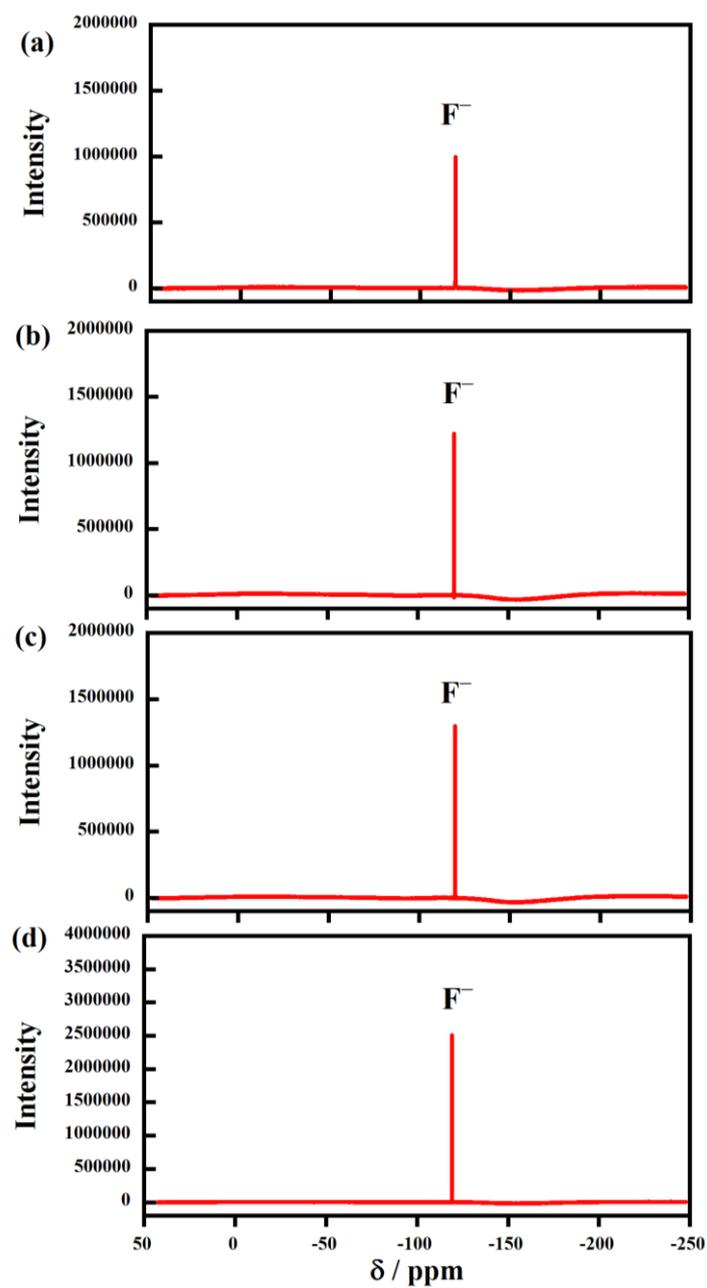


Fig. 8. ^{19}F -NMR spectra of the resulting reaction solutions from subcritical water treatment with 3.0 M of initial $[\text{KOH}]$ at 360 $^{\circ}\text{C}$ for (a) 6 h, (b) 12 h, (c) 15 h, and (d) 18 h.

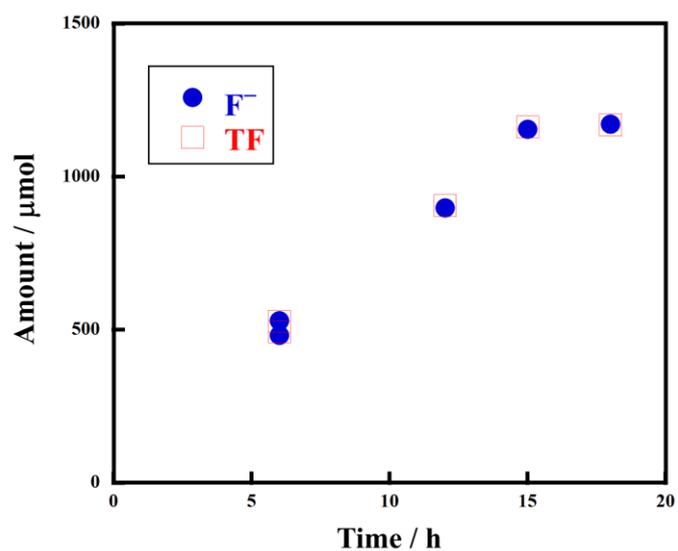


Fig. 9. Reaction-time dependences of the amounts of F^- and TF in the reaction solution. FEP (30.0 mg) was heated with 3.0 M of initial [KOH] in subcritical water at 360 °C for 6–18 h. For 6 h, two replicate experiments were performed.

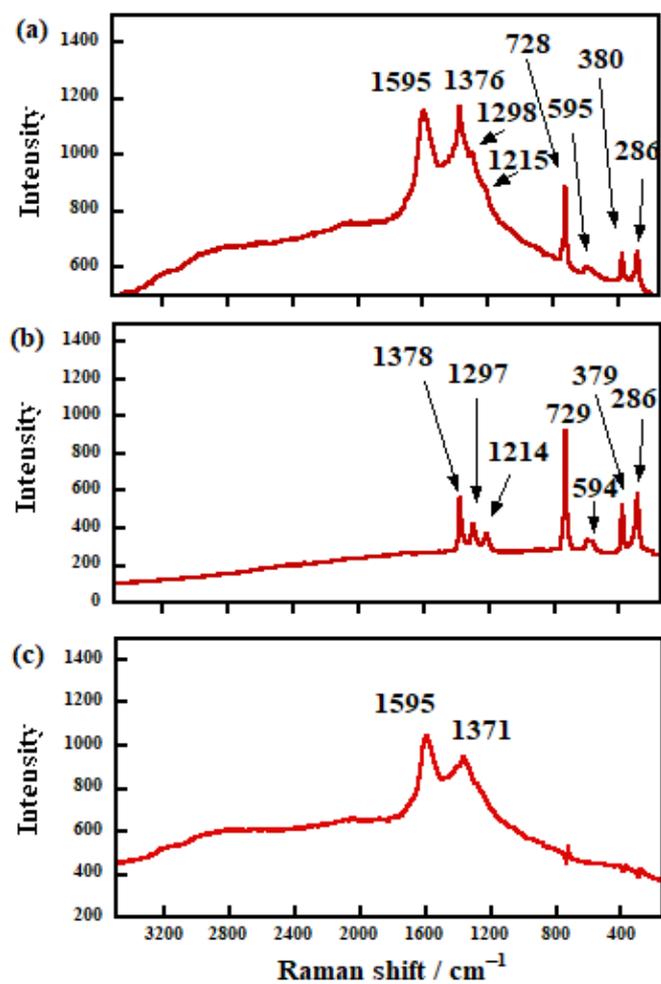


Fig. 10. Raman spectra of (a) the residue generated from reaction with 3.0 M of [KOH] at 360 °C for 6 h, (b) virgin FEP, and (c) the spectrum after subtracting the intensity due to FEP from (a).