Thermal degradation of fluoropolymers

Fluoropolymers break down via thermal decomposition to a number of different fluorinated degradation products, including carboxylic acids.

Ellis, et al. 2001. David A. Ellis*, Scott A. Mabury*, Jonathan W. Martin, Derek C. G. Muir, **Thermolysis of Fluoropolymers as a potential source of halogenated organic acids in the environment**, Letters to Nature , p. 321 Vol 412, 19July2001. Access at: https://www.nature.com/articles/35085548.pdf

> "Here we report that thermolysis of fluorinated polymers, such as the commercial polymers Teflon and Kel-F, can also produce trifluoroacetate and the similar compound chlorodifluoroacetate. This can occur either directly or indirectly via products that are known to degrade to the haloacetates in the atmosphere"
> "Thermolysis also leads to longer chain polyfluoro- and/or polychlorofluoro- (C3-C14) carboxylic acids which may be equally persistent."
> "Furthermore, we detected CFCs and fluorocarbons – groups that can destroy ozone and act as greenhouse gases, respectively – among the other thermal degradation products suggesting that continued use of fluoropolymers may also exacerbate stratospheric ozone –depletion and global warming."
> "Fluoropolymers are also incorporated into commercial products that may be exposed to high temperatures (such as the Teflonized engine additive Slick 50, teflonized frying pans and surgical syringes). By heating these commercial products, we found that the incorporated fluoropolymers decomposed in such a way as to produce the same products as the pure polymers, that is, TFA and/or CDFA along with numerous other perhalogenated acids."

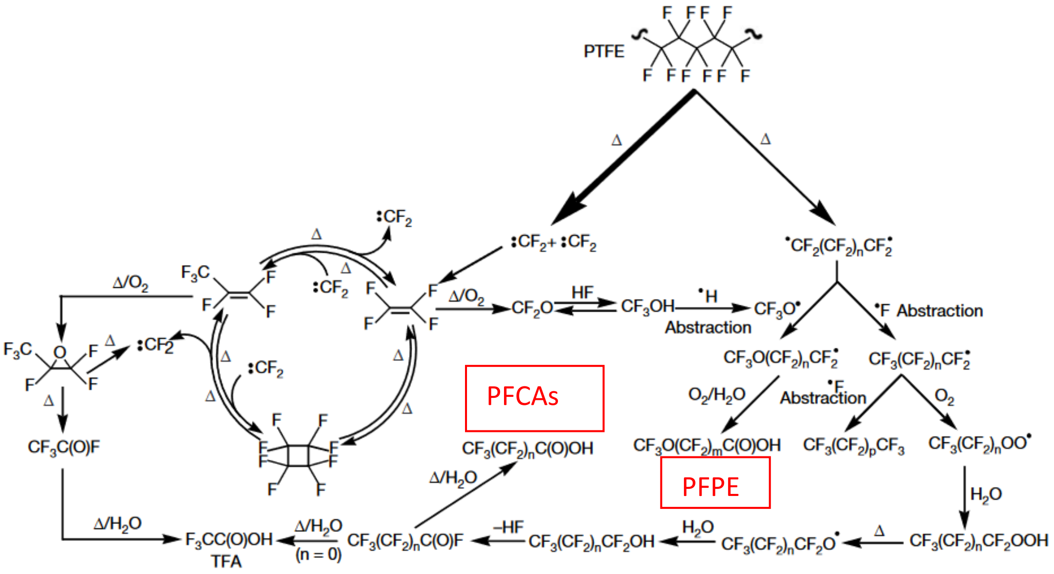

Figure 1 Proposed significant pathways in the thermal decomposition of fluoropolymers. The explicit major pathways for the production of TFA (trifluoroacetate) are shown. Evidence for the mechanism was obtained from this work and from previous observations[19,20,25,28,29]. As indicated by the bold arrow, the most significant step in the thermal decomposition is the formation of carbene radicals. Longer-chain diradicals are also formed, which can undergo fluorine abstraction or reaction with carbonyl fluoride to produce radical fluorinated alkanes ($p = 0$–4) or ethers. These radicals then react with constituents present in the air, oxygen and trace amounts of water, to form perfluorinated acids ($n = 0$–12, $m = 1$–7), the yield being inversely proportional to the number of carbon atoms in the chain. The distribution of product yield depends on temperature and the composition of the atmosphere. PTFE, polytetrafluoroethylene; Δ, heat.

Ref: Ellis, Mabury, Martin, Muir, 2001. Letters to Nature, Thermolysis of fuoropolymers as a potential source of halogenated organic acids in the environment, Nature, Vol 412, p 321.

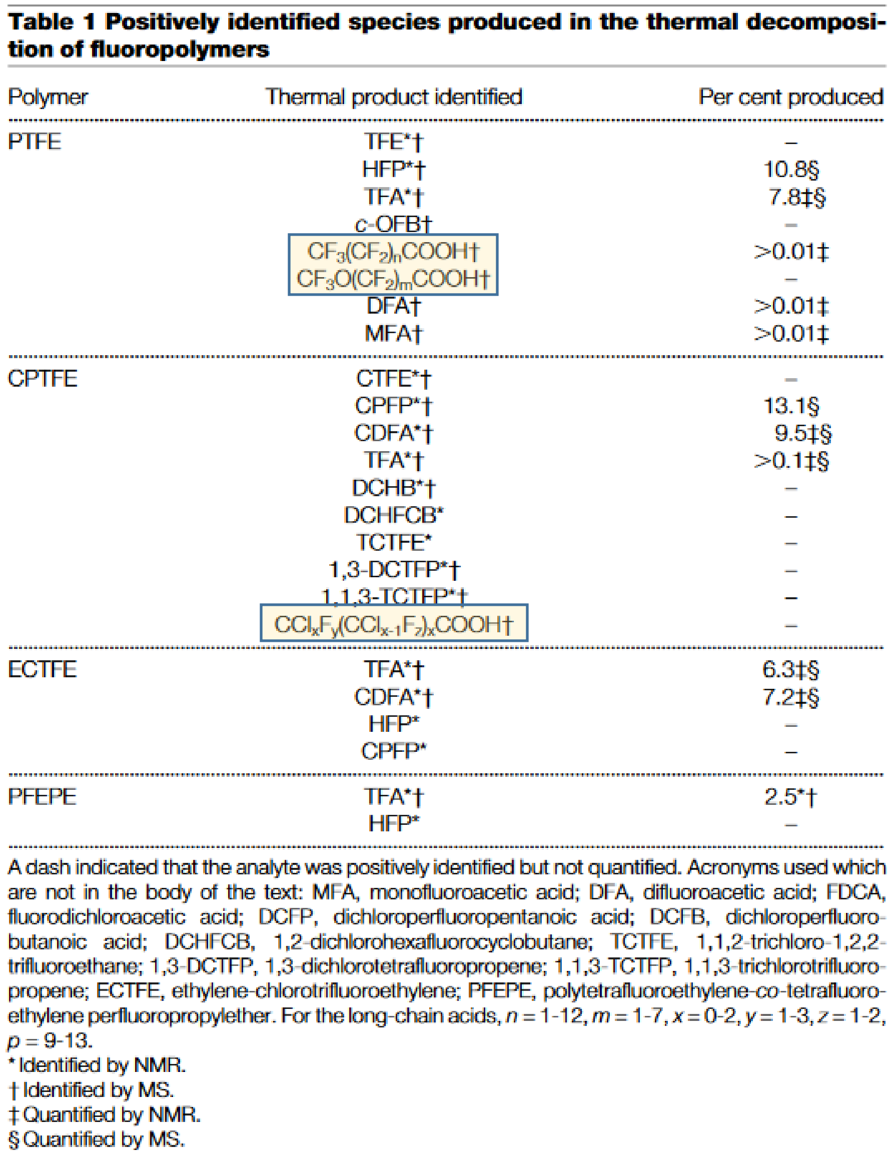

Table 1 Positively identified species produced in the thermal decomposition of fluoropolymers

Polymer	Thermal product identified	Per cent produced
PTFE	TFE*†	–
	HFP*†	10.8§
	TFA*†	7.8‡§
	c-OFB†	–
	$CF_3(CF_2)_nCOOH$†	>0.01‡
	$CF_3O(CF_2)_mCOOH$†	–
	DFA†	>0.01‡
	MFA†	>0.01‡
CPTFE	CTFE*†	–
	CPFP*†	13.1§
	CDFA*†	9.5‡§
	TFA*†	>0.1‡§
	DCHB*†	–
	DCHFCB*	–
	TCTFE*	–
	1,3-DCTFP*†	–
	1,1,3-TCTFP*†	–
	$CCl_xF_y(CCl_{x-1}F_z)_xCOOH$†	–
ECTFE	TFA*†	6.3‡§
	CDFA*†	7.2‡§
	HFP*	–
	CPFP*	–
PFEPE	TFA*†	2.5*†
	HFP*	–

A dash indicated that the analyte was positively identified but not quantified. Acronyms used which are not in the body of the text: MFA, monofluoroacetic acid; DFA, difluoroacetic acid; FDCA, fluorodichloroacetic acid; DCFP, dichloroperfluoropentanoic acid; DCFB, dichloroperfluorobutanoic acid; DCHFCB, 1,2-dichlorohexafluorocyclobutane; TCTFE, 1,1,2-trichloro-1,2,2-trifluoroethane; 1,3-DCTFP, 1,3-dichlorotetrafluoropropene; 1,1,3-TCTFP, 1,1,3-trichlorotrifluoropropene; ECTFE, ethylene-chlorotrifluoroethylene; PFEPE, polytetrafluoroethylene-*co*-tetrafluoroethylene perfluoropropylether. For the long-chain acids, $n = 1\text{-}12$, $m = 1\text{-}7$, $x = 0\text{-}2$, $y = 1\text{-}3$, $z = 1\text{-}2$, $p = 9\text{-}13$.

* Identified by NMR.

† Identified by MS.

‡ Quantified by NMR.

§ Quantified by MS.

Ref: Ellis, Mabury, Martin, Muir, 2001. Letters to Nature, Thermolysis of fuoropolymers as a potential source of halogenated organic acids in the environment, Nature, Vol 412, p 321. [With carboxylic acids highlighted]

Fluoropolymers can break down via thermal decomposition during processing, depending on the temperature and other conditions. Potential decomposition products include carboxylic acids.

Excerpts from: *Guide to safe handling of fluoropolymer resins* 5th ed. Society of the Plastics Industry BP-101; 2005

https://intechservices.com/content/SPI_Guide_for_Safe_Handling_of_Fluoropolymer_Resins.pdf

Health Effects of Decomposition products (p. 14-15)
"The type of decomposition product depends on the conditions under which heating occurs. Temperature, availability of oxygen, the physical form of the article, and the residence time at elevated temperatures are among the factors that determine the ultimate nature of the decomposition products. The four main types of products formed in the decomposition of fluoropolymers are fluoroalkenes, hydrogen fluoride, oxidation products, and low-molecular-weight fluoropolymer particulates. The presence of other monomers or additives in the fluoropolymer resin may change the nature of the decomposition products."

"For PTFE, NIOSH suggests in 1977 criteria document that the TFE [tetrafluoroethylene] monomer is the principle gaseous product at temps that just produce softening or melting (e.g. 625F or 330C). It may be residual monomer that is trapped in resin, or evolved as the resin structure changes. As temperature increases to 840F/450C in air, carbonyl fluoride and HF are main decomposition products. Carbonyl fluoride hydrolyzes rapidly in moist air to HF and CO2.
Small amounts of hexafluoropropylene may also be found; at 890F/475C perfluoroisobutylene has been detected as minor product. At 1470F/800C tetrafluoromethane begins to form."

Polymer Fume Fever (p. 15)
"The most common adverse effect associated with human exposure to fluoropolymer decomposition products is widely recognized as "polymer fume fever" (PFF)…. Johnston et al, found that overheating PTFE, 778°F (420°C), evolves fumes containing (excessive fluid in cells in the lungs) with hemorrhagic inflammation (severe irritation of the tissue with release of blood from small blood vessels)."

Other byproducts (p. 15)
Depending upon the type of fluoropolymer and finished product manufacturing conditions, it is theoretically possible that small quantities of residual gases, including perfluoroisobutylene (PFIB), hexafluoropropylene (HFP), tetrafluoroethylene (TFE), and hydrogen fluoride (HF) may be trapped and slowly evolve from resins as well as finished products. Testing of some finished products has confirmed that PFIB and HFP can be found in the finished products, but the conditions under which these compounds form, and in what quantities, has not been investigated. This emphasizes the importance of following manufacturer instructions in sintering and other finishing operations. These residual gases can accumulate in unventilated spaces (e.g., closed storage rooms, closed trucks, etc.) at levels that may be hazardous if the quantities of fluoropolymer materials and products stored are large. Therefore, it is important to ventilate these spaces before permitting personnel to enter."

Notes: TFE: reasonably anticipated to be a human carcinogen (11th RoC) and
PFIB: severe adverse effects pulmonary edema, ACGIH TLV-Ceiling = 0.01 ppm

Processing Hazards and Precautions (p. 19)

Heating fluoropolymers like PTFE to their melting point temperatures causes the polymer particles to melt and fuse together, eliminating voids that may result in weak points or flaws in the polymer structure. This process is termed heat treating, sintering or "coalescence" when applied to PTFE processing and is similar to the sintering process utilized in metallurgy…. Because of the high temperatures required to sinter PTFE and melt other fluoropolymers, hazardous decomposition products form in processing ovens. Regardless of their design (batch, conveyor, chain-on-edge), ovens used to process or heat-treat fluoropolymers must have mechanical (forced) ventilation with sufficient airflow to remove hazardous compounds from them during their operation and to keep them from entering the work area.

Additional References for Thermal Breakdown

Arito, et al 1977. Pyrolysis products of polytetrafluoroethylene and polyfluoroethylenepropylene with reference to inhalation toxicity, Am Occup Hyg Vol 20 pp 247-255.

> "Analysis of pyrolysis products of polytetrafluoroethylene (PTFE) and polyfluoroethylenepropylene (PFEP) and the influence of pyrolysis conditions on the pyrolysis products were investigated to evaluate the inhalation toxicity of those pyrolysis products. Both polymers were pyrolysed at various temperatures in a flow of nitrogen and air, either dry or humid. The pyrolysis products were analysed by infrared spcctrometry and combined gas chromatographymass spectrometry. In pyrolysis of both polymers in a nitrogen stream, octofluoroisobutylene was identified in addition to the main products such as tctrafluoroethylene, hexafluoropropylene and octofluorocyclobutane. The main pyrolysis products of both polymers in an air stream were carbonyl fluoride and trifluoroacetyl fluoride. Tetrafluoroethylene and hexafluoropropylene were far less in quantity but octofluoroisobutylene was found only with PFEP. Perfluoroalkanes were produced by oxidative pyrolysis of PTFE at high temperature. Effect of water vapour in the gas flow on the product formation was significant only in oxidative pyrolysis. In the presence of water vapour, carbonyl fluoride was converted into hydrogen fluoride and carbon dioxide, while trifluoroacetyl fluoride was converted to trifluoroacctic acid and hydrogen fluoride."

Feng, et al 2015. Characterization of the thermolysis products of Nafion membrane: A potential source of perfluorinated compounds in the environment, Scientific Reports, 5:9859. DOI: 10.1038/srep09859.

> "The thermal decomposition of Nafion N117 membrane, a typical perfluorosulfonic acid membrane that is widely used in various chemical technologies, was investigated in this study….Notably, several types of perfluorinated compounds (PFCs) including perfluorocarboxylic acids were detected and identified. Based on these data, a thermolysis mechanism was proposed involving cleavage of both the polymer backbone and its side chains by attack of radical species."