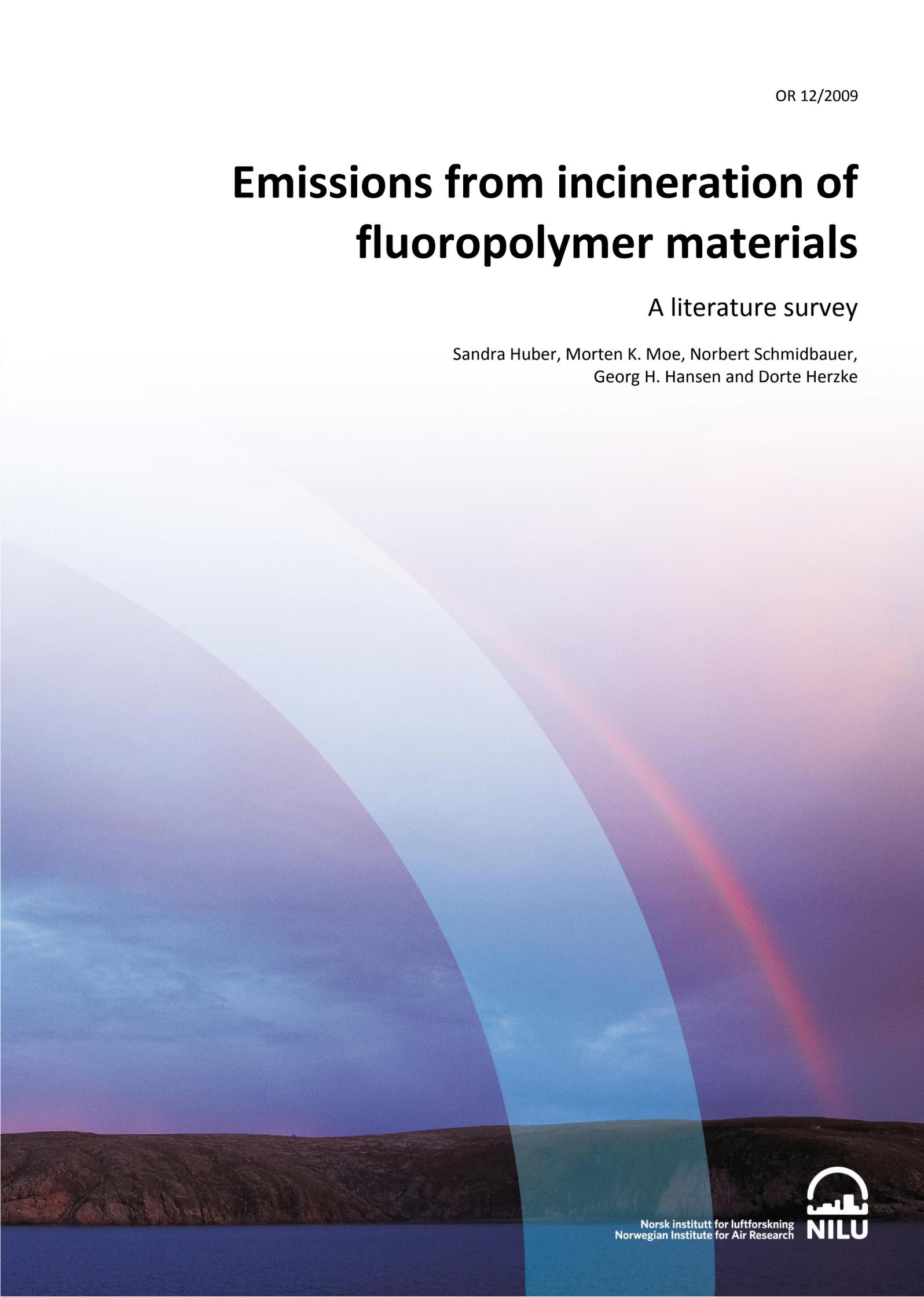


# Emissions from incineration of fluoropolymer materials

A literature survey

Sandra Huber, Morten K. Moe, Norbert Schmidbauer,  
Georg H. Hansen and Dorte Herzke





# **Emissions from incineration of fluoropolymer materials**

A literature survey

Sandra Huber, Morten K. Moe, Norbert Schmidbauer,  
Georg H. Hansen and Dorte Herzke



# Contents

	Page
<b>Table of content</b>	
<b>Contents.....</b>	<b>1</b>
<b>1 Summary .....</b>	<b>3</b>
<b>2 Abbreviations.....</b>	<b>5</b>
<b>3 Background and purpose.....</b>	<b>7</b>
<b>4 Types of fluoropolymers .....</b>	<b>9</b>
4.1 Perfluorinated polymers .....	9
4.2 Partially fluorinated polymers .....	10
4.3 Fluoroelastomers .....	11
4.4 Other fluorine containing polymers .....	12
4.4.1 Fluorinated Polyurethans .....	12
4.4.2 Hexafluoroisopropylidene-containing polymers .....	13
4.4.3 Polyfluoroacrylates and -methacrylates .....	13
4.4.4 Perfluoropolyethers .....	13
4.4.5 Perfluorinated ionomers .....	14
<b>5 Production and consumption of fluoropolymers .....</b>	<b>14</b>
5.1 Consumption of fluoropolymers .....	15
5.2 Consumption of fluoroelastomers .....	17
5.3 Future perspectives.....	18
<b>6 Thermal degradation of fluoropolymer materials .....</b>	<b>19</b>
6.1 Properties and stability of fluoropolymers .....	19
6.2 Thermal degradation experiments with fluoropolymers .....	24
<b>7 Greenhouse potential of fluoropolymer combustion products .....</b>	<b>31</b>
7.1 Thermal degradation products of fluoropolymers.....	31
7.2 Possible contribution of incineration of fluoropolymers to global warming.....	34
<b>8 Conclusions and evaluation of the need for further studies .....</b>	<b>36</b>
8.1 Recommendation on future investigations.....	36
<b>9 References .....</b>	<b>38</b>
<b>Appendix 1 : Review of the SFT report on PTFE .....</b>	<b>43</b>
<b>Appendix 2; List of Fluoropolymers.....</b>	<b>49</b>
<b>Appendix 3: List of intermediates produced by Daikin (Daikin     Industries, 2008). .....</b>	<b>55</b>



## 1 Summary

This report consists of two parts. (1) An overview of existing commercially available fluoro-polymer materials and their properties, application area, production and consumption levels is given, and (2) a review of the existing scientific literature on the possible formation of greenhouse gases upon fluoro-polymer incineration and the potential greenhouse effects.

Fluoropolymers are special plastics that are used in a great variety of applications because of their unique properties. They are used in e.g. cable coating, coated cookware, sports and extreme weather clothing, food handling and medical equipment. In 2004, the global consumption of fluoropolymers reached almost 133 000 tons.

Polytetrafluoroethylene (PTFE) is worldwide the most produced and consumed fluoro-polymer followed by polyvinylfluoride (PVF) and a co-polymer of tetrafluoroethylene and hexafluoropropylene (PVDF and FEP). Therefore, it is assumed that these also are the major fluoropolymers to end up in municipal waste incinerators, with minor contributions from a multitude of other recently introduced fluoro-polymers and -elastomers.

The literature survey was conducted by using comprehensive and widely appreciated search engines such as SciFinder, ISI Web of Knowledge, and PubMed, along with specialized technical books on fluoropolymers. Furthermore, homepages of fluoropolymer companies were scrutinized on their product range and applications. The report "Assessment of information assessable on Teflon and degradation products of Teflon (CAS 9002-84-0)" was reviewed and updated on missing and new literature (Tobiesen, 2005).

A considerable amount of scientific literature was found on the thermal stability and decomposition products of PTFE for temperatures between 400 and 600°C, the temperature range where PTFE and most other fluoro-polymers start to degrade. The main degradation products were found to be fluoroalkanes and alkenes, hydrogen fluoride, oxidation products (epoxides, aldehydes and acids), and fluoro-polymer particulates in this temperature range.

However, municipal waste incineration is carried out at about 850°C, and to our best knowledge, any emissions of fluoro-polymer degradation products from household waste incineration have not been monitored yet. On the laboratory scale the degradation of fluoro-polymers, primarily PTFE, has been investigated in the temperature range 700-1050°C, yielding CF<sub>4</sub> (PFC-14), CHF<sub>3</sub> (HFC-23), C<sub>2</sub>F<sub>6</sub> (PFC-116), tetrafluoroethene (TFE) and hexafluoropropene (HFP) as major products. The kind of compounds formed is strongly dependent on the incineration conditions like temperature, moisture, oxygen content, use of catalysts etc. Few studies have been published on the incineration degradation products of other fluoropolymers than PTFE.

The most potent greenhouse gases formed by fluoropolymer incineration are compounds containing C-F bonds, which absorb electromagnetic radiation in the

1000-1400  $\text{cm}^{-1}$  range where the atmosphere is rather transparent. Perfluoropolymers will therefore presumably produce the most efficient greenhouse gases upon incineration.

Incineration of fluoropolymer containing products has a great potential to contribute considerably to the total greenhouse gas emissions of Norway, but due to the lack of sound data on the fate of fluoropolymers in Norway as well as of the chemical reactions in the different types of MWI plants in Norway, no exact amounts can be given at this stage. On-site investigations for revealing a realistic impression on the compounds formed in Norwegian municipal incinerators are necessary in order to assess the extent and the composition of the organofluorine emissions. In addition, a quantitative life cycle assessment for the imported PTFE and other fluoropolymers should be conducted to fill knowledge gaps about the fate of fluoropolymers in Norway.

The scientists Dr. Sandra Huber, Dr. Morten K. Moe, Dr. Norbert Schmidbauer, Dr. Georg H. Hansen and Dr. Dorte Herzke contributed to the report.

## 2 Abbreviations

1,1,3-TCTFP	1,1,3-TriChloroTriFluoroPropene
1,3-DCTFP	1,3DiChloroTetraFluoroPropene
6F	Hexafluoroisopropylidene
BMA	Butyl methacrylate
CDFA	ChloroDiFluoroAcetic acid
CFC	ChloroFluoroCarbon
<i>c</i> -OFB	OctaFluoro <i>cyclo</i> -Butane
CPFP	ChloroPentaFluorPropene
CPTFE	ChloroPolyTriFluoroEthylene
CTFE	chlorotrifluoroethylene
CTFE	ChloroTriFluoroEthylene
DCFA	DiChloroFluoroAcetic acid
DCHB	1,2-DiChloroHexafluorocycloButane
DFA	DiFluoroAcetic acid
E	Ethylene
ECTFE	co-polymer of ethylene (E) and ChloroTriFluoroEthylene (CTFE)
EFEP	co-polymer of ethylene (E), tetrafluoroethylene (TFE) and hexafluoropropylene (HFP)
EHA	Ethylhexyl acrylate
ETFE	co-polymer of Ethylene (E) and TetraFluoroEthylene (TFE), ethylene tetrafluoroethylene
EVE	Esther Vinyl Ether
FDD	FluoroDibenzoDioxine
FDF	FluoroDibenzoFuran
FEP	co-polymer of tetrafluoroethylene (TFE) and hexafluoropropylene (HFP)
GC-MS	Gas Chromatography Mass Spectrometry
GWP	Global Warming Potential
HCFC	HydroChloroFluoroCarbon
HFC	HydroFluoroCarbon
HFIB	HexaFluoroIsoButylene
HFIBO	HexaFluoroIsoButylene Oxide
HFIFA	1,1,1,3,3,3-hexafluoroisopropyl $\alpha$ -fluoroacetate
HFIMA	1,1,1,3,3,3-hexafluoroisopropyl methacrylate
HFP	HexaFluoroPropylene
HFPO	HexaFluoroPropylene Oxide
HPFP	1-HydroPentaFluoroPropene
HTE	co-polymer of Hexafluoropropylene (HFP), Tetrafluoroethylene (TFE) and Ethylene
IPCC	Inter-governmental Panel on Climate Change
MA	Methyl acrylate
MFA	MonoFluoroAcetic acid
MFA	co-polymer of tetrafluoroethylene (TFA) and perfluoromethylvinylether (PMVE)
MTFA	MethylTriFluoroAcrylate
MW	Molecular Weight
MWI	Municipal Waste Incinerator

NIOSH	National Institute for Occupational Safety and Health
NMR	Nuclear Magnetic Resonance
P	Propene
PAVE	PerfluoroAlkyl VinylEther
PCTFE	Poly ChloroTriFluoroEthylene
PDMS	PolyDiMethylSiloxane
PEVE	PerfluoroEthyl VinylEther
PFA	PerFluoroAlkan
PFA	PerFluoroAlkoxy; co-polymer of tetrafluoroethylene (TFE) and perfluoropropyl vinyl ether (PPVE)
PFA7	Poly-2,2'3,3',4,4',5,5',6,6',7,7',7"-tridecafluoroheptylacrylate
PFMA7	Poly-2,2'3,3',4,4',5,5',6,6',7,7',7"-tridecafluoroheptylmethacrylate
PFBE	PerFluoroButylEthylene
PFCA	PerFluoroCarboxylic Acid
PFEPE	co-polymer of polytetrafluoroethylene (PTFE) and tetrafluoroethylene perfluoropropylether
PFIB	PerFluoroIsoButene
PFOA	PerFluoroOctanoic Acid
PFPE	PerFluoroPolyEther
PHFIFA	Poly(1,1,1,3,3,3-hexafluoroisopropyl $\alpha$ -fluoroacetate)
PHFIMA	Poly(1,1,1,3,3,3-hexafluoroisopropyl methacrylate)
PMNFHS	PolyMethylNonaFluoroHexylSiloxane
PMTFPS	PolyMethylTriFluoroPropylSiloxane
PMVE	PerfluoroMethylVinylEther
PPVE	PerfluoroPropyl VinylEther
PSEPVE	Perfluoro-2-(2-fluoroSulfonylEthoxy) PropylVinylEther
PTFE	PolyTetraFluoroEthylene
PTFEMA	Poly(2,2,2-trifluoroethyl methacrylate)
PVDF	Poly Vinylidene Fluoride
PVF	PolyVinyl Fluoride
RF	Radiative Forcing
SAR	Second Assessment Report
SFT	Norwegian Pollution Control Authority
SSB	Statistics Norway
TAR	Third Assessment Report
TCTFE	1,1,2-TriChloro-1,2,2-TriFluoroEthane
TFA	TriFluoroAcetic acid
TFE	TetraFluoroEthylene
TFEMA	2,2,2-trifluoroethyl methacrylate
TFEO	TetraFluoroEthylene Oxide
TFE-P	co-polymer of TetraFluoroEthylene (TFE) and Propylene
TFMAA	$\alpha$ -(TriFluoroMethyl) Acrylic Acid
TFP	3,3,3-TriFluoroPropylene
TH	Time Horizon
THV	terpolymer of Tetrafluoroethylene (TFE), Hexafluoropropylene (HFP) and Vinylidene Fluoride (VF <sub>2</sub> /VDF)

VDF, VF <sub>2</sub>	Vinylidene Fluoride (1,1-difluoroethylene)
VOC	Volatile Organic Compound
XFDA	Poly(1H,1H,2H,2H-perfluorodecyl acrylate)
XFDMA	Poly(1H,1H,2H,2H-perfluorodecyl methacrylate)

### 3 Background and purpose

Fluoropolymers are crucial parts of our daily lives, often in invisible ways. They are special plastics being chemically inert, non-wetting, very slippery, nonstick, highly fire resistant, high temperature resistant, highly weather resistant and regarded as nontoxic. Fluoropolymers are used in a multitude of ways as in cookware and food handling (e.g. bakeries), sports and extreme weather military clothing, medical equipment, silicon chip and pharmaceutical manufacturing, motor oil additives, house and car air conditioning, and wiring to laptop computers, cell phones, aircrafts, fire alarms and data communications, under-hood in cars and down-hole oil wells, and high temperature filters for coal plants (Fluoropolymer Division, 2008).

In 2004, the global consumption of fluoropolymers reached almost 133 000 tons and exceeded a value of \$2.5 billion (Fluoropolymer Division, 2008). Will et al. announced in a marked report that the global trade of fluoropolymers reached about 60 000 tons, representing 46% of total consumption in 2005. Western Europe consumed 23 900 tons PTFE, 6 800 tons PVDF and 4 700 tons of other fluoropolymers in 2005 (Will et al., 2005).

In today's society large amounts of disposed products end up as waste. Incineration is one state of the art method for waste treatment, while landfill is still the most used. In 2006, 1 889 000 tons of waste were deposited in Norwegian landfills and 847 000 tons of waste (31% by mass) were incinerated (Table 1) (<http://www.ssb.no/avfhand/>).

Additionally, the total amount of waste produced in Norway has been increasing continuously. Paper (including coated paper and cardboard), plastic and textiles are the main waste types containing fluoropolymers and other fluorinated organic compounds, all of them increasing steadily (for more details see: <http://www.ssb.no/avfregno/>).

*Table 1 Waste amounts in Norway in 2006 in 1 000 tons:*

<b>Waste type (2006)</b>	<b>Paper</b>	<b>Plastics</b>	<b>Textiles</b>
Recycling	670	63	13
Biological treatment	-	-	-
Incineration	216	193	64
Landfill	147	123	44
Other treatment	199	91	0

According to the data given by SSB, 17.5% of paper, 41% of plastics and 53% of disposed textiles were incinerated in 2006 in Norway, summing up to 470 000 tons of potentially fluoropolymer containing waste.

With the upcoming ban of landfilling biological decomposable waste, an increasing part of products containing fluoropolymers like coated paper, will end up in municipal waste incineration (MWI) plants in the future ([http://www.sft.no/artikkel\\_\\_\\_43096.aspx?cid=10621](http://www.sft.no/artikkel___43096.aspx?cid=10621)). However, it is difficult to estimate an approximately amount of fluoropolymer content in domestic waste and the subsequent amount fluoropolymers incinerated. A quantitative life-cycle assessment on the imported fluoropolymers could provide a better estimate for this. Import and export of waste into and out of Norway occur as well, relying on waste treatment regulations in the target country. In order to estimate any global contributions of Norwegian waste incineration to global warming, the whole picture must be assessed.

During the combustion process the waste undergoes thermal degradation which results in more and/or less stable degradation products. The previous SFT report "Assessment of information assessable on Teflon and degradation products of Teflon (CAS 9002-84-0)" revealed that upon incineration of PTFE, carbonyl fluoride ( $\text{COF}_2$ ), trifluoroacetic acid (TFA), tetrafluoroethene (TFE), and hydrogen fluoride (HF) are emitted.  $\text{COF}_2$  is highly toxic and has an atmospheric half-time of approximately two weeks. HF is a strong inorganic corrosive which shows a high reactivity with other molecules in the atmosphere as well as a tendency for wet deposition and particle binding. In addition, other compounds such as perfluorinated carbons (PFC) can be produced by combustion of fluoropolymer materials; however, their magnitude and potential to contribute to global warming, are at present not thoroughly assessed.

The aim of this literature study was to:

1. Review the current state of knowledge on the emission and formation of greenhouse gases during combustion of fluoropolymer materials.
  - i. Critical review and update of SFT report "Miljøvurdering av miljøinformasjon vedrørende Teflon og nedbrytningsprodukter fra Teflon (Cas nr 9002-84-0)".
  - ii. Theoretical presentation of formation of greenhouse gases during combustion of other fluoropolymer materials which are in use besides PTFE.
  - iii. Conclusion of requirements for further experimental work regarding this study.
2. If 1.iii. shows that further work related to this study is necessary, a concept on how to perform controlled in-vitro experiments in the lab to test whether greenhouse gases are formed during combustion of fluoropolymer material will be presented. In addition, on-site air sampling in incineration treatment plants could be of interest. This concept will also include an approximate estimation of costs performing the suggested experiments.

## 4 Types of fluoropolymers

Fluoropolymers are produced and sold worldwide by several manufacturers and are essential to a variety of technologies and products. They are a versatile family of engineering materials, often exhibiting a broader range of applications compared to nonfluorinated substitutes. Fluoropolymers are among the few plastic materials that can withstand the temperatures inside ovens and the engine compartments of aircrafts. They have high resistance to a broad range of fuels, solvents and corrosive chemicals. These unique properties provide critical performance characteristics needed to prevent fire, fluid emission, electrical overloading or similar emergencies in many high performance applications. In addition, for virtually all of these applications, fluoropolymers are one of the very few materials that meet system performance needs in high temperature and harsh chemical environments (The Society of the Plastic Industry, 2005).

Major industries using/applying fluoropolymers and -elastomers are aerospace, military, automotive, transportation, chemical and petrochemical processing, semiconductor and electronics manufacturing, telecommunications, power generation, pollution control and consumer housewares (Fluoropolymer Division, 2008).

Among the fluoropolymer materials four groups can be distinguished: (i) perfluorinated polymers; (ii) partially (or poly-) fluorinated polymers; (iii) fluoroelastomers; and (iv) other fluorine containing polymers. All four groups will be described more closely in the chapters 4.1-4.4 below.

### 4.1 Perfluorinated polymers

The discovery of polytetrafluoroethylene (PTFE) in 1938 by Roy Plunkett of DuPont Company started the era of fluoropolymers. In 1950 DuPont commercialized PTFE as Teflon<sup>®</sup> (Figure 1). Since then a large number of other fluorine containing polymers have been developed, primarily in the last three decades. Some of them are derivatives of the original PTFE and some contain other elements, such as chlorine, silicon, or nitrogen, and represent a large group of materials with broad industrial applicability.

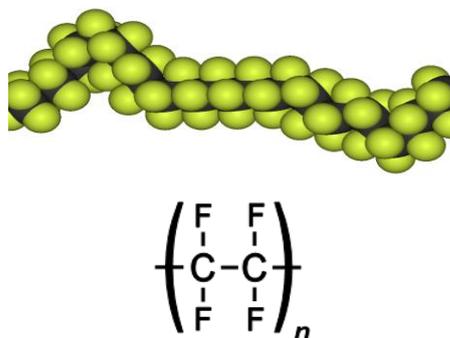


Figure 1: 3D model of a section of PTFE and structural formula of PTFE.

PTFE belongs to the group of perfluorinated polymers and is generally superior to other fluoropolymers with respect to properties and performances. PTFE is a polymer consisting of recurring tetrafluoroethylen (TFE) monomer units  $[\text{CF}_2\text{-CF}_2]_n$  (Figure 1). After heating, the virgin resin forms a clear, coalescable gel at  $330^\circ\text{C}\pm 15^\circ\text{C}$ . Once produced, the gel point (often referred to as the melting point) is  $10^\circ\text{C}$  lower than that of the virgin resin (Scheirs, 1997). PTFE is sold as a granular powder, a fine powder, or an aqueous dispersion. In addition, it can be blended with water or other solvents and sprayed on metals or fabric. Chemical pipelining, wire insulation, or fuel hose tubing are examples of end products made from melted polymer, while cookware or roofing material illustrates end uses of the dispersed product (The Society of the Plastic Industry, 2005).

Other perfluorinated polymers are:

*Perfluoroalkanes (PFA)* PFA resin is a polymer of TFE and a perfluorinated vinyl ether having the formula  $[(\text{CF}(\text{OR}_f)\text{-CF}_2)_x(\text{CF}_2\text{-CF}_2)_y]_n$  where  $\text{OR}_f$  represents a  $\text{C}_1\text{-C}_4$  perfluoroalkoxy group. PFA melts at  $\sim 300^\circ\text{C}$  and is melt processible. It is available in the form of pellets, powder, and as an aqueous dispersion (The Society of the Plastic Industry, 2005).

*MFA.* MFA is a copolymer of TFE and perfluoromethylvinylether (PMVE). MFA melts at  $280\text{-}290^\circ\text{C}$ . It is available in the form of translucent pellets and aqueous dispersions (The Society of the Plastic Industry, 2005).

## 4.2 Partially fluorinated polymers

Partly fluorinated polymers are:

*Ethylene- chlorotrifluoroethylene (ECTFE)* is a copolymer having the formula  $[(\text{CH}_2\text{-CH}_2)_x(\text{CFCl}\text{-CF}_2)_y]_n$ . ECTFE has a melting point range of  $220\text{-}245^\circ\text{C}$  and is melt processible. It is available in the form of translucent pellets and as a fine powder and is the most important chlorotrifluoroethylene (CTFE) copolymer (The Society of the Plastic Industry, 2005).

*Polychlorotrifluoroethylene (PCTFE)* is a polymer of CTFE with the formula  $(\text{CF}_2\text{-CFCl})_n$ . It has a melting point range of  $210\text{-}220^\circ\text{C}$  and is melt processible. It is available in pellet, granular and powder form (The Society of the Plastic Industry, 2005).

*Polyvinylidene fluoride (PVDF)* is a homopolymer of vinylidene fluoride ( $\text{VF}_2$ ) having the formula  $(\text{C}_2\text{H}_2\text{F}_2)_n$  or a copolymer of  $\text{VF}_2$  and hexafluoropropylene (HFP) having the formula  $[(\text{CF}(\text{CF}_3)\text{-CF}_2)_x(\text{C}_2\text{H}_2\text{F}_2)_y]_n$ . All are sold as PVDF copolymers. PVDF polymers/copolymers melt at  $90^\circ\text{-}178^\circ\text{C}$ , are melt processible, and are supplied in the form of powder, pellets, and dispersions (The Society of the Plastic Industry, 2005).

*Ethylene-tetrafluoroethylene (ETFE)* is a copolymer of ethylene and TFE having the formula  $[(\text{CF}_2\text{-CF}_2)_x(\text{CH}_2\text{-CH}_2)_y]_n$ . ETFE melts above  $220^\circ\text{C}$ . It is melt processible and is supplied in pellet and powder form (The Society of the Plastic Industry, 2005).

*Ethylene-tetrafluoroethylene-hexafluoropropylene (EFEP)* is a copolymer of ethylene, TFE and hexafluoropropylene (HFP) with the formula  $[(\text{CH}_2-\text{CH}_2)_x(\text{CF}_2-\text{CF}_2)_y(\text{CF}(\text{CF}_3)-\text{CF}_2)_z]_n$ . EFEP polymers melt at 155-200°C, it is melt processible and is supplied in pellet form (The Society of the Plastic Industry, 2005).

*Hexafluoropropylene, tetrafluoroethylene and ethylene copolymer (HTE)* is melt processible with melting points from 155-215°C depending on grade. It is available in pellets of agglomerate form (The Society of the Plastic Industry, 2005).

*The terpolymer of TFE, HFP and  $\text{VF}_2$  (THV)* has the formula  $[(\text{CF}_2-\text{CF}_2)_x(\text{CF}(\text{CF}_3)-\text{CF}_2)_y(\text{CH}_2-\text{CF}_2)_z]_n$ . THV is melt processible with melting points ranging from 115 to 180°C depending on its grade. It is available in pellet, agglomerate or as an aqueous dispersion (The Society of the Plastic Industry, 2005).

Melt-processible partially fluorinated copolymers, like FEP, PVDF/PVF, PFA/MFA, ETFE/ECTFE/PCTFE, or CTFE-VFD, represent a large share of the fluoropolymer market (Will et al., 2005). A major application is wire and cable insulation. Injection moldable products such as PFA or MFA are widely used in high-performance, high purity fluid handling systems, such as those used in making semiconductor chips.

### 4.3 Fluoroelastomers

The third major category of fluoropolymers is fluoroelastomers, like  $\text{VF}_2$ , hexafluoropropylene (HFP) or tetrafluoroethylene (TFE). Fluoroelastomers were introduced commercially in 1955. As the name implies, fluoroelastomers are synthetic rubber-like materials. Fluoroelastomers are fluorine-containing polymers known for their exceptional resistance to heat, weathering, a wide variety of fluids and chemicals as well as for their excellent sealing and other mechanical properties. They are used in special performance applications where extreme temperature ranges and chemical attack are encountered.

The main constraints on the use of fluoroelastomers are costs due to the relatively complex technology of processing. The products generally have fairly low-temperature flexibility and low elasticity. The solvent resistance of fluoroelastomers is generally high; however, certain organic liquids may cause considerable swelling. In addition, fluoroelastomers are very sensitive to moisture and require a strictly controlled processing environment, which makes the processing of fluoroelastomers difficult.

Common names and producers of some main commercially available fluoroelastomers are presented in Table 2. Names and producers of some common fluoroelastomers. Table 2 (Ameduri et al., 2001):

*Table 2. Names and producers of some common fluoroelastomers.*

<b>Fluoroelastomer</b>	<b>Producer</b>
Daiel® 801 and 901	Daikin
Fluorel®	3M/ Dyneon
Technoflon®	Ausimont
SKF®-26	Russia
Viton®A and B	DuPont

Fluorinated monomers, which are the starting material to prepare these polymers, can be divided in two classes: i) VF<sub>2</sub>-based fluorocarbon elastomers, and ii) TFE-based fluorocarbon elastomers (perfluoroelastomers).

The most commonly used perfluoroelastomer is perfluoromethylvinylether (PMVE) due to its favorable polymerization properties. Perfluoroelastomers are high-performance elastomers with exceptional chemical resistance properties and high-temperature stability (up to 300°C) and can be used for all applications where the properties of regular fluoroelastomers are not sufficient.

Viton A, a copolymer of VF<sub>2</sub> and HFP containing 68% fluorine, was originally introduced commercially to the market in 1958. Viton B, a terpolymer including TFE, containing 68% fluorine, was introduced shortly after Viton A and provided a significant improvement in heat and fluid resistance. Today, about 50 years after the introduction of the first commercial grade, there exist a wide range of copolymers and terpolymers with fluorine levels as high as 70%.

Perfluoroelastomers are used mainly in high performance O-rings. The major global producers of fluorocarbon elastomers are DuPont, Dyneon, Solvay Solexis and Daikin.

#### **4.4 Other fluorine containing polymers**

##### **4.4.1 Fluorinated Polyurethans**

Polyurethans are perhaps the most versatile polymers. Materials with a wide variety of physical and chemical properties can be formulated from the many commercially available and relatively inexpensive polyisocyanates and polyols. Introducing fluorine into polyurethane resins brings about changes in properties similar to those seen when other polymers are fluorinated. Chemical, thermal, hydrolytic, and oxidative stability are enhanced, and the polymer becomes more permeable to oxygen. Surfaces treated with fluorinated polyurethans are biocompatible.

Fluorourethans are widely used in modern chemical technology, like in products ranging from hard, heat-resistant electrical components to biologically compatible surgical adhesives. The most common use is in surface coatings for industrial and residential structures, automobiles, ships and aircraft. They are also widely used in medical products and as surface-enhancing treatments for leather, textiles and carpets. Properties of a particular fluorourethane are determined by the raw materials and manufacturing processes used. Useful generalizations about properties cannot be made without considering the use for which the material is designed (Scheirs, 1997). Typical applications are surface coatings, surface

treatments of leather, textile and other substrate, cladding for optical fibers, etc. (Drobny, 2001).

#### **4.4.2 Hexafluoroisopropylidene-containing polymers**

Monomers containing the hexafluoroisopropylidene (6F) group have found worldwide application in the synthesis of high-performance polymers. These polymers show dramatic improvement of properties when compared to non-fluorinated analogues. In general the presence of the 6F group in a polymer increases solubility, oxidative and thermal stability, optical transparency, flame resistance and resistance to UV mediated degradation, while decreases crystallinity, dielectric constant, water absorption and surface energy.

Numerous applications for polymers containing hexafluoroisopropylidene groups have been suggested, including water and heat resistant coatings, fibers, adhesives and even dental prostheses. The high cost of these materials, however, limits their use to small-scale and speciality applications such as microelectronics, aerospace and medical devices (Scheirs, 1997).

#### **4.4.3 Polyfluoroacrylates and -methacrylates**

The earlier progress in supersonic aviation necessitated the need to develop ‘organic’ glasses which exceed the current capabilities of acrylics such as poly(methylmethacrylate) in terms of heat and impact resistance. Fluoroalkyl  $\alpha$ -fluoroacrylate polymers are characterized by a higher glass transition temperature, enhanced heat resistance, good mechanical strength and flexibility in comparison with the widely used fluoroalkyl methacrylate polymers. Polymers and copolymers of fluoroalkyl acrylates and fluoroalkyl methacrylates have the most practical use. They are used in the production of plastic lightguides, resists, water-, oil- and dirt-repellent coatings and in other advanced applications (Scheirs, 1997, Drobny, 2001). Foraperle® products are fluorinated acrylic copolymers used for the treatment of paper, paperboard, and leather ([www.dupont.com](http://www.dupont.com)). The monomeric components of Foraperle 390 are butyl methacrylate (BMA), 2-ethylhexyl methacrylate (EHA), and 1H,1H,2H,2H-perfluorodecyl acrylate (XFDA) (Lazzari, 2009).

#### **4.4.4 Perfluoropolyethers**

Perfluoropolyethers (PFPEs) are a class of low molecular weight polymers (500-15 000 Dalton) that were originally developed in the mid 1960s. Their molecular structure, comprising only carbon, fluorine and oxygen, makes these materials useful for applications under extreme conditions, in the presence of aggressive chemicals and in oxidizing environments. They have approximately the same chemical stability as PTFE in most cases. PFPEs are liquids at room temperature with very low volatility and their viscosity shows little temperature dependence. In addition, they show almost no shear thinning even at very high shear rates. PFPEs are excellent lubricants. They are produced by a variety of different polymerizations techniques. The basis repeat units are  $\text{CF}_2\text{O}$ ,  $\text{CF}_2\text{CF}_2\text{O}$ ,  $\text{CF}_2\text{CF}_2\text{CF}_2\text{O}$  and  $\text{CF}(\text{CF}_3)\text{CF}_2\text{O}$  while the terminal groups of the polymer chain can be  $\text{CF}_3\text{O}$ ,  $\text{C}_2\text{F}_5\text{O}$  and  $\text{C}_3\text{F}_7\text{O}$ . The structure depends on the method used for synthesis.

Fluorolink, Fomblin, Galden and H-Golden are typical trade names for PFPE products manufactured by Solvay Solexis; whereas Demnum, Daifloil, Optodyne Unidyne and Daifree are manufactured by Daikin. Additionally PFPEs are used as intermediates in polymer synthesis in order to produce polyurethanes, elastomers, epoxy and polyester resins, stratifying polymers and paint additives (Scheirs, 1997).

#### 4.4.5 Perfluorinated ionomers

This group resins is based on copolymers of TFE and perfluorinated vinyl ether containing a terminal sulfonyl fluoride group. The commercial products are available mainly in the membrane form, from DuPont as NAFION membranes and from Ashai Glass as FLEMION membranes. Major areas of application are in the field of aqueous electrochemistry. The most important application for perfluorinated ionomers is as a membrane separator in chloralkali cells. They are also used in reclamation of heavy metals from plant effluents and in regeneration of the streams in the plating and metals industry. The resins containing sulfonic acid have been used as powerful acid catalysts (Drobny, 2001). Appendix 3 lists various kinds of fluorinated intermediates used and produced during fluoropolymer production.

Appendix 2 gives an overview over key fluoropolymers, reprocessed PTFE and melts, filled compounds, concentrates, coatings, and fluoroelastomers, plus the material suppliers and their trademarks.

## 5 Production and consumption of fluoropolymers

In 2004, the world consumption of fluoropolymers reached almost 133 000 tons and exceeded a value of \$2.5 billion (Figure 2).

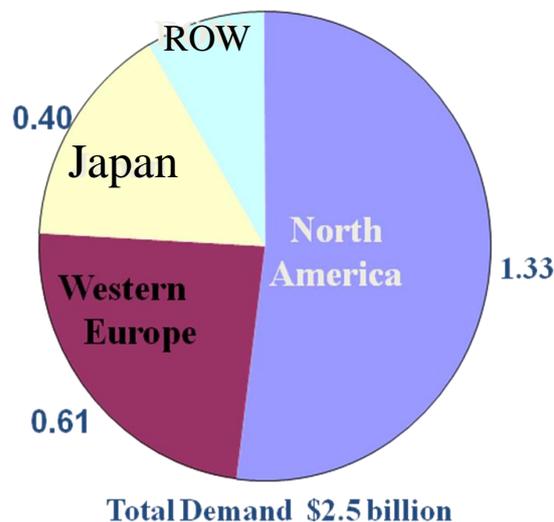


Figure 2: Global market demand of fluoropolymers in the year 2004 (Fluoropolymer Division, 2008). ROW: rest of the world.

Western Europe consumed in 2004 23 900 tons PTFE, 6 800 tons PVDF and 4 000 tons of other fluoropolymers (Will et al., 2005). An overview over the worldwide distribution pattern of the different fluoropolymers is shown in Figure 3.

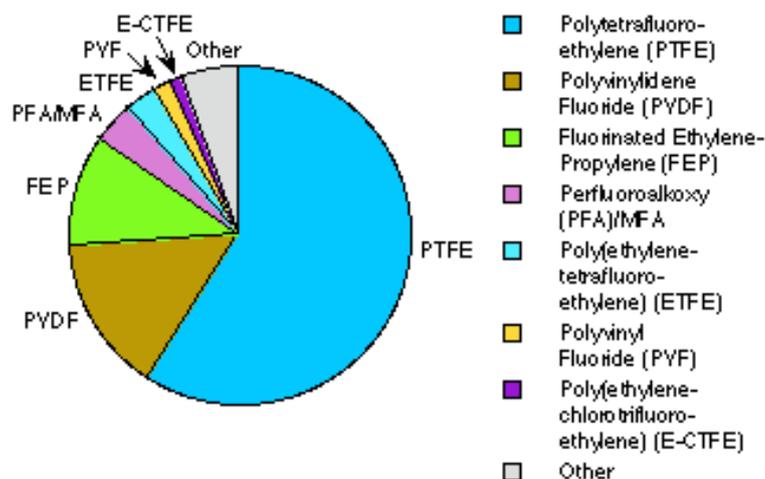
**World Consumption of Fluoropolymers—2004**

Figure 3: World consumption of Fluoropolymers in 2004 (Will et al., 2005).

By summing up all types of consumed fluoropolymers 34 700 tons were consumed in Western Europe in 2004. That is a consumption of fluoropolymers of 0.09 kg/capita (for a population of 370 million in Western Europe). By using a population of 4.7 million people in Norway as a calculation basis, the theoretical Norwegian consumption of fluoropolymers in 2004 was roughly 441 tons. However, the Substances in Preparations In the Nordic countries (SPIN) database reported the use of only 1.7 tons of PTFE in Norway in 2006 in chemical products and preparations, compared to 292 tons for Sweden. The consumption of fluoropolymers is still increasing worldwide, so the Norwegian consumption is expected to have increased accordingly.

According to Ring et al. there have never been any fluoropolymer manufacturing sites in Scandinavia. Western European production sites are based in France, Germany, Italy, Netherlands and UK with total capacity of 46 800 tons in 2007 (Ring et al., 2002). US production in 2007 was higher at 158 200 tons including all fluoropolymer types. In the last years other parts of the world have become quite important. Japan produced 35 800 tons and China is an especially important expanding market. The entire rest of the world (excluding Western Europe, US and Japan) produced 25 700 tons in 2007 with China/South Korea/Taiwan contributing with 19 300 tons (Will et al., 2005).

## 5.1 Consumption of fluoropolymers

### *PTFE*

The total PTFE market in the USA and Canada was approximately 24 600 tons in 1999. The various forms of PTFE and their respective market shares and market sector breakdowns are listed in Table 3.

Table 3: Various forms of PTFE, their respective market shares and market sector breakdowns in 1999 (Scheirs, 2001). Tpa: tons per annum.

<b>Market Share of the various forms of PTFE (approximately 24 600 tpa)</b>	
<b>Granular resins</b>	<b>33% (8 200-10 000 tpa)</b>
Chemical processing	38%
Mechanical	38%
Electrical	12%
Semiconductor manufacture	8%
Laminates	3%
Other	1%
<b>Fine powders</b>	<b>26% (6 400-7 000 tpa)</b>
Textile laminates	26%
Wire and Cable	23%
Tubing	22%
Automotive	21%
Other	8%
<b>Aqueous dispersions</b>	<b>22% (5 400-6 000 tpa)</b>
Consumer and industrial coatings	28%
Coated fiberglass and fabrics	25%
Fibres	17%
Printed circuit boards	14%
Imprgnated items	13%
Antidusting and others	3%
<b>Micronized powders</b>	<b>19% (4 600-4 800 tpa)</b>
Ink and coating	60%
Plastics	35%
Grease and lubricant	3%
Others (e.g. rubbers)	2%

### FEP

The annual US consumption of the copolymer of tetrafluorethylene and hexafluoropropylene (FEP) was approximately 15 000 tons per year in 1999 (Scheirs, 2001), making the FEP the second most important fluoropolymer after PTFE. The three main markets for FEP resins are wire and cable insulation, tube and film, and lining applications for pipes, valves and chemical storage tanks (Table 4).

Table 4: Market sector breakdown for FEP in 2000 (Scheirs, 2001).

<b>Total</b>	<b>15000 tons</b>
Wire and Cable	80%
Tube and film	10%
Lining application	6%
Others	4%

### PVDF

The third most consumed fluoropolymer in the USA is PVDF with an annual consumption of approximately 9 500 tons. The main markets for PVDF resins (Table 5) are architectural coatings on buildings, chemical process industry equipment, molded/extruded products such as tanks, pipes, etc., for semiconductor manufacture and wire and cable insulation (Scheirs, 2001).

Table 5: Market Sector breakdown for PDVF in 2000 (Scheirs, 2001).

Total	9500 tons
Architectural coatings	40%
CPI/semiconductor manufacture	40%
Wire and cable insulation	20%

ETFE, PFA and ECTFE are only minor fluoropolymers with a consumption between 2 300 and 2 000 tons per year.

More information on production and consumption levels of fluoropolymers also can be found in the Marketing Research Report of Will et al., 2005 or in Parker, 2006.

## 5.2 Consumption of fluoroelastomers

Perfluoroelastomers represent a production of only a few thousand kilograms a year. However, they are growing at a fast pace in terms of applications and introduction of new composition to meet industrial needs. They represent less than 1% of the total fluoroelastomer field, dominated by VDF-base copolymers (Ameduri et al., 2001). More detailed information on world production and consumption of fluoroelastomers can be found in the Marketing Research Report of Inoguchi et al., 2006.

North America is the dominant producer and consumer of fluoroelastomers, followed by Western Europe, Japan and the remainder of Asia (Table 6).

Table 6: Consumption of fluoroelastomers per region in 1998 (Scheirs, 2001)

Region	Consumption (tons)
USA and Canada	21 000
EU	15 000
Japan/Asia	4 000

Inoguchi estimated a global demand for fluoroelastomers of 23 000 tons in 2006, with a market value estimated at about \$1.3 billion. This is half of the PTFE marked value. The United States, Western Europe and Asia accounted for 99% of world consumption of fluoroelastomers in 2006 (Inoguchi et al., 2006).

The automotive industry is by far the largest consumer of fluoroelastomers (Table 7) with applications including O-rings, valve stem seals, shaft seals, and extrusion for fuel hosing and tubing. (Scheirs, 2001).

*Table 7: Fluoroelastomer consumption by industry sector in 2000 (Scheirs, 2001)*

<b>Fluoroelastomer consumer</b>	<b>Share</b>
Automotive	65%
Mechanical	15%
Chemical process industry	10%
Aerospace	7%
Other	3%

### **5.3 Future perspectives**

From 2004 to 2009, the average annual increase in world consumption of PTFE will be approximately 6.0% per year while for other fluoropolymers the increase will average about 5.3% per year (Will et al., 2005). As emerging design trends increasingly require superior performance characteristics, fluoropolymers will continue to replace other materials in demanding applications that justify their generally higher costs.

Among major fluoropolymer types, fastest growth is expected for PVDF resins, as strong nonresidential construction will boost demand for PVDF-based architectural coatings. Gains in demand for FEP will be driven by an improved market for wire and cable, where FEP is used as a jacketing and insulation material. Demand for fluoroelastomers will benefit from an improved motor vehicle output and a revived aerospace market. The most rapid gains for fluoropolymers will be found in smaller-volume resins, which include a number of high value products used in fast-growing applications. For example, a strong semiconductor market will increase the demand for PFA polymers, which are used in microelectronics processing equipment. Double-digit growth in solar energy products will fuel gains for PVF films used in the production of photovoltaic modules. Also, the demand for perfluorosulfonic acid polymers (such as DuPont's NAFION) will be driven by a rapid rise in fuel cell shipments.

Electrical and electronic products are expected to be the largest and fastest growing market for fluoropolymers through 2011, accounting for 37 percent of total demand by value. Gains will be driven by a robust turnaround in the wire and cable market, continued increases in semiconductor shipments and double-digit growth in fuel cell spending. Transportation applications will benefit from increasing motor vehicle production, although cost-cutting measures by automotive producers will restrain the demand for costly fluoropolymer resins. Industrial equipment markets for fluoropolymers will advance at the slowest pace, due in part to weakness in the chemical processing industry. However, value gains will be limited by heightened competition from low-cost foreign imports, especially commodity PTFE resins from Russia and China (Freedonia, 2007).

The global trend shows that fluoropolymer use is increasing (OECD report, 2007). Further and more detailed information about the estimated future demands can be found in Freedonia, 2007.

## 6 Thermal degradation of fluoropolymer materials

One of the main questions in this report is whether fluoropolymer combustion may produce greenhouse gases. To assess this, an overview over the literature data on the formation of fluoropolymer combustion products is presented.

Definition of thermal processes: *Pyrolysis* is formally defined as chemical decomposition of organic materials by heating in the absence of oxygen or any other reagents, except possibly steam. *Thermolysis* is a chemical reaction whereby a chemical substance breaks up into at least two chemical substances when heated. *Combustion* (or burning) is a complex sequence of exothermic chemical reactions between a substance (the fuel) and a gas (the oxidizer) to release heat or heat and light in the form of either a glow or flames. Combustion normally occurs in contact with oxygen. *Incineration* is the process of destroying something through fire.

Although fluoropolymers are among the most thermally stable plastics, they will start to generate toxic air contaminants at, or slightly above, their recommended processing temperatures. Manufacturers recommend the use of local exhaust ventilation during processing operations because of this property. The rate of formation rises as temperatures increase and may cause sufficient degradation of the polymer to produce particulate fume as well as toxic gaseous by-products (The Society of the Plastic Industry, 2005).

Temperature, availability of oxygen, the physical form of the product and the residence time at elevated temperature and whether a catalyst is present, are some of the factors determining the ultimate nature and amount of the decomposition products.

The four main types of decomposition products formed are fluoroalkanes (among these PFCs), hydrogen fluoride (HF), oxidation products, and fluoropolymer particle matter. The presence of other monomers or additives in the fluoropolymer resin may change the nature of the decomposition product (The Society of the Plastic Industry, 2005).

### 6.1 Properties and stability of fluoropolymers

Various fluoropolymers possess different physical and chemical properties. Table 8 displays melting temperature, typical continuous use temperature and processing temperature for some polymers (The Society of the Plastic Industry, 2005). In table 7, fluoropolymers and their main decomposition products at defined temperatures are listed in the order of decreasing stability. The order ETFE<FEP<PFA<PTFE was confirmed by experiments published by The Society of the Plastic Industry, 2005. For example, PTFE will endure 2.3 years at 260 °C until failure due to degradation (Ellis et al., 2001). Generally, the polymers should not be exposed to elevated temperatures as they will start an accelerating decomposition when exposed to conditions above their recommended processing temperature.

Table 8. Typical melting points, continuous use and processing temperatures of polymers (The Society of the Plastic Industry, 2005).

Polymer	Typical melting temperature (°C)	Typical continuous use temperature (°C)	Typical processing temperature (°C)
PTFE	330	260	380
PFA	305	260	380
MFA	280	249	360
FEP	260	205	360
ETFE	220-270	150	310
ECTFE	230	140-150	280-310
THV	120-230	70-130	171-310
TEH	160-210	105-150	200-290
EFEP	158-195	100-150	220-260
PCTFE	215	120	265
PVDF	170	150	232
PVDF copolymer	115-170	100-150	232-249

**PTFE.** PTFE is extremely inert and stable up to 250°C. Above this temperature, it decomposes very slowly, with a reported weight loss of 0.004%/h at 371°C. Processing of PTFE above 400°C is not recommended. The inhalation of PTFE fumes may cause “polymer fume fever” (Drobny, 2001). Depropagation (unzipping) to form monomer competes with chain radical transfer reactions, and the dominant pathway depends on the structure of the fluoropolymer. The high bond strength of the C–F bond makes depolymerization the dominant mechanism. In partially fluorinated fluoropolymers, on the other hand, the lower bond energies of C–H and C–Cl bonds increase the likelihood of chain transfer reactions (Scheirs, 1997).

**FEP.** FEP is considerably less thermally stable than PTFE and starts to degrade at temperatures above 200°C (Drobny, 2001; Scheirs, 1997). There are two stages in the degradation of FEP (Drobny, 2001). The first involves the preferential elimination of HFP from the backbone at a rate four times faster than depolymerization of PTFE. In the second step the remaining backbone undergoes decomposition at the same rate as PTFE (Drobny, 2001; Scheirs, 1997).

**PFA.** PFA is more stable than FEP because of the presence of stable ether groups in the side chain which serves as a spacer and eliminates steric strain at the branching point (Scheirs, 1997). However, PFA (e.g. Teflon PFA 340) can degrade during the processing or use at high temperatures due to the presence of reactive end groups (e.g., –COF and –CH<sub>2</sub>OH). The result is cross-linking reactions and an increase in the molecular weight distribution (MWD) when the unstable end groups decompose to form radicals, which then undergo radical recombination reactions (Drobny, 2001; Scheirs, 1997). PFA resins can be processed at temperatures up to 445°C (Drobny, 2001).

**PVDF.** PVDF is considerably less thermally stable than PTFE but much more stable than PVF or PCTFE (Drobny, 2001; Scheirs, 1997).. Certain inorganic compounds (SiO<sub>2</sub>, TiO<sub>2</sub>, Sb<sub>2</sub>O<sub>3</sub>, often used as additives) can catalyze its decomposition at temperatures above 375°C (Drobny, 2001; Scheirs, 1997).

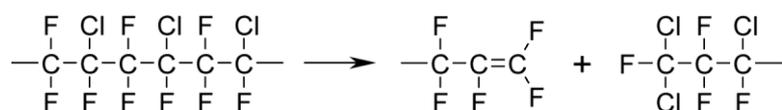
**ETFE.** ETFE degradation is autocatalytic and similar to that of PVDF and is accompanied by the evolution of HF. Iron and transition metal salts can accelerate

the degradation of ETFE by dehydrofluorination and oligomers formation (Drobny, 2001; Scheirs, 1997). Cu salts have been found to stabilize the polymer. ETFE decomposes readily at temperatures above 380°C (Drobny, 2001). Crosslinked ETFE insulation turns yellow after just a few days at 220°C, and after two months' ageing the insulation had turned brown. The oxidative stability of ETFE has been related to the oxidative degradation of tandem ethylene linkages. For example  $-\text{CF}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CF}_2-$  is less oxidative stable than  $-\text{CF}_2-\text{CF}_2-\text{CH}_2-\text{CH}_2-\text{CF}_2-\text{CF}_2-$  because the shielding effect provided by the fluorine atoms does not extend over more than one C-C bond length so that the methylene groups near the centre of the tetramethylene sequence have almost the same susceptibility to oxidative attack as those in polyethylene (Scheirs, 1997).

**PVF.** PVF decomposes in air at temperatures above 350°C by dehydrofluorination (Drobny, 2001). Unlike PTFE, the fluorine deficient PVF does not yield appreciable amounts of monomer during pyrolysis. Instead, HF is the major product of PVF thermal degradation, and it occurs at 350°C (Scheirs, 1997). At approximately 450°C backbone cleavage occurs (Drobny, 2001). Benzene is also a major degradation product of PVF and is formed by chain scission and subsequent cyclization (Scheirs, 1997). PVF films discolor at high temperatures, but retain considerable strength after heat-aging at 217°C (Drobny, 2001; Scheirs, 1997).

**ECTFE.** ECTFE has a thermal stability comparable to ETFE and can be stabilized by the addition of an ionomer, which considerably reduces dehydrofluorination and dehydrochlorination reactions and suppress the discoloration of the polymer (Drobny, 2001).

**PCTFE.** PCTFE can start to degrade at temperatures as low as 250°C. The mechanism of thermal degradation of PCTFE is a chain scission and leads to terminal unsaturation (Drobny, 2001; Scheirs, 1997).



**Fluoroelastomers.** Fluoroelastomers, such as Kalrez (copolymer of TFE and PMVE), can maintain their thermal stability to temperatures as high as 300°C or even higher, with a maximum continuous service temperature of 315°C. Moreover, instead of hardening, the elastomer becomes more elastic with aging (Drobny, 2001).

**Fluorocarbon elastomers.** Fluorocarbon elastomers, such as copolymers of VDF and HFP, typically have a maximum continuous service temperature of 215°C. Some metal oxides may cause dehydrofluorination at a temperature of 150°C or even lower. Copolymers of VDF and CTFE (e.g., Kel-F) have a maximum long-term service temperature of 200°C. Fluorocarbon elastomers based on copolymers

of VDF/HPFP (hydropentafluoropropylene) and terpolymers of VDF/HPFP/TFE have lower thermal stability than copolymers of VDF/HFP because they have a lower fluorine content than the latter (Drobny, 2001).

*Table 9: List of fluoropolymers and their main decomposition products at defined temperatures found in the literature. In parenthesis: PFC-code*

Polymer	Temperature	Main products	Reference	
PTFE	450°C	COF <sub>2</sub> HF	(The Society of the Plastic Industry, 2005)	
	400-500°C	TFE HFP PFIB	(Waritz, 1975)	
	500°C	HFP TFA	(Ellis et al., 2001)	
	530°C	CF <sub>4</sub> (PFC-14) C <sub>2</sub> F <sub>6</sub> (PFC-116) TFE HFP <i>c</i> -C <sub>4</sub> F <sub>8</sub> ( <i>c</i> -OFB) (PFC-318)	(Chen et al., 1991)	
	550°C <sup>#</sup>	CF <sub>2</sub> O C <sub>6</sub> F <sub>2</sub> CF <sub>3</sub> CFO C <sub>5</sub> F <sub>4</sub> CF <sub>3</sub> CF <sub>2</sub> CFO (CF <sub>2</sub> ) <sub>3</sub> O <sub>2</sub>	(Kitahara, 2009)	
	600-700°C	TFE <i>c</i> -C <sub>4</sub> F <sub>8</sub> ( <i>c</i> -OFB) (PFC-318)	(Bhadury et al., 2007)	
	750-800°C	HFP	(Bhadury et al., 2007)	
	850-900°C	PFIB	(Bhadury et al., 2007)	
	800°C	CF <sub>4</sub> (PFC-14)	(The Society of the Plastic Industry, 2005)	
	>900°C	C <sub>2</sub> F <sub>6</sub> (PFC-116)	(The Society of the Plastic Industry, 2005)	
	850°C	HFP TFE	(Garcia et al., 2007)	
	750-1050°C	C <sub>2</sub> F <sub>6</sub> (PFC-116) CF <sub>4</sub> (PFC-14)	(Garcia et al., 2007)	
	ETFE	350°C	COF <sub>2</sub> PFBE TFE CO	(The Society of the Plastic Industry, 2005)
	ECTFE	500°C	TFA CDFA	(Ellis et al., 2001)
FEP	400°C	COF <sub>2</sub> CHF <sub>3</sub> (HFC-23) HFP TFE PFIB	(The Society of the Plastic Industry, 2005)	
PFA	400°C	COF <sub>2</sub>	(The Society of the Plastic Industry, 2005)	
PFEPE	500°C	TFA	(Ellis et al., 2001)	
CPTFE/ PCTFE	500°C	CPFP CDFA	(Ellis et al., 2001)	
PTFE/PFA + PTFE/FEP	800°C	CH <sub>4</sub> CHF <sub>3</sub> (HFC-23) C <sub>2</sub> F <sub>6</sub> (PFC-116)	(Clarke et al., 1992)	

Polymer	Temperature	Main products	Reference
		TFE HFP	
<b>PTFEMA</b>	600°C	TFEMA <sup>§</sup>	(Lazzari et al., 2009)
<b>PHFIFA</b>	600°C	HFIFA <sup>§</sup>	(Lazzari et al., 2009)
<b>PHFIMA</b>	600°C	HFIMA <sup>§</sup>	(Lazzari et al., 2009)
<b>TFEMA/MA</b>	600°C	TFEMA <sup>§</sup> MA	(Lazzari et al., 2009)
<b>XFDA/BMA</b>	600°C	Butane BMA 1H,1H,2H-perfluorodecene <sup>§</sup> XFDA <sup>§</sup>	(Lazzari et al., 2009)
<b>XDFMA/EHA</b>	600°C	1H,1H,2H-perfluorodecene <sup>§</sup> 2-ethylhexene 2-ethylhexanol XFDMA <sup>§</sup> EHA	(Lazzari et al., 2009)
<b>XDFMA/EMA/MA</b>	600°C	MA 1H,1H,2H-perfluorodecene <sup>§</sup> EMA 1H,1H,2H,2H-perfluorodecanol <sup>§</sup> XFDMA	(Lazzari et al., 2009)
<b>Foraperle* fluorinated acrylic copolymer.</b>	<b>a</b> 600°C	CO <sub>2</sub> Butene Butyl methacrylate 2-ethylhexene 2-ethylhexanol 2-ethylhexyl methacrylate 1H,1H,2H-perfluorodecene 1H,1H,2H,2H-perfluorodecanol 1H,1H,2H,2H-perfluorodecyl acrylate 1H,1H,2H,2H-perfluorodecyl methacrylate 1H,2H,2H-perfluorodecanal	(Lazzari et al., 2009)
<b>PFA7</b>	650°C	Monomer Fluorinated alcohol Perfluorocyclohexane C <sub>6</sub> F <sub>12</sub> Light products <sup>♠</sup>	(Zuev, 2006)
<b>PFMA7</b>	650°C	Monomer Light products <sup>♠</sup>	(Zuev, 2006)

<sup>#</sup> Oxidative pyrolysis, i.e. pyrolysis in air.

<sup>\*</sup> The composition is not known.

<sup>§</sup> Identified through direct interpretation of mass spectra since commercially available electronic libraries did not include these compounds

<sup>♠</sup> Light products include CO<sub>2</sub>, H<sub>2</sub>O, C<sub>2</sub>F<sub>4</sub>, C<sub>2</sub>F<sub>2</sub>H<sub>2</sub>.

## 6.2 Thermal degradation experiments with fluoropolymers

The thermal stability and degradation properties of PTFE have been in the focus of the scientific community and the consumers for a long time. The temperature range where thermal degradation of fluoropolymers starts, was the most investigated endpoint. Only few studies focused on conditions relevant for waste incineration in Norway (temperatures at 850°C) and they will be discussed first. Additionally, the results are not always comparable due to different experimental set-up parameters, e.g., temperature, availability of oxygen, the physical form of the article, and the residence time at the elevated temperature, making the drawing of a final conclusions challenging.

### *Experiments between 800 and 1000°C*

Bhadury et al. conducted a series of experiments where PTFE powder underwent flash pyrolysis under inert atmosphere ( $N_2$ ) in a quartz assembly (Figure 4a). The experimental set up is attractive for future investigations of PTFE pyrolysis products. TFE and *c*-OFB were most abundant at 600-700°C (Figure 4b), HFP at 750-800°C, perfluoroisobutylene (PFIB) at 850-900°C, and hexafluoroethane at temperatures above 950°C (Bhadury et al., 2007). The emitted compounds were identified by both GC-MS and  $^{19}F$  NMR.

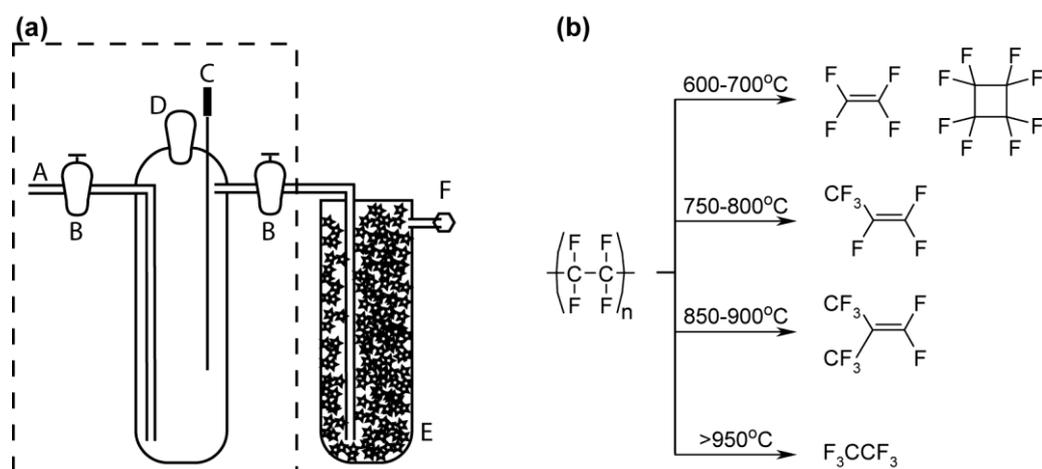


Figure 4: (a) Pyrolysis assembly. A: inlet for Nitrogen; B: stoppers; C: thermocouple; D: inlet for sample; E: filter with glass wool; F: outlet for gas sampling through tedlar bag. The dashed line indicates oven interior. (b) Generation of organofluorine compounds by flash pyrolysis of PTFE (Bhadury et al., 2007).

In the work of Garcia et al., the influence of the temperature as well as the reaction atmosphere on the products obtained in the thermal degradation of PTFE was evaluated. At 850 °C, pyrolysis of PTFE leads to extensive formation of hexafluoropropylene (HFP; 82%), although a significant yield of tetrafluoroethylene (TFE) was also obtained (12%). At fuel-rich combustion (oxygen supply) conditions at temperatures between 750 and 1050 °C, the main fluorine products are  $C_2F_6$  (PFC-116) and  $CF_4$  (PFC-14). 27 minor products, including long chain hydrocarbons ( $C_{14}$ - $C_{20}$ ), organic acids ( $C_8$ - $C_{16}$ ), alcohols, and

toluene were identified in the pyrolysis and combustion of PTFE. The formation of fluorinated compounds is highest at 750 and 850 °C and decreases at 950 and 1050 °C (Garcia et al., 2007). However, differences in the process parameters such as temperature, operation atmosphere and secondary reactions can lead to a quite different spectrum of the major degradation products.

A mechanism for the formation of unsaturated compounds under non-oxidative condition with further reaction of the primary combustion products by the introduction of oxygen is given in Figure 5.

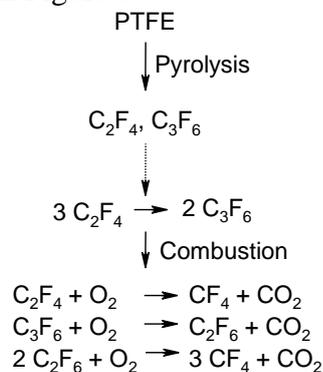


Figure 5: Proposed reaction mechanism for the thermal degradation of PTFE (Garcia et al., 2007).

In a full scale fire experiment with telecommunication cables insulated and jacketed with fluorinated materials (Teflon<sup>®</sup> FEP and/or Teflon<sup>®</sup> PFA) at 850 °C, Clarke et al. identified CF<sub>4</sub> (PFC-14), CHF<sub>3</sub> (HFC-23), C<sub>2</sub>F<sub>6</sub> (PFC-116), TFE, HFP, and small amounts of four carbon species as the most abundant compounds, which is in accordance with the findings of Garcia et al. (Clarke et al., 1992).

In Clarke's experiments, the formation of a maximum of 8.4 g CF<sub>4</sub> and 68 g C<sub>2</sub>F<sub>6</sub> from 100g PTFE was achieved at 850 °C. Similarly, Garcia reports 5.5 g CF<sub>4</sub> and 61 g C<sub>2</sub>F<sub>6</sub> for the same temperature and per PTFE amount. When run at 1050 °C, 9.3 g CF<sub>4</sub> and 12.5 g C<sub>2</sub>F<sub>6</sub> are formed according to Garcia et al (2007). Since these are the only available quantitative data described in the literature so far, taking relevant temperature conditions in MWI into consideration (e.g. 850 °C and above), any assessment concerning emissions of PFCs in Norwegian waste incinerators conditions must rely on these data until more appropriate data are available. The topic is further discussed in Chapter 7.

In addition to the degradation products mentioned above, Herzke (1998) identified several fluoro-dioxins and fluoro-benzofurans, besides other fluorinated aromatic compounds upon PTFE thermolysis (≤ 800°C), see Figure 6 for structures.

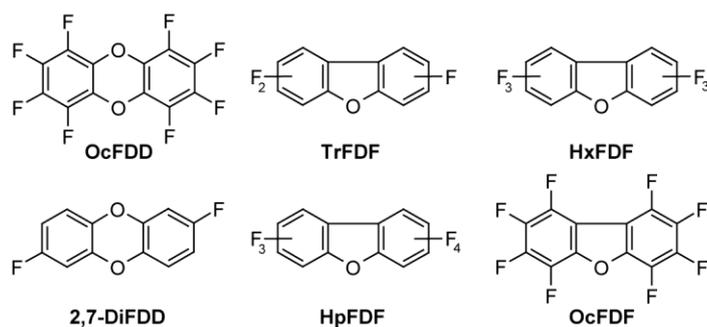


Figure 6. Fluorinated dioxins and benzofurans formed upon thermolysis of fluoropolymers Herzke (1998).

#### Experiments between 300 and 800°C

The National Institute for Occupational Safety and Health, USA, (NIOSH) suggested in its 1977 Criteria Document for PTFE that the TFE monomer is the principle gaseous product at temperatures that just produce softening or melting of the polymer (330°C). The TFE may be a residual monomer that is trapped in the resin particles or evolved as the resin structure changes with temperature (The Society of the Plastic Industry, 2005). As the PTFE temperature increases to approximately 450°C in air, carbonyl fluoride and hydrogen fluoride become the main decomposition products. Carbonyl fluoride hydrolyses in the presence of moist air to HF and carbon dioxide. Small amounts of HFP may also be found at 450°C. The highly toxic chemical, perfluoroisobutylene (PFIB), has been detected as a minor decomposition product at temperatures above 475°C. When the temperature reaches approximately 800°C, tetrafluoromethane (CF<sub>4</sub>) begins to form (The Society of the Plastic Industry, 2005).

In a weight loss experiment, PTFE was heated to 400-500°C, and the emitted gases were monitored by GC-MS (Waritz, 1975). In this temperature region, TFE, HFP and PFIB were the most abundant thermolysis products (Figure 7).

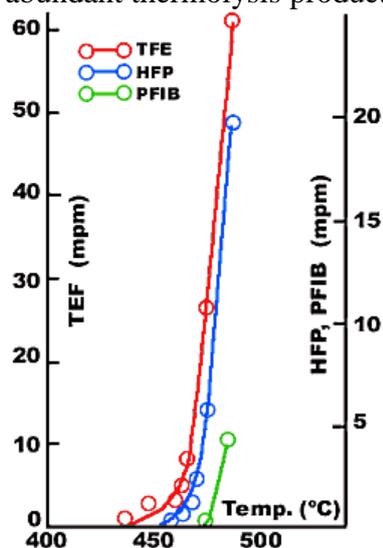


Figure 7: Evolution of (O) tetrafluoroethylene, (O) hexafluoropropylene, and (O) perfluoroisobutylene from polytetrafluoroethylene resin as a function of temperature (Waritz, 1975).

Kitahara et al. (2009) conducted oxidative pyrolysis of PTFE at 550°C and identified CF<sub>2</sub>O (100), C<sub>6</sub>F<sub>2</sub> (10), CF<sub>3</sub>CFO (21), C<sub>5</sub>F<sub>4</sub> (5), CF<sub>3</sub>CF<sub>2</sub>CFO (2), and (CF<sub>2</sub>)<sub>3</sub>O<sub>2</sub>. The relative intensities are given in parentheses.

DuPont conducted a weight loss experiment of six fluoropolymer resins. The resins were heated for 1-24 h (The Society of the Plastic Industry, 2005), results are presented in Table 8 (The Society of the Plastic Industry, 2005). Formation of PFIB, even in small amounts, is noted because of its high toxicity (2 h LC<sub>50</sub> for rats is 1 ppm). PFIB was formed from FEB at 400°C, whereas 525°C was required to produce PFIB from PTFE. This difference is presumably due to the branched chain of FEB (Baker, 1993; The Society of the Plastic Industry, 2005). These experiments also indicate the following thermal stability: ETFE<FEP<PFA<PTFE.

*Table 10: Comparison of one hour thermogravimetry (TGA) weight loss with weight of evolved gases. Weight of evolved gases as % of sample of evolved gases as % of sample. HFP is hexafluoropropylene and PFBE is perfluorobutylethylene (Baker, 1993; The Society of the Plastic Industry, 2005).*

Resin	Temp °C	TGA% wt. loss	PFIB	TFE	HFP	HCF <sub>3</sub>	PFBE	COF <sub>2</sub>	CO
ETFE 200	350	5.3	n.d.	0.06	n.d.	n.d.	0.3	2.5	0.06
FEP 100	400	2.5	0.003	0.06	0.38	0.19	n.d.	1.2	n.d.
PFA 340	400	0.43	n.d.	n.d.	n.d.	n.d.	n.d.	0.53	n.d.
PFA 440	400	0.26	n.d.	n.d.	n.d.	n.d.	n.d.	1.2	n.d.

Yamada et al. investigated the fate of a fluorotelomer-based polymer under incineration conditions to determine whether perfluorooctanoic acid (PFOA) is formed as a thermal degradation product. The main aim was to investigate the thermal degradation of a fabric treated with a fluorotelomer-based acrylic polymer under laboratory conditions conservatively representing typical combustion conditions of time, temperature, and excess air level in a municipal incinerator. Thermal testing was initiated at 600 °C. The decomposition of the “Telomer” (CF<sub>2n+1</sub>CH<sub>2</sub>CH<sub>2</sub>-X) functionality resulted in the formation of compounds containing the ·CF<sub>2</sub>CH-CH<sub>2</sub> fragment in greater amounts with increasing temperature. Additionally, the authors report that the combustion tests of the treated and untreated article at 1000°C showed no detectable levels of PFOA (Yamada et al., 2005).

Ellis et al. characterized the structures of compounds released upon thermolysis (up to 500°C) of different fluoropolymers. From all the polymers investigated, C<sub>2</sub>-C<sub>14</sub> perfluorocarboxylic acids and [per]chlorofluoro-carboxylic acids and their terminal -OCF<sub>3</sub> ethers were observed, along with the low molecular weight compounds dichlorofluoro acetic acid (DCFA), chlorodifluoroacetic acid (CDFA), difluoroacetic acid (DFA), monofluoroacetic acid (MFA), HFP, chloropentafluoropropene (CPFP), and fluoroformaldehyde (F<sub>2</sub>C=O) (Ellis et al., 2003).

Lazzari and colleagues (2009) subjected the partially fluorinated methacrylic polymer Foraperle 390 to 600°C for ten seconds, and 11 major products were identified. The non-fluorinated degradation products were CO<sub>2</sub>, butene, butyl methacrylate, 2-ethylhexene, 2-ethylhexanol, and 2-ethylhexyl methacrylate. The fluorinated products were 1H,1H,2H-perfluorodecene, 1H,1H,2H,2H-perfluorodecanol, 1H,1H,2H,2H-perfluorodecyl acrylate, 1H,1H,2H,2H-perfluorodecyl methacrylate, and 1H,2H,2H-perfluorodecanal.

Thermolysis of the fluorinated side chain acrylic polymers Poly-2,2'3,3',4,4',5,5',6,6',7,7',7''-tridecafluoroheptylacrylate (PFA7) and Poly-2,2'3,3',4,4',5,5',6,6',7,7',7''-tridecafluoroheptylmethacrylate (PFMA7) at 550 and 650°C was reported by Zuev et al. (Zuev, 2006). The major products were the monomer, and "alcohol" and perfluorocyclohexane (C<sub>6</sub>F<sub>12</sub>). Light products, such as CO<sub>2</sub>, H<sub>2</sub>O, C<sub>2</sub>F<sub>4</sub>, and C<sub>2</sub>F<sub>2</sub>H<sub>2</sub>. There was observed a shift towards lighter products at increased temperature.

TFE, HFP and *cyclo*-octafluorobutane (*c*-OFB) were the main gases produced upon thermolysis of the pure fluorinated polymer and of the commercially available products tested (Table 9). TFA and CDFA were the main acids to be observed in the thermolysis of fluoro- and chlorofluoro-polymers, while other longer-chain perhalogenated acids were also identified. A mechanism for the formation of TFA caused by thermal degradation of PTFE at 500°C, is given in Figure 8: Proposed reaction mechanisms involved in the thermolysis of a fluoropolymer. The explicit major pathways for the production of TFA are shown. As indicated by the bold arrow, the most significant step in the thermal decomposition is the formation of carbene radicals. 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. A Δ indicates heat. (Ellis et al., 2001). Figure 8. The mechanism is supported by key products observed by several other studies and the additional products observed in this investigation. It is hypothesized that the thermolysis of PTFE and other polyfluorinated polymers is a major contributor to the steadily increased measured concentrations of TFA in urban environment precipitation. The other products formed upon thermolysis of such polymers, PFCA, F<sub>3</sub>CO-PFCA and PFA may contribute to global warming, as discussed below. The global warming potential of TFA is unknown.

*Table 11: Identified products identified upon thermolysis of fluoro- and chlorofluoro-polymers at up to 500°C. A dash indicates that the analyte was positively identified but not quantified. PTFE: polytetrafluoroethylene (Teflon); CPTFE: chloro-polytrifluoroethylene (Kel-F); ECTFE: ethylene-chlorotrifluoroethylene; PFEPE: polytetrafluoroethylene-co-tetrafluoroethylene perfluoropropylether (Ellis et al., 2001).*

<b>Polymer</b>	<b>Thermal product identified (acronyms/formula and full name)</b>		<b>% produced</b>
<i>PTFE</i>	TFE	Tetrafluoroethene	-
	HFP	Hexafluoropropene	10.8
	TFA	Trifluoroacetic acid	7.8
	<i>c</i> -OFB	Octafluoro cyclobutane	-
	CF <sub>3</sub> (CF <sub>2</sub> ) <sub>n</sub> COOH	Perfluorinated carboxylic acid	>0.01
	F <sub>3</sub> CO(CF <sub>2</sub> ) <sub>m</sub> COOH	Trifluoromethoxy perfluorinated carboxylic acid	-
	DFA	Difluoroacetic acid	>0.01
	MFA	Monofluoroacetic acid	>0.01
<i>CPTFE/ PCTFE</i>	CTFE	Chloro-trifluoroethene	-
	CPFP	Chloro-pentafluoropropene	13.1
	CDFA	Chlorodifluoroacetic acid	9.5
	TFA	Trifluoroacetic acid	>0.1
	DCHB	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	-
CF <sub>3</sub> (CF <sub>2</sub> ) <sub>n</sub> COOH	Perfluorinated carboxylic acid	-	
<i>ECTFE</i>	TFA	Trifluoroacetic acid	6.3
	CDFA	Chloro-difluoroacetic acid	7.2
	HFP	Hexafluoropropene	-
	CPFP	Chloro-pentafluoropropene	-
<i>PFEPE</i>	TFA	Trifluoroacetic acid	2.5
	HFP	Hexafluoropropene	-

Thermolysis of Teflon, Kel-F, and other fluoro- and chlorofluoropolymers can produce TFA and chlorodifluoroacetate (CDFA), either directly or indirectly via products that are known to degrade to these haloacetates in the atmosphere. Figure 8 shows proposed reaction mechanisms involved in the thermolysis of a fluoropolymer. The onset of thermal degradation of fluoropolymers is known to initiate cleavage of the backbone and subsequent rearrangement to produce significant amounts of TFA and CDFA. Thermolysis also leads to longer chain polyfluoro and/or polyfluorochloro (C<sub>3</sub>-C<sub>14</sub>) carboxylic acid, compounds known to be persistent. Finally, Ozone depleting substances like CFCs and greenhouse gases like fluorocarbons, are among other thermal degradation products. This suggests that thermolysis of fluoro- and fluorochloro-polymers may contribute to ozone depletion and global warming (Ellis et al., 2001).



## 7 Greenhouse potential of fluoropolymer combustion products

### 7.1 Thermal degradation products of fluoropolymers

One aim of the present study was to discuss whether greenhouse gases are formed during fluoropolymer combustion. Some or all of the greenhouse gases discussed in Chapter 6 may also have other sources. These sources may be natural, primarily volcanic emissions (Francis et al., 1998; Gribble, 1995), or anthropogenic, such as HFC and HCFC cooling gases (Jordan, 1999), anesthetic gases, use in aluminum industry or metal coating as well as agrochemicals (Key et al., 1997; Ellis et al., 2000), and their degradation products.

A number of atmospheric constituents influence the earth's climate through radiative forcing (RF); these are called greenhouse gases. Radiative forcing is a measure of the change of balance of incoming and outgoing energy in the Earth-atmosphere system. This radiative balance controls the Earth's surface temperature and the thermal variability throughout most of the atmosphere. The term 'forcing' indicates that the Earth's radiative balance is pushed away from its normal/initial state (Forster et al., 2007). Hence, a positive RF implies global warming, whereas a negative RF causes global cooling.

To be able to compare the impact of various factors on climate, the Intergovernmental Panel on Climate Change (IPCC) in 1990 introduced the term Global Warming Potential (GWP). The GWP of a compound  $i$  is the time-integrated global mean RF of a pulse emission of 1 kg of this compound relative to the RF of 1 kg of the reference gas  $\text{CO}_2$  ( $r$ ). The UNFCCC have required use of GWPs for many years for the calculation of countries' greenhouse gas emissions (National Inventory Reports), and the GWPs listed in the Third Assessment Report (TAR) of the IPCC were adopted for use in the Kyoto Protocol (Forster et al., 2007). The GWP of component  $i$  is defined by (Forster et al., 2007; Blowers et al., 2008):

$$GWP_i = \frac{\int_0^{TH} RF_i(t) dt}{\int_0^{TH} RF_r(t) dt}$$

where  $TH$  is the time horizon and  $t$  denotes time. The radiative efficiencies (radiative forcing per unit amount/mixing ratio) for well-mixed greenhouse gases are given in Table 12.

The greenhouse gases formed upon incineration of fluoropolymers are covered either by the Montreal or the Kyoto protocols, as indicated in Table 10.

Table 12: Names, chemical formula, abundances, lifetimes, radiative forcings (given as  $W m^{-2}$ ) and GWP relative to  $CO_2$ . The GWP were calculated in the Third Assessment Report in a 100 year perspective. (IPCC report: Forster et al., 2007; IPCC, 2001).

Gas	Chemical formula	Abundance (ppt)			Lifetime (years)	Radiative forcing <sup>a</sup>	GWP# 100 years
		2005	1998	1750			
<i>Other important greenhouse gases</i>							
Carbon dioxide [K]	CO <sub>2</sub>	3.79·10 <sup>6</sup>	3.66·10 <sup>6</sup>	2.75·10 <sup>6</sup>	50?	1.68	1
Methane [K]	CH <sub>4</sub>	1774	1745	700	12	0.48	23
Sulfur hexafluoride [K]	SF <sub>6</sub>	5.6	4.2	0	3200	0.0029	22200
CFC-11 [K]	CFCl <sub>3</sub>	251	268	0	45	0.063	4600
CFC-12 [K]	CF <sub>2</sub> Cl <sub>2</sub>	538	533	0	100	0.17	10600
<i>Gases relevant for fluoropolymer incineration</i>							
CFC-13 [M]	CClF <sub>3</sub>	NA	4	0	640	0.009 <sup>§</sup>	14000
CFC-113 [M]	CCl <sub>2</sub> FCClF <sub>2</sub>	79	84	0	85	0.024	6000
HFC-23 [K]	CHF <sub>3</sub>	18	14	0	260	0.0033	12000
PFC-14 [K]	CF <sub>4</sub>	74	80	40	50000	0.0034	5700
PFC-116 [K]	C <sub>2</sub> F <sub>6</sub>	2.9	3.0	0	10000	0.0008	11900
PFC-318 [K]	c-C <sub>4</sub> F <sub>8</sub>	NA	NA	NA	3200	NA	10000
<i>Total long lived greenhouse gases</i>						2.63	
Total CFC						0.27	
Total HCFC						0.04	
Total Montreal gases						0.32	
Other Kyoto gases (HFCs + PFCs + SF <sub>4</sub> )						0.017	
Halocarbons						0.34	

<sup>a</sup>  $W m^{-2}$ , values taken from Third assessment report

[M] Gas covered by the Montreal protocol

[K] Gas covered by the Kyoto protocol

<sup>§</sup> Sum for CFC-13, CFC-114, and CFC-115 and the halons.

\* Percent change in RF for the period 1998-2005

# GWP taken from TAR (IPCC, 2001)

When discussing the GWPs of the fluoropolymer degradation products, it is convenient to divide them into three categories: stable neutral (saturated), unstable neutral (unsaturated), and ionic and polar compounds:

- i) Short-chained saturated, neutral, and stable perfluoro (PFCs), chlorofluoro (CFCs), and hydrofluoro (HFCs) compounds have long half-lives, a property important for exhibiting a significant GWP. These compounds are postulated to affect global climate by acting as greenhouse gases with GWPs between 5700 and 14000 (Table 10).

- ii) Unstable unsaturated neutral compounds formed during combustion of fluoropolymers are short lived in the atmosphere. They do not contribute to global warming and are not covered by the TAR.
- iii) Polar and ionic compounds such as long-lived halocarboxylic acids, e.g. TFA. They are expected to be removed from the atmosphere through wet and dry deposition. The GWP of this group is negligible due to the short atmospheric lifetime.

*Short-chain saturated, neutral, and stable degradation products; PFC, CFC, and HFC*

The fluoropolymer combustion products CO<sub>2</sub>, CF<sub>4</sub> (PFC-14), C<sub>2</sub>F<sub>6</sub> (PFC-116), *c*-OFB (PFC-318), CHF<sub>3</sub> (HFC-23), CClF<sub>3</sub> (CFC-13), and TCTFE (CFC-113) are greenhouse gases covered by the TAR. DCHB (1,2-dichlorohexafluorocyclobutane) is not covered by the TAR, but being a saturated CFC, it should be considered as a greenhouse gas with a GWP comparable to the other CFC gases discussed in the TAR. Fluorocarbons efficiently absorb infrared radiation, particularly in the 1000-1400 cm<sup>-1</sup> spectral range, where the atmosphere originally is relatively transparent (Tuazon et al., 1993; McCulloch, 2003). Table 12 shows the GWP of the greenhouse gases listed in the TAR (IPCC, 2001). CF<sub>4</sub> (PFC-14), C<sub>2</sub>F<sub>6</sub> (PFC-116), *c*-OFB (PFC-318), CHF<sub>3</sub> (HFC-23), CClF<sub>3</sub> (CFC-13), and TCTFE (CFC-113) all have very long atmospheric lifetimes and GWPs considerably larger than that of CO<sub>2</sub> (even though the large uncertainty regarded the lifetime of CO<sub>2</sub>). The PFCs, CFCs, and HFCs possibly formed during fluoropolymer waste incineration (see chapter 6) might therefore have a considerable potential to influence the greenhouse effect when emitted in large amounts.

The RF due to these compounds depends on the quantities and absorptivities of the released atmospheric gases, and in this respect carbon dioxide dominates because of the large quantities emitted. The total global RF values presented in the 2007 IPCC report were  $+0.017 \pm 0.002 \text{ W m}^{-2}$  for the group consisting of HFC, PFC and SF<sub>6</sub>,  $+0.32 \pm 0.03 \text{ W m}^{-2}$  for the group consisting of CFC, HCFC and chlorocarbons, and  $+1.66 \pm 0.17 \text{ W m}^{-2}$  for CO<sub>2</sub>. Thus, the accumulation of fluorocarbons in the atmosphere will enhance the warming of the atmosphere, but compared to CO<sub>2</sub> their contribution is small.

*Unstable unsaturated degradation products*

Neutral unsaturated degradation products with a short atmospheric lifetime, i.e., TFE, HFP, CTFE, CPFP, 1,3-DCTFP, 1,1,3-TCTFP, and PFIB will not have a considerable affect on the global warming. TFE and HFP have atmospheric half-lives of 1.9 and 6 days, respectively. No atmospheric half-lives are reported for the combustion products CTFE, CPFP, 1,3-DCTFP, 1,1,3-TCTFP, and PFIB. The unsaturated compounds have the potential to react with OH radicals (OH<sup>•</sup>) in the troposphere to eventually produce TFA or other PFCA (100% conversion) in a manner similar to that of HFP and TFE in Figure 9 above (Ellis et al., 2001).

*Polar and ionic degradation products*

PFCA and TFA are minor products emitted to the atmosphere from thermolysis of fluoropolymers (Hurley et al., 2004). The global warming potential of TFA is unknown, but it should be lower than CO<sub>2</sub> given its short atmospheric life-time.

PFCA, including TFA, and HF are removed from the atmosphere through wet or dry deposition (Jordan, 1999).

PFCA, including TFA, and HF are removed from the atmosphere through wet or dry deposition. Model calculations predicted a global mean TFA concentration in precipitation in Europe of about 14 ng/L in 1995 and 120 ng/L in 2010. Already in 1999, TFA was found at 10-200 ng/L in precipitation and 60-600 ng/L in surface water. It is hypothesized that the thermolysis of PTFE and other polyfluorinated polymers is a major contributor to the steadily increasing concentrations of TFA in urban environment precipitation. The global warming potential of TFA is unknown, but it should be lower than CO<sub>2</sub> given its short atmospheric life-time (Jordan and Frank, 1999).

In addition to the anthropogenic sources, considerable natural sources of TFA and other fluoroorganics are known. Volcanic emissions are reported to contain several fluoroorganic compounds, and a summary is provided by Gribble and references therein (Gribble, 2002). One other possible source is seafloor hydrothermal vents (Scott et al., 2005). In most cases, the identified compounds have not been quantified, thus it is difficult to estimate (except for HF) the volcanic contribution to the atmospheric content of fluoro- and fluorochloro-organic compounds.

The anthropogenic emissions of the non-greenhouse gas HF are primarily due to coal combustion, and from the ceramics and metal industries (Caddle, 1980). Assuming that all of the  $0.123 \cdot 10^{12}$  g annually manufactured fluoropolymers (Herzke et al., 2007) are combusted to HF, this will only account for 3% of the total anthropogenic HF emission. According to the "Guide to the Safe Handling of Fluoropolymer Resins" incineration for waste disposal is only recommended if the incinerator is fitted and permitted to scrub out HF and other acidic combustion gases, which is the case for all Norwegian incineration plants by legislation.

## **7.2 Possible contribution of incineration of fluoropolymers to global warming**

Does incineration of household waste containing fluoropolymers contribute significantly to the total national emissions of green house gases in Norway? Do these incineration products increase the atmospheric content of CFC, PFC, and HFC, and hence contribute to global warming?

In order to contribute to global warming the fluoropolymers must be incinerated and the produced greenhouse gases must be released into the environment. The annual Norwegian fluoropolymer consumption is estimated to a maximum of 441 tons on the basis of the European consumption of fluoropolymers. However, the amount ending in Norwegian incinerators remain largely unknown, due to lack of data on amounts and types of fluoropolymers applied on products (inventory needed), the amounts of fluoropolymer containing products ending up at Norwegian MWIs as well as amounts of exported waste containing fluoropolymers, incinerated in other countries. In addition, it is unclear how much PFC is emitted via municipal waste incinerators in Norway and it is unknown if the cleaning procedures of the exhaust are sufficient for removing PFCs.

There exist only two studies where the emissions from thermal degradation of fluoropolymers have been quantified (Clarke, 1992; Garcia, 2007).

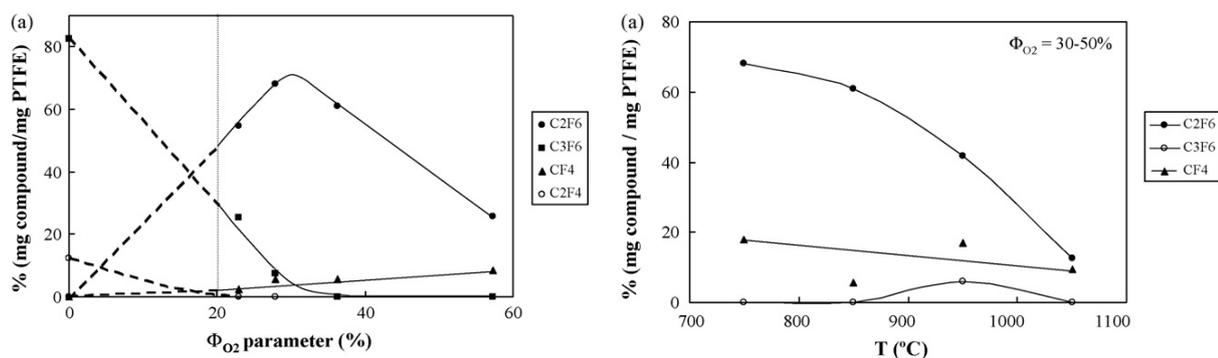


Figure 9: Impact of oxygen and temperature on the formation of PFCs after the combustion of PTFE (from Garcia et al., 2007)

As shown in figure 9, at 850°C and 30-50% oxygen present, C<sub>2</sub>F<sub>6</sub> and CF<sub>4</sub> are formed in considerable yields.

However, no reports or studies exist where fluoropolymers are incinerated together with other waste, and it has not been reported that HFC, CFC and PFC have been identified in municipal incineration plant emissions so far.

This literature study has revealed that it is not possible to provide reliable estimates for the magnitude of emissions of fluorine-containing green house gases produced from fluoropolymers in Norwegian municipal incinerators.

In summary, incineration of fluoropolymer containing products has a great potential contributing to a certain degree to the emissions of greenhouse gases of Norway, but due to the lack of sound data on the fate of fluoropolymers in Norway as well as of the chemical reactions in the different types of MWI plants in Norway, **no exact amounts can be given at this stage**. However, according to Garcia et al. (2007), PFC can be formed during the combustion of fluoropolymers. Due to the high GWP (5700 and 11900, respectively, for PFC-14 and 116) a potential significant input to the national CO<sub>2</sub> equivalent budget might be possible and needs to be investigated.

## 8 Conclusions and evaluation of the need for further studies

PTFE is worldwide the most produced and consumed fluoropolymer followed by PVDF and FEP. Therefore, it is assumed that these are also the main fluoropolymers which end up in the municipal waste incinerators. However, a broad spectrum of other fluorine containing polymers and fluoroelastomers are currently introduced into our society with increasing volumes and applications. In future years, they will end up in the domestic and industrial waste as well.

The thermolytic stability and degradation properties of PTFE have been in the focus of the scientific community and the consumers for a long time already with not always agreeing conclusions due to differing experimental conditions as for example temperature, availability of oxygen, the physical form of the investigated article, and the residence time at elevated temperature. The main products of PTFE incineration at temperatures between 750 and 1050°C, relevant for Norwegian waste incineration plants, are CF<sub>4</sub> (PFC-14), CHF<sub>3</sub> (HFC-23), C<sub>2</sub>F<sub>6</sub> (PFC-116), TFE and HFP. Only a few studies have been conducted where the yields of these compounds in relation to thermolysis conditions have been investigated. The most potent greenhouse gases formed by fluoropolymer combustion are compounds containing C–F bonds, which absorb electromagnetic radiation in the spectral range 1000-1400cm<sup>-1</sup>, namely CF<sub>4</sub> (PFC-14), C<sub>2</sub>F<sub>6</sub> (PFC-116), TFE, and HFP. The latter two are rapidly degraded in the atmosphere and do not contribute to global warming. The GWP of CF<sub>4</sub> (PFC-14) and C<sub>2</sub>F<sub>6</sub> (PFC-116) are 5 700 and 11 900, respectively (TAR; IPCC, 2001).

Since all kinds of quantifications of possible emissions rely on only few studies on that subject, realistic emission numbers cannot be achieved, and can only be determined through direct measurement of exhaust from MWIs.

Additionally Norwegian waste is not only handled in Norway. Waste export to other countries (mainly Europe) for incineration purposes occurs, with other regulations for MWI plant emissions, adding to any global inputs. To make the picture more complex Norway is importing waste as well from several countries with no information on the content of fluoropolymers (Miljøstatus Norge).

No information was available regarding on-site measurements of decomposition products of fluoropolymers in municipal incinerators. **On-site investigations for revealing a realistic impression on the compounds formed in Norwegian municipal incinerators are necessary in order to assess the extent and the composition of the organofluorine emissions.**

### 8.1 Recommendation on future investigations

As documented above, the results and conclusions concerning the thermal degradation products of fluoropolymers varies severely, depending on experimental set-up. Applied temperatures, oxygen content, moisture, other gases and metals reacting as catalysts might influence the outcome of the experiments dramatically without reflecting the conditions in an incinerator correctly. Hence it is not recommended to run laboratory incineration experiments on fluoropolymer materials. Experimental incineration cannot be compared directly to waste

incinerators due to the complex mixture of waste burned in a municipal waste incinerator. Even between the incinerators differences in construction, especially in air pollution control filter systems, lead to different emission values. Therefore, on-site studies in Norwegian waste incinerators are recommended.

Sampling should be performed in different types of incinerators for comparing emission values between different constructions. A known fluoropolymer content of the waste incinerated during sampling would be of help in order to quantify emitted amounts of greenhouse gases. Already installed sample equipment for air monitoring can be used in some incinerators. Waste is often sorted and therefore the incinerators are run in different modes. It is recommended to investigate the decomposition products within these different incineration runs, in order to gain more and distinguished information on waste composition and their related degradation products.

The waste incinerators proposed for sampling are given in Table 13.

*Table 13: Waste incinerators suggested to be included in future investigations.*

<b>Type of incinerator</b>	<b>The localization of the incinerator</b>
Large MWI	Brobekk Klemetsrud
Small MWI	Senja
Dangerous waste MWI	NORCEM Brevik

Standard air sampling in the chimney at standard sampling point  
6 samples per location to cover different days and varying modes of incineration

Following analytes and groups of analytes are recommended:

- Hydrogenfluoride (HF)
- Chlorofluorocarbons (CFCs)
- Hydrochlorofluorocarbons (HCFCs)
- Hydrofluorocarbons (HFCs)
- Perfluorinated compounds (PFCs)

Sampling methods and analysis for HF, CFCs, HCFCs, HFCs and some PFCs (e.g. SF<sub>6</sub>, C<sub>2</sub>F<sub>6</sub>) are established and included in the proposed costs. Methods for sampling and analysis of some PFCs; e.g., TFE and HFP, are not commercially available and have to be developed.

Finally, a life cycle assessment of the imported fluoropolymers should be conducted to obtain more reliable estimates for the amount of fluoropolymers that is incinerated and hence the potential amount of greenhouse gases emitted due to fluoropolymer incineration. The incineration of Norwegian waste in other countries and the import and fate of international waste should be part of that study as well. The determined amounts may be used in an extrapolatory manner to estimate the total amount of the annually emitted amount of fluoro-containing gases in Norway. Further the amount of CCIF<sub>3</sub> (CFC-13), CF<sub>4</sub> (PFC-14), C<sub>2</sub>F<sub>6</sub> (PFC-116), and *c*-OFB (PFC-318) originating from fluoropolymer incineration must be related to the total national and global emissions of these compounds and other greenhouse gases, a topic which is beyond the scope of the present work.

## 9 References

- Acerboni, G., Beukes, J.A., Jensen, N.R., Hjorth, J., Myhre, G., Nielsen, C.J. and Sundet, J.K. (2001) Atmospheric degradation and global warming potentials of three perfluoroalkenes. *Atmos. Environ.*, 35, 4113-4123.
- Ameduri, B., Boutevin, B. and Kostov, G. (2001) Fluoroelastomers: synthesis, properties and applications. *Prog. Polym. Sci.*, 26, 105-187.
- Baker, Jr. B.B. and Kasprzak, D.J. (1993) Thermal degradation of commercial fluoropolymers in air. *Polym. Degrad. Stab.*, 42, 181-188.
- Bhadury, P.S., Singh, S., Sharma, M. and Palit, M. (2007) Flash pyrolysis of polytetrafluoroethylene (teflon) in a quartz assembly. *J. Anal. Appl. Pyrol.*, 78, 288-290.
- Blowers, P., Moline, D.M., Tetrault, K.F., Wheeler, R., Ronald, X. and Tuchawena, S.L. (2008) Global warming potentials of hydrofluoroethers. *Environ. Sci. Tech.*, 42, 1301-1307.
- Boucher, M., Ehmler, T. J. and Bermudez, A.J. (2000) Polytetrafluoroethylene gas intoxication in broiler chickens. *Avian Dis.*, 44, 449-453.
- Cadle, R.D. (1980) A comparison of volcanic with other fluxes of atmospheric trace gas constituents. *Rev. Geophys.*, 18, 746-752.
- Chen, D.M., Hsieh, W.H., Snyder, T.S., Yang, V., Litzinger, T.A. and Kuo, K.K. (1991) Combustion behavior and thermophysical properties of metal-based solid fuels. *J. Propul. Power*, 7, 250-257.
- Clarke, F.B., Vankuijk, H., Valentine, R., Makovec, G.T., Seidel, W.C., Baker, B.B., Kasprzak, D.J., Bonesteel, J.K., Janssens, M. and Herpol, C. (1992) The toxicity of smoke from fires involving perfluoropolymers: full-scale fire studies. *J. Fire Sci.*, 10, 488-527.
- Daikin Industries (2008) URL: <http://www.daikin.com/index.html>.
- Drobny, J.G. (2001) Technology of fluoropolymers. Boca Raton, CRC press LLC.
- Ebnesajjad S. (2008) Introduction to fluoropolymers. URL: <http://fluoroconsultants.com/sitebuildercontent/sitebuilderfiles/introductiontofluoropolymers.pdf>.
- Ellis, D.A. and Mabury, S.A. (2000) The aqueous photolysis of TFM and related trifluoromethylphenols. An alternate source of trifluoroacetic acid in the environment. *Environ. Sci. Tech.*, 34, 632-637.
- Ellis, D.A., Martin, J.W., Muir, D.C.G. and Mabury, S.A. (2003) The use of F-19 NMR and mass spectrometry for the elucidation of novel fluorinated acids and atmospheric fluoroacid precursors evolved in the thermolysis of fluoropolymers. *Analyst*, 128, 756-764.
- Ellis, D.A., Mabury, S.A., Martin, J.W. and Muir, D.C.G. (2001) Thermolysis of fluoropolymers as a potential source of halogenated organic acids in the environment. *Nature*, 412, 321-324.

- European Environment Agency (2008) Air pollution by ozone across Europe during summer 2007. Copenhagen, European Environment Agency (Technical report No 5/2008).
- Fluoropolymer Division (2007) Fpd material suppliers. URL: <http://www.fluoropolymers.org/index.htm>.
- Fluoropolymer Division (2008) URL: <http://www.fluoropolymers.org/index.htm>.
- Forbes, N.A. (1997) PTFE toxicity in birds. *Vet. Rec.*, 140, 512.
- Forster, P., Ramaswamy, V., Artaxo, P., Bernsten, T., Betts, R., Fahey, D.W., Haywood, J., Lean, J., Lowe, D.C., Myhre, G., Nganga, J., Prinn, R., Raga, G., Schulz, M. and, Van Dorland, R. (2007) Changes in atmospheric constituents and in radiative forcing. In: *Climate change 2007: The physical science basis. Contribution of Working Group I to the fourth assessment report of the Intergovernmental Panel on Climate Change*. Ed. by: Solomon, S. et al. Cambridge, United Kingdom and New York, NY, USA, Cambridge University Press. pp. 129-234.
- Francis, P., Burton, M.R. and Oppenheimer, C. (1998) Remote measurements of volcanic gas compositions by solar occultation spectroscopy. *Nature*, 396, 567-570.
- Frank, H., Christoph, E.H., Holm-Hansen, O. and Bullister, J.L. (2002) Trifluoroacetate in ocean waters. *Environ. Sci. Tech.*, 36, 12-15.
- Freedonia (2007) Fluoropolymers. US industry study with forecasts for 2001 & 2016. Cleveland, Freedonia Group.
- Garcia, A.N., Viciano, N. and Font, R. (2007) Products obtained in the fuel-rich combustion of PTFE at high temperature. *J. Anal. Appl. Pyrol.*, 80, 85-91.
- Gribble, G. (1995) Volcanic CFCs-response. *Environ. Sci. Tech.*, 29, A8-A8.
- Herzke, D. (1998) Polyfluorinated dibenzo-p-dioxines and benzofuranes: Synthesis, properties, analyses, formation and toxicology. Berlin, Technical University of Berlin.
- Herzke, D., Schlabach, M., Mariussen, E., Uggerud, H. and Heimstad, E. (2007) A literature survey on selected chemical compounds. Oslo, Norwegian Pollution Control Authority (TA-2238/2007).
- Hurley, M.D., Sulbaek Andersen, M.P., Wallington, T.J., Ellis, D.A., Martin, J.W. and Mabury, S.A. (2004) Atmospheric chemistry of perfluorinated carboxylic acids: reaction with OH radicals and atmospheric lifetimes. *J. Phys. Chem. A*, 108, 615-620.
- Inoguchi, Y. and Loechner, U. (2006) Fluoroelastomers. CEH marketing research report. SRI Consulting.
- IPPC (2001) Climate Change 2001: The scientific basis. Contribution of Working Group I to the third assessment report of the Intergovernmental Panel on Climate Change. Ed. by: Houghton, J.T. et al. Cambridge, United Kingdom and New York, NY, USA, Cambridge University Press.
- Johns, K. and Stead, G. (2000) Fluoroproducts - the extremophiles. *J. Fluor. Chem.*, 104, 5-18.

- Jordan, A. and Frank, H. (1999) Trifluoroacetate in the environment. Evidence for sources other than HFC/HCFCs. *Environ. Sci. Tech.*, *33*, 522-527.
- Key, B.D., Howell, R.D. and Criddle, C.S. (1997) Fluorinated organics in the biosphere. *Environ. Sci. Tech.*, *31*, 2445-2454.
- Kitahara, Y., Takahashi, S., Kuramoto, N., Šála, M., Tsugoshi, T., Sablier, M. and Fujii, T. (2009) Ion attachment mass spectrometry combined with infrared image furnace for thermal analysis: Evolved gas analysis studies. *Anal. Chem.*, *81*, 3155-3158.
- Ko, M.K.W., Sze, N.D., Rodríguez, J.M., Weistenstein, D.K., Heisey, C.W., Wayne, R.P., Biggs, P., Canosa-Mas, C.E., Sidebottom, H.W. and Treacy, J. (1994) CF<sub>3</sub> chemistry: potential implications for stratospheric ozone. *Geophys. Res. Lett.*, *21*, 101-104.
- Koch, E.C. (2002) Metal-fluorocarbon-pyrolants IV: Thermochemical and combustion behaviour of magnesium/teflon/viton (MTV). *Propellants, Explos., Pyrotec.*, *27*, 340-351.
- Mashino, M., Ninomiya, Y., Kawasaki, M., Wallington, T.J. and Hurley, M.D. (2000) Atmospheric chemistry of CF<sub>3</sub>CF=CF<sub>2</sub>: kinetics and mechanism of its reactions with OH radicals, Cl atoms, and ozone. *J. Phys. Chem. A*, *104*, 7255-7260.
- McCulloch, A. (2003) Fluorocarbons in the global environment: a review of the important interactions with atmospheric chemistry and physics. *J. Fluor. Chem.*, *123*, 21-29.
- OECD (2007) Report of an OECD workshop on perfluorocarboxylic acids (PFCAs) and precursors. Paris, OECD (ENV/JM/MONO(2007)11).
- Papadimitriou, V.C., Talukdar, R.K., Portmann, R.W., Ravishankara, A.R. and Burkholder, J.B. (2008) CF<sub>3</sub>CF[double bond, length as m-dash]CH<sub>2</sub> and (Z)-CF<sub>3</sub>CF[double bond, length as m-dash]CHF: temperature dependent OH rate coefficients and global warming potentials. *Phys. Chem. Chem. Phys.*, *10*, 808-820.
- Parker, M.P. (2006) The world market of fluoropolymers in primary forms: a 2007 global trade perspective. San Diego, Icon group international.
- Posner, S., Herzke, D., Poulsen, P.B. and Jensen, A.A. (2007) PFOA in Norway – Survey of national sources, 2007. Oslo, Norwegian Pollution Control Authority (TA-2354/2007).
- Powley, C.R., Michalczyk, M.J., Kaiser, M.A. and Buxton, L.W. (2005) Determination of perfluorooctanoic acid (PFOA) extractable from the surface of commercial cookware under simulated cooking conditions by LC/MS/MS. *Analyst*, *130*, 1299-1302.
- Richardson, M. (1991) Teflon toxicity from heat lamps. *J. Assoc. Avian Vet.*, *5*, 192.
- Ring, K.L., Kalin, T. and Kishi, A. (2002) Fluoropolymers. CEH marketing research report. SRI Consulting.
- Scheirs, J. (2001) Fluoropolymers: technology, markets and trends. Rapra industry analysis report. Rapra Technology.

- Scheirs, J. (1997) Modern fluoropolymers. Chichester, John Wiley & Sons.
- Scott, B.F., Macdonald, R.W., Kannan, K., Fisk, A., Witter, A., Yamashita, N., Durham, L., Spencer, C. and Muir, D.C.G. (2005) Trifluoroacetate profiles in the Arctic, Atlantic, and Pacific oceans. *Environ. Sci. Tech.*, 39, 6555-6560.
- SPIN (2008) SPIN Substances in Products in the Nordic Countries. URL: [www.spin2000.net](http://www.spin2000.net)
- Tobiesen, A. (2006) Assessment of information assessible on Teflon and degradation products of Teflon (Cas 9002-84-0). Oslo, SFT-NIVA (In Norwegian).  
URL: [http://www.sft.no/nyheter/dokumenter/teflon\\_miljorisiko\\_niva.pdf](http://www.sft.no/nyheter/dokumenter/teflon_miljorisiko_niva.pdf)
- The Society of the Plastics Industry (2005) The guide to the safe handling of fluoropolymer resins – fourth edition. Bp-101. Washington, SPI.
- Tuazon, E.C. and Atkinson, R. (1993) Tropospheric transformation products of a series of hydrofluorocarbons and hydrochlorofluorocarbons. *J. Atmos. Chem.*, 17, 179-199.
- Waritz, R.S. (1975) An industrial approach to evaluation of pyrolysis and combustion hazards. *Environ. Health Perspect.*, 11, 197-202.
- Will, R., Kaelin, T. and Kishi, A. (2005) Fluoropolymers. CEH marketing research report. SRI Consulting.
- Yamada, T., Taylor, P.H., Buck, R.C., Kaiser, M.A. and Giraud, R.H. (2005) Thermal degradation of fluorotelomer treated articles and related materials. *Chemosphere*, 61, 974-984.
- Zuev, V. V., Bertini, F. and Audisio, G. (2006) Investigation on the thermal degradation of acrylic polymers with fluorinated side-chains. *Polymer Degrad. Stabil.*, 91, 512-516.



## **Appendix 1 : Review of the SFT report on PTFE**



Review of the report "Miljøvurdering av miljøinformasjon vedrørende Teflon og nedbrytningsprodukter fra Teflon (Cas 9002-84-0)". Remarks are given in respect to the chapters of the report.

### **Background**

- Up-to-date produced amounts for Teflon and other fluoro- and chlorofluoropolymers are included in chapter 4.4 Production and consumption of fluoropolymers.

### **Emissions caused by the use of Teflon products**

- Additionally to Washburn's experiments another research group, which included also DuPont researchers, came to the same results that no PFOA is extractable during the cooking procedure with commercial cookware (Powley et al., 2005). How hot can cookware become by inobservant use? An in-vivo cooking study to check the extractable fluorinated amount by cooking different kind of meals with different lipid and water content could be interesting. But since only literature from major PTFE producers is available independent studies are needed to assess the total potential of PTFE to form hazardous degradation products.
- Depending on the fluoropolymer and finished product manufacturing conditions, it is theoretically possible that small quantities of residual gases, including perfluoroisobutylene (PFIB), hexafluoropropylene (HFP), tetrafluoroethylene (TFE) and hydrogenfluoride (HF) may be trapped and slowly evolve from resins as well as finished products. Testing some finished products has confirmed that PFIB and HFP can be found in the finished products, but the conditions under what these compounds form and in what quantities, has not been investigated. These 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 (The Society of the Plastic Industry, 2005).
- Heat lamp bulbs which are often used for animal breeding were found to be PTFE coated. The surface temperatures are around 200°C (Boucher et al., 2000). PTFE toxicosis from heat lamps has been reported in captive raptors (Forbes, 1997), birds at the San Antonio Zoo (Richardson, 1991), broiler chickens and on a duck research farm (Boucher et al., 2000).

### **Emissions caused by waste handling**

- 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 (HF), 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 (The Society of the Plastic Industry, 2005).

- As the PTFE temperature increases to approximately 450°C in air, carbonyl fluoride (COF<sub>2</sub>) and hydrogen fluoride (HF) become the main decomposition products. Carbonyl fluoride hydrolyzes rapidly in the presence of moist air to hydrogen fluoride and carbon dioxide (CO<sub>2</sub>). Small amounts of hexafluoropropylene (HFP) may also be found at these temperatures. The highly toxic chemical, perfluoroisobutylene (PFIB), has been detected as a minor product at temperatures above 475°C. When temperatures reach approximately 800°C, tetrafluoromethane begins to form (The Society of the Plastic Industry, 2005).
- Koch, 2002, could show that at 460°C an exothermal decomposition reaction accompanied by weight loss starts and is completed at approximately 610°C where all of the starting material has been consumed (100% weight loss). The constituents of the thermal decomposition reaction in air are mainly COF<sub>2</sub>, tetrafluoroethylene (C<sub>2</sub>F<sub>4</sub>) and difluorocarbene (CF<sub>2</sub>). In presence of humidity also hydrogen-containing products such as fluoroform (CHF<sub>3</sub>) and HF are formed. In addition thermal decomposition has been studied in vacuum. Under this condition the decomposition is an endothermic process yielding a mixture of the monomer and acyclic as well as cyclic fluorocarbons. Under argon gas the decomposition starts at 512°C and in nitrogen at 486°C. Similarly decomposition under inert atmosphere is an endothermic process yielding a similar product distribution as under vacuum. The distribution of PTFE decomposition products at temperatures between 727 and 472°C are CF<sub>2</sub> as major product, CF<sub>4</sub>, solid carbon (C<sub>8</sub>) and atomic fluorine. It has been found that release of gaseous products upon thermal treatment of PTFE may be suppressed by addition of nonvolatile basic compounds such as calcium hydroxide (Ca(OH)<sub>2</sub>) and sodium hydroxide (NaOH) (Boucher et al., 2000, Koch, 2002).
- In the “Guide to the Safe Handling of Fluoropolymer Resins” (The Society of the Plastic Industry, 2005) a regulatory information for waste disposal is advised. Preferred options are recycling and landfill. Incinerate only if the incinerator is fitted and permitted to scrub out HF and other acidic combustion gases.

#### **TFA**

- The environmental fate of TFA is adequately described. There are no new reports describing novel degradation pathways of TFA. TFA therefore still must be regarded as persistent.
- Volcanic emissions are reported to contain several fluoroorganic compounds, and a summary is provided by Gribble (Gribble 2002) and references therein. TFA is found at higher concentrations than what can be accounted for. Therefore TFA is believed to have a major non-anthropogenic source, but this has yet to be identified (Gribble 2002), although this is disputed (Ellis et al., 2001). One possible source is seafloor hydrothermal vents (Scott et al., 2005). In most cases, the identified compounds have not been quantified, thus it is difficult to estimate (except for HF) the volcanic contribution to the atmospheric content of fluoro- and fluorochloro-organic compound. However, considered the very large volumes of volcanic emissions, they cannot be

neglected and might exceed emissions caused by fluoropolymer-thermolysis considerably.

- The environmental effects of TFA towards plants and aquatic organisms are thoroughly described.

#### **Fate of degradation products of Teflon after pyrolysis ’**

The research group of Garcia et al (2007) carried out thermal degradation of PTFE in a horizontal tubular reactor. The influence of the temperature and the reaction atmosphere on the degradation products generated has been studied. Different runs (pyrolysis and fuel rich atmosphere) in the range 750–1050 °C were performed. In pyrolysis runs, only C<sub>2</sub>F<sub>4</sub> and C<sub>3</sub>F<sub>6</sub> as perfluorocarbon compounds were found. Under oxidative conditions, C<sub>2</sub>F<sub>6</sub>, C<sub>3</sub>F<sub>6</sub> and CF<sub>4</sub> were detected, varying their percentages as a function of temperature and oxygen proportion in the atmosphere. A low percentage of semivolatiles were also analyzed in all the cases studied, although only few fluorinated compounds were identified in this group.

- The atmospheric lifetimes of gaseous 1-4-carbon PFCAs and PFOA have been examined and are thought to be dependent on removal by wet and dry deposition rather than removal by reaction with hydroxyl radicals. Atmospheric lifetimes for gaseous PFOA of a few days to several weeks have been estimated.
- PFCAs resist degradation via oxidation, hydrolysis or reduction.

#### **Conclusions**

- The conclusion claiming that normal use of teflon lined cooking vessels do not emit hazardous compounds is supported.
- No additional data on waste incineration treatment plants and the forming of PTFE degradation gasses in these plants is available in the literature.



## **Appendix 2; List of Fluoropolymers**



Appendix II-I: List of fluoromono and -polymer compounds mainly used in the world marked.

Type	Chemical name	CAS No.	Chemical formula
<b><u>Fluoromonomers:</u></b>			
TrFE	trifluoroethylene	359-11-5	C <sub>2</sub> HF <sub>3</sub>
TFE	tetrafluoroethylene	116-14-3	CF <sub>2</sub> =CF <sub>2</sub>
TFP	3,3,3-trifluoropropylene	677-21-4	C <sub>3</sub> H <sub>3</sub> F <sub>6</sub>
HFP	hexafluoropropylene	9003-53-6	C <sub>3</sub> F <sub>6</sub>
HFPO	Hexafluoropropylene Oxide	428-59-1	C <sub>3</sub> F <sub>6</sub> -O
PFBE	perfluorobutylethylene	19930-93-4	C <sub>6</sub> H <sub>3</sub> F <sub>9</sub>
PVF	polyvinyl fluoride	24981-14-4	C <sub>2</sub> H <sub>3</sub> F
VDF, VF <sub>2</sub>	vinylidene fluoride	75-38-7	C <sub>2</sub> H <sub>2</sub> F <sub>2</sub>
PVDF	polyvinylidene fluoride	24937-79-9	(C <sub>2</sub> H <sub>2</sub> F <sub>2</sub> ) <sub>n</sub>
PMVE	perfluoromethyl vinyl ether	1187-93-5	C <sub>14</sub> H <sub>24</sub> O <sub>2</sub>
PEVE	perfluoroethyl vinyl ether	10493-43-3	C <sub>4</sub> H <sub>3</sub> F <sub>5</sub> O
PPVE	perfluoropropyl vinyl ether	1623-05-8	C <sub>5</sub> F <sub>10</sub> O
PSEPVE	Perfluoro-2-(2-fluorosulfonylethoxy) Propyl Vinyl Ether	16090-14-5	FSO <sub>2</sub> CF <sub>2</sub> CF <sub>2</sub> OCF(CF <sub>3</sub> )CF <sub>2</sub> OCF=CF <sub>2</sub>
EVE	Esther vinyl ether	63863-43-4	
CTFE	chlorotrifluoroethylene	79-38-9	C <sub>2</sub> ClF <sub>3</sub>
DFDCE	1,2-difluoro-1,2-dichloroethylene	598-88-9	C <sub>2</sub> Cl <sub>2</sub> F <sub>2</sub>
PCDFE	1,1-dichloro-2,2-difluoroethylene	79-35-6	C <sub>2</sub> Cl <sub>2</sub> F <sub>2</sub>
HFIB	hexafluoroisobutylene	382-10-5	C <sub>4</sub> H <sub>2</sub> F <sub>6</sub>
HFIBO	Hexafluoroisobutylene epoxide	31898-68-7	cyclo-C(CF <sub>3</sub> ) <sub>2</sub> CH <sub>2</sub> O-

Type	Chemical name	CAS No.	Chemical formula
<b><u>Fluoropolymers:</u></b>			
ETFE	Ethylene-tetrafluoroethylene copolymer	68258-85-5	$(\text{CF}_2\text{-CF}_2)_m\text{-(CH}_2\text{-CH}_2)_n$
ECTFE	ethylene-chlorotrifluoroethylene copolymer	25101-45-5	$[(\text{CH}_2\text{-CH}_2)_x\text{-(CFCl-CF}_2)_y]_n$
PCTFE	Polychlorotrifluoroethylene	9002-83-9	$(\text{CF}_2\text{-CFCl})_n$
FEP	tetrafluoroethylene-hexafluoropropylene copolymer	25067-11-2	$[(\text{CF}(\text{CF}_3)\text{-CF}_2)_x(\text{CF}_2\text{-CF}_2)_y]_n$
PFA	Perfluoroalkoxyethylene (perfluoroalkoxyalkane)	26655-00-5	$-(\text{CF}_2\text{-CF}_2)_m\text{-(CF}_2\text{-CF)}_n\text{-}$   ORf
PTFE	polytetrafluoroethylene	9002-84-0	$(\text{CF}_2\text{-CF}_2)_n$
EFEP	Copolymer of ethylene, TFE and HFP	25038-71-5	$[(\text{CH}_2\text{-CH}_2)_x\text{-(CF}_2\text{-CF}_2)_y(\text{CF}(\text{CF}_3)\text{-CF}_2)_z]_n$
TFE-P	Copolymer of TFE and propylene	-	
HTE	Copolymer of HFP, TFE and ethylene	-	
MTFA	methyltrifluoroacrylate	392-41-6	
TFMAA	$\alpha$ -(Trifluoromethyl) acrylic acid		
MFA	Copolymer of TFE and PMVE	957766-98-2	
THV	Terpolymer of TFE, HFP, VDF	25190-89-0	

Appendix II-II: This table lists the key fluoropolymers, reprocessed PTFE and melts, filled compounds, concentrates, coatings, and fluoroelastomers, plus the material suppliers and their trademarks (Fluoropolymer Division, 2007).

### FLUOROPOLYMERS

Code	Fluoropolymer Type	Supplier	Trade Name
PTFE	Polytetrafluoroethylene (Homopolymer of TFE)	<a href="#">AGC Chemicals Americas, Inc.</a>	Fluon®
		<a href="#">Daikin America, Inc.</a>	Daikin-Polyflon™
		<a href="#">DuPont</a>	Teflon®
		<a href="#">Dyneon</a>	Dyneon™
		<a href="#">Flontech USA LLC</a>	Flontech®
		<a href="#">Heroflon USA</a>	Heroflon™
		<a href="#">KC America</a>	FluoroPlast™
FEP	Fluorinated ethylene-propylene (Copolymer of TFE and HFP)	<a href="#">Daikin America, Inc.</a>	Neoflon™
		<a href="#">DuPont</a>	Teflon®
		<a href="#">Dyneon</a>	Dyneon™
		<a href="#">KC America</a>	FluoroPlast™
PFA	Perfluoroalkoxy (Copolymer of TFE and PPVE)	<a href="#">Whitford Corp.</a>	Dykor®
		<a href="#">AGC Chemicals Americas, Inc.</a>	Fluon®
		<a href="#">Daikin America, Inc.</a>	Neoflon™
		<a href="#">DuPont</a>	Teflon®
MFA	Copolymer of TFE and PMVE	<a href="#">Dyneon</a>	Dyneon™
		<a href="#">Solvay Solexis</a>	Hyflon®
		<a href="#">Whitford Corp.</a>	Dykor®
		<a href="#">KC America</a>	FluoroPlast™
PCTFE	Polychlorotrifluoroethylene (Homopolymer of CTFE)	<a href="#">Daikin America, Inc.</a>	Neoflon™
PVDF	Polyvinylidene fluoride  (Homopolymers of VF2) (Copolymers of VF2 and HFP) Homopolymers & Copolymers  (Homopolymers of VF2)	<a href="#">Solvay Solexis</a>	Hylar®, Hylar 5000®
		<a href="#">Dyneon</a>	Dyneon™
		<a href="#">Arkema Inc.</a>	Kynar®, Kynar 500®
		<a href="#">Arkema Inc.</a>	Kynar Flex®, Kynar Powerflex®
		<a href="#">Solvay Solexis</a>	Solef® PVDF
PVF	Polyvinyl fluoride	<a href="#">Dyneon</a>	Dyneon™
		<a href="#">Whitford Corp.</a>	Dykor®
ETFE	Ethylene tetrafluoroethylene (Copolymer of TFE & ethylene)	<a href="#">DuPont</a>	Tedlar®
		<a href="#">AGC Chemicals Americas, Inc.</a>	Fluon®
		<a href="#">Daikin America, Inc.</a>	Neoflon™
ECTFE	Ethylene chlorotrifluoroethylene	<a href="#">DuPont</a>	Tefzel®
		<a href="#">Dyneon</a>	Dyneon™
THV	Terpolymer of TFE, HFP, VF2	<a href="#">Solvay Solexis</a>	Halar®
Micropowders & Additives	Low Molecular Wt. PTFE, FEP	<a href="#">Dyneon</a>	Dyneon™
		<a href="#">AGC Chemicals Americas, Inc.</a>	Fluon®
	<a href="#">Solvay Solexis</a>	Algoflon®, Polymist®	
	<a href="#">Daikin America, Inc.</a>	Daikin-Polyflon™	
	<a href="#">Dyneon</a>	Dyneon™, Dynamar™	
Lube Powders	Low Molecular Weight PTFE	<a href="#">DuPont</a>	Zonyl® Fluoroadditives
		<a href="#">DuPont Dow Elastomers</a>	Viton Free Flow®
	Polytetrafluoroethylene	<a href="#">Heroflon USA</a>	Heroflon™
		<a href="#">Shamrock Technologies</a>	SST™

Code	Fluoropolymer Type	Supplier	Trade Name
Reprocessed Melts	Repelletized fluoropolymer melts	<a href="#">Jeneet, Inc.</a>	
Filled Compounds	PTFE with various fillers	<a href="#">AGC Chemicals Americas, Inc.</a> <a href="#">Dyneon</a> <a href="#">Flontech USA LLC</a> <a href="#">Heroflon USA</a> <a href="#">Solvay Solexis</a>	Fluon® Dyneon™ Flontech® Heroflon™ Algoflon®
Color Concentrates		<a href="#">AGC Chemicals Americas, Inc.</a> <a href="#">Chromatics</a>	Fluon®
Foam Concentrates		<a href="#">AGC Chemicals Americas, Inc.</a> <a href="#">Chromatics</a>	Fluon®
Coatings (Powders & Formulations)	ETFE, PFA PTFE, PFA, MFA PVDF PTFE dispersions FEP, PFA, ETFE PTFE, FEP, PFA, & ETFE patented blends  ECTFE, MFA, PFA, PVDF PFA, PVDF, PPS coating powders PTFE dispersions Reinforced PTFE coatings	<a href="#">AGC Chemicals Americas, Inc.</a> <a href="#">Akzo Nobel Non-Stick Coatings</a> <a href="#">Arkema Inc.</a> <a href="#">Dyneon</a> <a href="#">Daikin America, Inc.</a> <a href="#">DuPont Finishes</a>  <a href="#">DuPont Finishes</a> <a href="#">Solvay Solexis</a> <a href="#">Whitford Corp.</a> <a href="#">Whitford Corp.</a> <a href="#">Whitford Corp.</a>	Fluon® Chemlon®, Matrix®, Skandia®, Tri-Tanium®, Ceram®, Marlite® Kynar®, Kynar 500® Dyneon™ Neoflon™ Teflon®, Autograph®, Teflon® FEP, PFA, ETFE powder, Teflon-S® powder, Teflon® PTFE & ETFE primers Teflon® PTFE liquids, Teflon® FEP, PFA, ETFE liquids Teflon-S® One Coat primer liquids Halar®, Hyflon®, Hylar®, Solef® Dykor® 800 Series Xylan®, Xylan Plus®, Eclipse®, Excalibur® & Quantum™ Quantum 2™, QuanTanium®

#### FLUROELASTOMERS

Code	Fluoroelastomer Type	Supplier	Trade Name
	Copolymers of VF2 and HFP	<a href="#">Dyneon</a> <a href="#">Daikin America, Inc.</a> <a href="#">DuPont Dow Elastomers</a> <a href="#">Solvay Solexis</a>	Dyneon™ Dai-el™ Viton® Tecnoflon®
	Terpolymers of VF2, HFP, & TFE	<a href="#">Daikin America, Inc.</a> <a href="#">Dyneon</a> <a href="#">DuPont Dow Elastomers</a> <a href="#">Solvay Solexis</a>	Dai-el™ Dyneon™ Viton® Tecnoflon®
	Copolymers of TFE and propylene	<a href="#">AGC Chemicals Americas, Inc.</a> <a href="#">Dyneon</a>	AFLAS® (TM of Asahi Glass) Dyneon™
	Copolymers of TFE & perfluorinated vinyl ethers	<a href="#">Daikin America, Inc.</a> <a href="#">DuPont Dow Elastomers</a> <a href="#">Solvay Solexis</a>	Dai-el Perfluor™ Kalrez®, Zalak® Tecnoflon®
	Terpolymers of TFE, propylene, VF2	<a href="#">AGC Chemicals Americas, Inc.</a> <a href="#">Dyneon</a>	AFLAS® (TM of Asahi Glass) Dyneon™
	Thermoplastic elastomers	<a href="#">Daikin America, Inc.</a>	Dai-el Thermoplastics™

**Appendix 3: List of intermediates produced by  
Daikin (Daikin Industries, 2008).**



Category	Chemical name	Structure	CAS No.	ENCS	EINECS	TSCA
ALCOHOLS	1H,1H,5H-octafluoropentanol	$H(CF_2)_4CH_2OH$	355-80-6	2-285	206-593-4	355-80-6
	2,2-bis(trifluoromethyl)propanol	$(CF_3)_2C(CH_3)CH_2OH$	2927-17-5	---	---	---
	2,2,3,3,3-pentafluoropropanol	$CF_3CF_2CH_2OH$	422-05-9	2-3364	207-012-7	422-05-9
	1H,1H,9H-hexadecafluorononanol	$H(CF_2)_8CH_2OH$	376-18-1	2-286	206-806-0	376-18-1
CARBOXYLIC ACID	7H-dodecafluoroheptanoyl chloride	$H(CF_2)_6COCl$	41405-35-0	2-3425	---	---
	trifluoroacetic acid anhydride	$(CF_3CO)_2O$	407-25-0	2-1187	206-982-9	407-25-0
	ethyl trifluoroacetate	$CF_3CO_2C_2H_5$	383-63-1	2-3532	206-851-6	383-63-1
IODIDES	perfluoroethyl iodide	$CF_3CF_2I$	354-64-3	---	206-566-7	354-64-3
	2-(perfluorooctyl)ethyl iodide	$F(CF_2)_8CH_2CH_2I$	2043-53-0	---	218-053-5	2043-53-0
	heptafluoro-2-iodopropane	$(CF_3)_2CFI$	677-69-0	---	211-643-3	677-69-0
	perfluorooctyl iodide	$F(CF_2)_8I$	507-63-1	2-90	208-079-5	507-63-1
	hexadecafluoro-1,8-diiodooctane	$I(CF_2)_8I$	335-70-6	---	---	---
	dodecafluoro-1,6-diiodohexane	$I(CF_2)_6I$	375-80-4	---	206-794-7	---
OLEFINS	(perfluorooctyl)ethylene	$F(CF_2)_8CH=CH_2$	21652-58-4	2-3594*	244-503-5	---
	chlorotrifluoroethylene	$CF_2=CFCl$ (CTFE)	79-38-9	2-113	201-201-8	---
	hexafluoropropene	$CF_3CF=CF_2$ (HFP)	116-15-4	2-116	204-127-4	116-15-4
METHACRYLATES	2,2,3,3,3-pentafluoropropyl methacrylate	$CF_3CF_2CH_2OOC C(CH_3)=CH_2$	45115-53-5	2-1031	256-191-8	45115-53-5
	2,2,3,3-tetrafluoropropyl methacrylate	$H(CF_2)_2CH_2OOC C(CH_3)=CH_2$	45102-52-1	2-1031	256-189-7	---
	2,2,2-trifluoroethyl methacrylate	$CF_3CH_2OOC C(CH_3)=CH_2$	352-87-4	2-1031	206-525-3	352-87-4
	3-(perfluoro-5-methylhexyl)-2-hydroxypropyl methacrylate	$(CF_3)_2CF(CF_2)_4CH_2CH(OH)CH_2OOC C(CH_3)=CH_2$	16083-81-1	---	---	---
EPOXIDES & ETHERS	3-perfluorooctyl-1,2-epoxypropane	$F(CF_2)_8CH_2CH-CH_2$ 	38565-53-6	---	254-006-5	---
	hexafluoropropene oxide	HFPO 	428-59-1	2-3337	207-050-4	428-59-1
HALOALKANES	chlorodifluoromethane	$CHClF_2$ (R-22)	75-45-6	2-93	200-871-9	75-45-6
	bromofluoromethane	$CH_2BrF$ (31 B1)	373-52-4	---	---	---
	dibromofluoromethane	$CHBr_2F$ (21 B2)	1868-53-7	---	---	---
OTHERS	2,2-bis(4-hydroxyphenyl)hexafluoropropane	BisAF 	1478-61-1	4-1335	216-036-7	---
	2,2-bis(3,4-anhydrodicarboxyphenyl)hexafluoropropane	6FDA 	1107-00-2	---	214-170-0	1170-00-2
	hexafluoroacetone	$CF_3COCF_3$	684-16-2	2-581	211-676-3	684-16-2
	1,1,2,3,3,3-hexafluoro-1-diethylamino-propane	$CF_3CHFCF_2N(C_2H_5)_2$	309-88-6	---	---	---





REFERENCE: O-1080990-108099  
DATE: 14.12.2009  
ISBN: 978-82-425-2085-2 (printed)  
978-82-425-2086-9 (electronic)

NILU is an independent, nonprofit institution established in 1969. Through its research NILU increases the understanding of climate change, of the composition of the atmosphere, of air quality and of hazardous substances. Based on its research, NILU markets integrated services and products within analyzing, monitoring and consulting. NILU is concerned with increasing public awareness about climate change and environmental pollution.

REFERENCE: O-108099  
DATE: 14.12.2009  
ISBN: 978-82-425-2085-2 (printed)  
978-82-425-2086-9 (electronic)

NILU is an independent, nonprofit institution established in 1969. Through its research NILU increases the understanding of climate change, of the composition of the atmosphere, of air quality and of hazardous substances. Based on its research, NILU markets integrated services and products within analyzing, monitoring and consulting. NILU is concerned with increasing public awareness about climate change and environmental pollution.



Norsk institutt for luftforskning  
Norwegian Institute for Air Research