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Assessment of Fluoropolymer Production and Use With Analysis of Alternative Replacement Materials



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SAVANNAH RIVER NATIONAL LABORATORY



Duke



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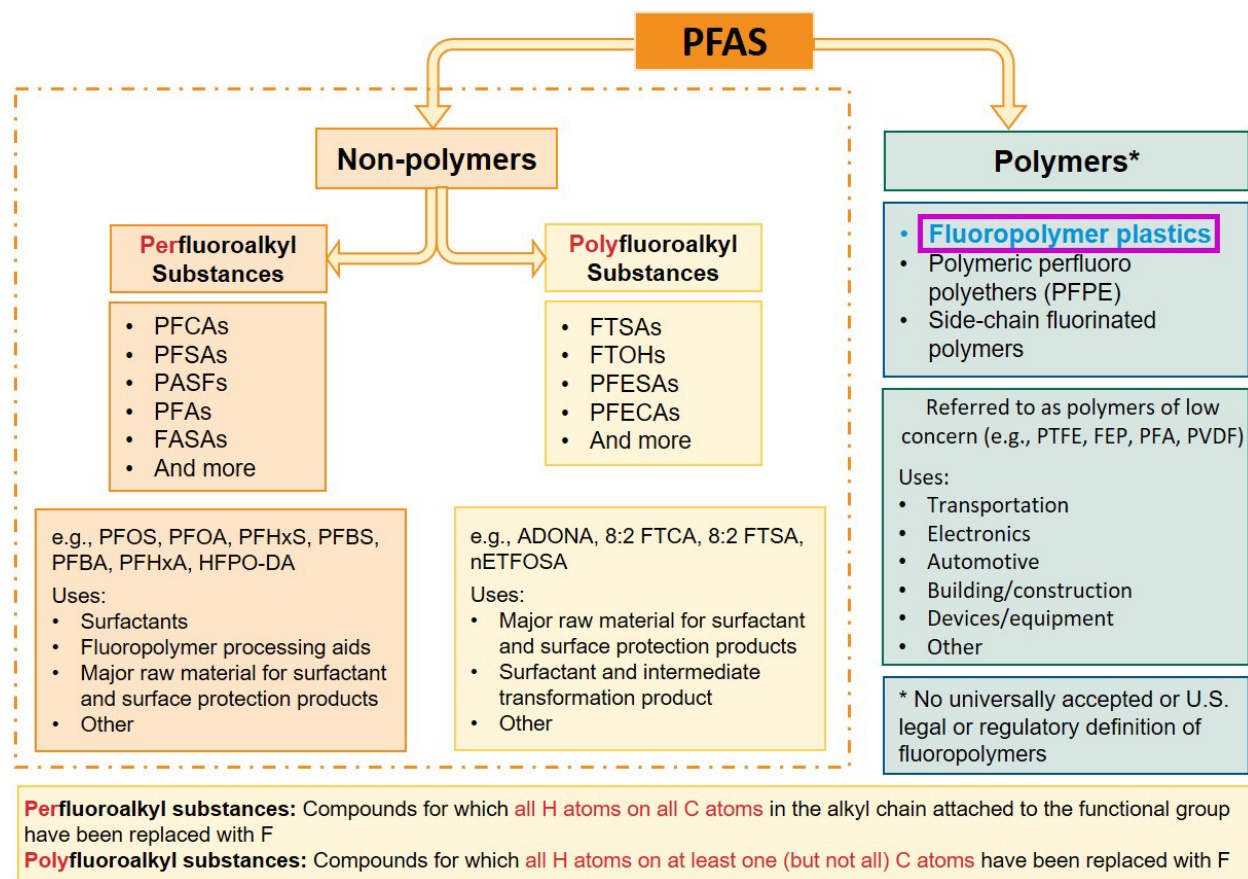
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EXECUTIVE SUMMARY

This report focuses on fluoropolymers, which are a subgroup of the much larger class of fluorinated chemicals known as per- and polyfluoroalkyl substances (PFAS). Clearly distinguishing fluoropolymers is important to understanding their distinctive chemical properties, associated risks and benefits, and roles in commerce. In this report, the factors that are considered in a lifecycle assessment (LCA) of fluoropolymers will be discussed. These include the manufacturing of fluoropolymers, their use in industry, and available replacement technologies. Emphasis is placed on fluoropolymer plastics because of their extensive use in the commerce sectors considered here, specifically aerospace, automotive, battery, building construction, chemical processing, electronics, infrastructure, semiconductor, solar panel, and wind energy industries.

The thousands of individual PFAS that have been developed divide into two classes: non-polymeric PFAS, consisting of a single unit (monomer), and polymeric PFAS, consisting of a chain of smaller repeating units (Figure ES-1). Non-polymeric PFAS (single molecule PFAS) are further divided into perfluoroalkyl and polyfluoroalkyl substances. These non-polymeric PFAS have a relatively small molecular weight and particle size. Extensive use of non-polymeric PFAS, such as the aqueous film-forming foam (AFFF) used for firefighting, has resulted in environmental contamination. Non-polymeric PFAS also are often used in the production of polymeric PFAS, including fluoropolymers. Non-polymeric PFAS are persistent and mobile in a variety of media, including water, air, soils, and sediments. This mobility increases the dispersion of non-polymeric PFAS in the environment and can lead to concerns about biological uptake and accumulation in plants and animals, with potential human health impacts.

Recent scientific and public concern has focused on the commercial use and fate of non-polymeric PFAS (e.g., perfluorooctane sulfonic acid [PFOS] and perfluorooctanoic acid [PFOA]) and the potential release of low molecular weight non-polymeric PFAS during the life cycle of polymeric PFAS.



Source: ITRC, 2022, “PFAS — Per- and Polyfluoroalkyl Substances,” Report No. PFAS-1, Interstate Technology and Regulatory Council, Washington, D.C.

Figure ES-1. Per- and Polyfluoroalkyl Substances Family Tree and Classification

PFAS, including fluoropolymers, are a research priority of federal health and environmental agencies, including the Agency for Toxic Substances and Disease Registry,¹ Centers for Disease Control and Prevention,² U.S. Environmental Protection Agency,³ National Institute of Environmental Health Sciences,⁴ and National Institute for Occupational Safety and Health.⁵ However, the environmental fate and impacts of non-polymeric and polymeric PFAS (not identified as fluoropolymers) are beyond the scope of this study.

¹ ATSDR, 2023, “Per- and Polyfluoroalkyl Substances (PFAS) and Your Health: Pease Study,” Agency for Toxic Substances and Disease Registry, Atlanta, Georgia.

² CDC, 2022, “Per- and Polyfluorinated Substances (PFAS) Factsheet,” Centers for Disease Control and Prevention, Atlanta, Georgia.

³ EPA, 2023a, “Increasing Our Understanding of the Health Risks from PFAS and How to Address Them,” U.S. Environmental Protection Agency, Washington, D.C.

⁴ NIEHS, 2023, “PFAS Research,” National Institute of Environmental Health Sciences, Durham, North Carolina.

⁵ NIOSH, 2022, “Per- and polyfluoroalkyl substances (PFAS),” National Institute for Occupational Safety and Health, Washington, D.C.; <https://www.cdc.gov/niosh/topics/pfas>.

Fluoropolymers include three subgroups of polymerized PFAS that are high molecular weight polymers and copolymers⁶ that consist of a carbon backbone with fluorine atoms directly bonded to the carbon atoms. Fluoropolymers are generally not soluble in water. The other two subgroups of polymerized PFAS include oligomeric⁷ perfluoropolyether (PFPE) compounds (used largely as chemically resistant lubricant oils and greases) and side-chain fluorinated polymers (used for surface protection and coatings mainly in fabrics, textiles, and apparel articles, and for food contact paper and paperboard). There is no globally accepted definition of either PFAS or the fluoropolymer subgroup, which challenges clarity in attribution of potential benefits, impacts, and controls; however, in this report, the discussion is focused on fluoropolymer plastics (as defined in Section 3.0⁸), which are considered distinct from fluorinated side-chain polymers and oligomeric PFPEs because of differing structural properties and uses. Oligomeric PFPEs contain a carbon and oxygen polymer backbone, with fluorine atoms directly attached to the carbon atoms. Side-chain fluorinated polymers branch off of a non-fluorinated polymer backbone. Due to their molecular structure, fluoropolymer plastics have unique physical and chemical properties that have led to wide-spread integration into many sectors of modern commerce, including aerospace, automotive, chemical processes and storage, infrastructure, solar and wind energies, electronics, and many others. Fluoropolymer plastics are emphasized in this report because of the overlap among the sectors of interest for this report and typical fluoropolymer uses.

Fluoropolymers can be chemically modified to optimize properties for specific applications, and many of these formulas are proprietary. Several fluoropolymers widely used in commerce include polytetrafluoroethylene (PTFE, also known as Teflon⁹), polychlorotrifluoroethylene (PCTFE), fluorinated ethylene propylene (FEP), polyvinyl fluoride (PVF), perfluoroalkoxy (PFA), ethylene tetrafluoroethylene (ETFE), ethylene chlorotrifluoroethylene (ECTFE), Nafion,¹⁰ and polyvinylidene fluoride (PVDF).

Table ES-1 and Table ES-2 summarize fluoropolymer properties and uses. Fluoropolymers are thermally and chemically stable, electrically non-conductive, flame retardant, and water-repellent, making them useful in a wide range of applications. Fluoropolymers can also be used in multiple forms, including as lubricants, coatings, sheeting, and additives. As an example of their versatility, fluoropolymers can be found in the coating on electrical wiring, seals and gaskets, fuel lines, and anti-vandal paint. Fluoropolymers are also used in tank and piping liners, valves, pumps, and personal protective equipment; their non-stick and weather resistance properties are also desirable in these applications. The unique properties of fluoropolymers make them long-lasting, stable, and resistant to chemical or biological breakdown, while still being light-weight and adaptable. Fluoropolymers enhance the durability, safety, and longevity of a wide range of products. Some applications use multiple fluoropolymers or fluoropolymers blended with other fluorinated or non-fluorinated polymers.

⁶ In this report, terpolymers (i.e., those copolymers obtained from three monomers) are grouped in the copolymer class.

⁷ Oligomers comprise the same monomers as polymers, but their chain is much shorter.

⁸ In the context of this report, fluoropolymer plastics include both thermoplastic (rigid materials formed by heating or machining) and elastomeric (flexible material) forms and refer to water-insoluble, solid-state materials (either hard or soft), composed of fluoropolymers and useful for fabrication of physical articles.

⁹ Teflon is a registered trademark of The Chemours Company FC, LLC (formally DuPont), Wilmington, Delaware.

¹⁰ Nafion is trademark of The Chemours Company FC, LLC (formerly DuPont), Wilmington, Delaware.

Table ES-1. Typical Applications of Fluoropolymers for Different Industry Sectors

Industries	Functions	Forms
Automotive	Mechanical property, thermal property, chemical property, and friction property	O-rings, gaskets, valve stem seals, shaft seals, linings for fuel hoses, power steering, and transmission
Chemical	Chemical resistance, mechanical property, thermal property, and weather stability	Coatings for heat exchangers, pumps, diaphragms, impellers, tanks, reaction vessels, autoclaves, containers, flue duct expansion joints, and heavy-wall solid pipe and fittings
Electrical/electronic	Dielectric constant, flame resistance, and thermal stability	Electrical insulation, flexible printed circuits, ultra-pure components for semiconductor manufacture
Architectural and domestic	Weatherability, flame retardancy, friction property, thermal stability	Water-repellent fabric, architectural fabric, non-stick coatings for cookware, and fiberglass composite for construction
Engineering	Mechanical property, thermal stability, chemical stability, weatherability, and surface energy	Seats and plugs, bearings, non-stick surfaces, coatings for pipes, fittings, valve and pump parts, and gears
Medical	Surface energy, biological stability, mechanical property, chemical resistance	Cardiovascular grafts, ligament replacement, and heart patches

Source: Teng, H., 2012, "Overview of the Development of the Fluoropolymer Industry," *Applied Sciences*, 2(2), pp 496–512.

Alternative materials and technologies have been identified for some specific uses of fluoropolymers. However, because of the combination of beneficial properties of fluoropolymers, no alternatives have been identified that could replace fluoropolymers in many, or over a broad range, of applications in the sectors considered in this report. As industry research and development and commercial pilot projects progress, substitutes for fluoropolymers in additional applications may be developed.¹¹

¹¹ Toloken, S., 2023, "An 'enormous' push to find PFAS replacements in manufacturing," *Plastics News*, Detroit, Michigan.

Table ES-2. Selected Fluoropolymers and Example Uses for Sectors of Interest

Industries end uses	Transportation		Chemical		Telecommunications		Infrastructure construction and architecture	Renewable energy		
	Auto-motive	Aero-space	Oil and gas	Chemical process industry (CPI)	Electronics and semiconductors	Internet and wireless communications		Energy production	Hydrogen production	Energy storage
Fluoropolymer Thermoplastics										
PTFE	•	•	•	•	•	•	•	•	•	•
ETFE	•	•	•	•	•	•	•	•		•
FEP	•	•	•	•	•			•		
PFA	•	•	•	•	•			•		
PVDF homopolymer	•	•	•	•	•	•	•	•	•	•
PVDF copolymer	•	•		•	•	•	•		•	•
ECTFE copolymer		•	•	•	•	•	•			
ECTFE terpolymer			•	•						
PCTFE		•			•					
FEVE	•	•			•		•			
EFEP	•			•	•					
CPT	•				•					
THV	•	•		•	•		•	•		•
Fluoropolymer Elastomers										
FEPM	•	•	•	•	•		•	•		
FKM	•	•	•	•	•		•	•	•	•
FFKM		•	•	•	•					
Specialty Fluoropolymers										
Amorphous		•		•	•	•			•	•
Ionomer	•			•	•			•	•	•

Source: Based on Henry et al., 2018, “A critical review of the application of polymer of low concern and regulatory criteria to fluoropolymers,” and Korzeniowski et al., 2023, “A critical review of the application of polymer of low concern regulatory criteria to fluoropolymers II: Fluoroplastics and fluoroelastomers,” *Integrated Environmental Assessment and Management*.

CPT	= chlorotrifluoroethylene-perfluoroalkoxy-tetrafluoroethylene.	FEVE	= fluoroethylene-vinyl ether.
ECTFE	= ethylene chlorotrifluoroethylene.	FFKM	= TFE-PMVE perfluoroelastomer.
EFEP	= ethylene-tetrafluoroethylene-hexafluoropropylene.	FKM	= fluorine Kautschuk material.
ETFE	= ethylene tetrafluoroethylene.	PCTFE	= polychlorotrifluoroethylene.
FEP	= fluorinated ethylene propylene.	PFA	= perfluoroalkoxy polymer.
FEPM	= trifluoroethylene-propylene copolymer.	PTFE	= polytetrafluoroethylene.
		PVDF	= polyvinylidene fluoride.
		THV	= TFE-HFP-VF2.

A life cycle assessment of every fluoropolymer is not practical because of the variety of fluoropolymers and the large number of applications for each type of fluoropolymer. While a quantitative comparative life cycle assessment of a limited number of important fluoropolymers and their alternatives would be useful, it is instructive to consider, as done in this report, specific phases of the life cycle of fluoropolymers and identify the most important potential routes for environmental releases, exposures, and adverse impacts.

The most important life cycle phases of fluoropolymers are production, use, recycling, and disposal:

- **Production** – Non-polymeric PFAS polymerization aids are nonreactive additives that are used in fluoropolymer synthesis. In some fluoropolymers, the non-polymeric PFAS act as raw materials. During fluoropolymer synthesis, most of the polymerization aid is recycled or recovered, with the remaining fraction of non-polymeric PFAS being emitted or disposed of with the effluent wastewater or waste. Typical polymerization aids used in industry are PFOA, perfluorononanoic acid (PFNA), and hexafluoropropylene oxide dimer acid (HFPO-DA).

A very low concentration of the processing aid is likely to remain incorporated with the fluoropolymer and may be emitted during downstream processing (parts forming or coatings) or use. Use of fluorinated processing aids has resulted in environmental releases and contamination proximate to production sites. Current and evolving fluoropolymer production has focused on reducing or eliminating the use of PFAS as processing aids and placing stringent controls on remaining non-polymeric PFAS as part of fluoropolymer production. Monitoring and discharge limits at wastewater treatment plants have also resulted in reductions in the quantities of PFAS released to the environment from production processes.

- **Use** – Residual, non-polymeric PFAS present in fluoropolymers from incomplete separation of processing aids during production may be leached from fluoropolymers in contact with water or other liquids; however, water or liquid contact does not occur during many fluoropolymer uses. Reduction or elimination of the use of fluorinated polymerization aids and increased focus on minimizing residual non-polymeric PFAS present in fluoropolymers should reduce or eliminate release of non-polymeric PFAS during use. The formation and environmental transport of fluoropolymer microplastics during fluoropolymer use in outdoor applications with potentially abrasive conditions (e.g., external building or solar panel coatings) and the presence of microplastic fluoropolymers in environmental systems (e.g., surface waters or biota) have not been studied.
- **Recycling** – Recycling of fluoropolymers in most circumstances is impractical because the fluoropolymer is embedded in a product and not readily separated as an initial recycling processing step. In cases where fluoropolymer recycling is practical (e.g., with scrap from forming products), non-polymeric PFAS formed during material softening by irradiation subsequently may be volatilized during processing or released through water contact.
- **Disposal** – Because recycling of fluoropolymers is often impractical, landfilling is frequently used. Studies examining the release of non-polymeric PFAS from landfills are confounded by the range of products and waste disposed of, which contain an unknown quantity and range of non-polymeric and polymeric PFAS in addition to fluoropolymers; thus, source attribution has not been possible. Studies examining the fate of fluoropolymers during incineration have been limited to analysis of a European rotary kiln pilot-scale incinerator, which indicated absence of PFAS in the exhaust gas. However, the primary combustion chamber was not representative of municipal solid waste incinerators in the U.S., which typically have less efficient moving grate combustion chambers, and therefore, the potential for PFAS residuals in the bottom ash from incomplete combustion is unknown.

The life cycle and cost-benefit understanding of fluoropolymers is at an early stage and still rapidly evolving. Industrial research and development into possible replacements of fluoropolymers is relatively recent, as is public health and environmental research into the impacts of fluoropolymers. Robust findings take many years to develop, even when prioritized by the government and private sector.

Carrying out an exhaustive cost-benefit analysis of removing fluoropolymers from the U.S. supply chain and replacing them with alternative materials presents several practical limitations. Fluoropolymers are used in thousands of end-use applications, and potential trade-offs would need to be considered for a significant number of those applications. In many instances, necessary data are not publicly available. However, much insight could be gained from well-done life cycle assessment and cost-benefit analysis case studies on a limited number of important fluoropolymers and alternatives. The barriers to overcome are the lack of detailed quantitative information on fluoropolymer production, use, and benefits in specific applications, and the associated environmental and public health impacts in the different stages of the life cycle. Similarly, getting access to analogous comprehensive information on substitute materials if used in the same applications is challenging. In addition, such case studies would likely require access to proprietary data about fluoropolymers, alternatives, and applications to be evaluated.

Removing fluoropolymers generally or from specific uses could lead to increased costs, not only in terms of raw material and manufacturing but also from equipment modifications and maintenance and compliance with or revision of industry standards. A transition to fluoropolymer alternatives may necessitate expensive retrofitting of existing infrastructure and machinery. In addition, restrictions in use of fluoropolymers may result in the loss of technological advances and innovation (e.g., in semiconductor and microelectronics production, and miniaturization and durability of products). With fluoropolymers playing an increasingly important role in the clean energy transition, efforts to replace fluoropolymers need to be studied carefully for effectiveness and affordability.

Overall, the key challenges and knowledge gaps in evaluating the comparative life cycle and cost-benefits of fluoropolymers versus alternative materials include the following:

- Limited number of alternative materials and technologies that provide acceptable performance as substitutes for fluoropolymers
- Lack of publicly available data on the life cycle of fluoropolymers and consequences of using alternative materials and processes
- Very limited amount of information on the environmental releases of fluoropolymer microplastics and non-polymeric PFAS during fluoropolymer production, product use, disposal, and recycling
- Lack of sufficient knowledge of the exposure pathways, fate and transport in the environment, and subsequent public health and environmental impacts of different fluoropolymers
- Lack of publicly available economic information regarding the supply chains, production, and use of fluoropolymers and alternatives
- Lack of transparency on fluoropolymer production processes used in other countries and the resulting impurities in materials that subsequently enter the U.S. supply chain (e.g., when non-polymeric PFOA is being used as the polymerization aid and may be released during subsequent end-product forming, use and disposal).

Importantly, the absence of clarity and agreement on the definition of the category of fluoropolymers confounds discourse and resolution of concerns associated with the materials.

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LIST OF ABBREVIATIONS

3D	three-dimensional
Å ³	cubic angstrom
ACA	American Coatings Association
ACM	acrylic rubber
ADONA	trade name for 4,8-dioxa-3H-perfluorononanoate
AEM	ethylene acrylic elastomer
AF	amorphous fluoropolymer
AFFF	aqueous film-forming foam
AGC	AGC Inc. (formerly Asahi Glass Co., Ltd.)
AiT	AI Technology Inc.
APFN	ammonium perfluorononanoate
APFO	ammonium perfluorooctanoate
ATSDR	Agency for Toxic Substances and Disease Registry
BA	Bachelor of Arts
BAE	Biosystems and Agricultural Engineering
BCEEM	Board-Certified Environmental Engineering Member
BE	Bachelor of Engineering
BS	Bachelor of Science
C	carbon
C ₂ F ₄	tetrafluoroethylene
CAGR	compound annual growth rate
CAS	Chemical Abstracts Service
CBA	cost-benefit analysis
CDC	Centers for Disease Control and Prevention
CED	cumulative energy demand
CEH	Chemical Economics Handbook
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
CF	characterization factor
CH ₄	methane
Chemours	The Chemours Company FC, LLC
CITS	Center for International Trade and Security
CMAQ	Community Multiscale Air Quality
CMC	carboxymethyl cellulose
CO ₂	carbon dioxide
CPI	chemical process industry
CPT	chlorotrifluoroethylene-perfluoroalkoxy-tetrafluoroethylene
CPVC	chlorinated polyvinyl chloride
CRESP	Consortium for Risk Evaluation with Stakeholder Participation
CST	crystalline silicotitanate

CTFE	chlorotrifluoroethylene
Da	dalton
DEQ	Department of Environmental Quality
DOD	U.S. Department of Defense
DOE	U.S. Department of Energy
DOE-EHSS	U.S. Department of Energy, Office of Environment, Health, Safety and Security
DOE-EM	U.S. Department of Energy, Office of Environmental Management
DOECAP-AP	Department of Energy Consolidated Audit Program – Accreditation Program
ECHA	European Chemicals Agency
ECTFE	ethylene chlorotrifluoroethylene
EFEP	ethylene-tetrafluoroethylene-hexafluoropropylene
EHSS	U.S. Department of Energy, Office of Environment, Health, Safety and Security
EHSS-21	U.S. Department of Energy, Office of Sustainable Environmental Stewardship
EM	U.S. Department of Energy, Office of Environmental Management
EMAB	Environmental Management Advisory Board
EPA	U.S. Environmental Protection Agency
EPDM	ethylene propylene diene monomer
EPR	ethylene propylene rubber
ES&H	Environment, Safety and Health
ETFE	ethylene tetrafluoroethylene
EVOH	ethylene vinyl alcohol resin
EXAFS	extended X-ray absorption fine structure
F	fluorine
FASA	fluoroalkyl sulfonamide
FEP	fluorinated ethylene propylene
FEPM	trifluoroethylene-propylene copolymer
FEVE	fluoroethylene-vinyl ether
FFKM	TFE-PMVE perfluoroelastomer
FFRDC	Federally Funded Research and Development Center
FKM	fluorine Kautschuk material
FLCAC	Federal Life Cycle Assessment Commons
FP	fluoropolymer
FPA	fluoropolymer processing aid
FR	Federal Register
FRP	fiber-reinforced plastic
FTCA	fluorotelomer carboxylic acid
FTOH	fluorotelomer alcohol
FTSA	fluorotelomer sulfonic acid
FVMQ	fluorosilicone
GREET	Greenhouse Gases, Regulated Emissions, and Energy Use in Technologies
GWP	global warming potential
H	hydrogen

HCl	hydrochloric acid
HDPE	high-density polyethylene
HFFR	halogen-free flame retardant
HFP	hexafluoropropylene
HFPO-DA	hexafluoropropylene oxide dimer acid
HNBR	hydrogenated nitrile butadiene rubber
IIASA	International Institute for Applied Systems Analysis
INSITE	Induced Spectral Interrogation Technology for the Environment
IPCC	Intergovernmental Panel on Climate Change
ISO	International Organization for Standardization
ITRC	Interstate Technology and Regulatory Council
LCA	life cycle assessment
LCC	life cycle costing
LCI	life cycle inventory
LCIA	life cycle impact assessment
LEAF	Leaching Environmental Assessment Framework
LLDPE	linear low-density polyethylene
MeHg	methylmercury
MFA	methyl fluoroacetate
MJ	megajoule
MJe	megajoule equivalents
MLIS	Master's in Library and Information Science
MS	Master of Science
MW	molecular weight
NAICS	North American Industry Classification System
NBR	nitrile butadiene rubber
NC	North Carolina
NC DEQ	North Carolina Department of Environmental Quality
nEtFOSA	N-ethyl perfluorooctane sulfonamide
NETL	National Energy Technology Laboratory
NIEHS	National Institute of Environmental Health Sciences
NIOSH	National Institute for Occupational Safety and Health
NMP	n-methyl-2-pyrrolidone
NNLEMS	Network of National Laboratories for Environmental Management and Stewardship
NNSA	National Nuclear Security Administration
NO _x	nitrogen oxides
NPDES	National Pollutant Discharge Elimination System
NRC	U.S. Nuclear Regulatory Commission
NREL	National Renewable Energy Laboratory
OECD	Organisation for Economic Co-operation and Development
P	propylene
PA	polyamide

PAA	polyacrylic acid
PAI	polyamideimide
PAN	polyacrylonitrile
PASF	perfluoroalkane sulfonyl fluoride
Pb	lead
PBI	polybenzimidazole
PBVE	perfluoro-3-butenylvinylether
PC	polycarbonate
PCR	product category rule
PCTFE	polychlorotrifluoroethylene
PDD	perfluoro-2,2-dimethyl-1,3-dioxole
PE	polyethylene
PEEK	polyetheretherketone
PEG	polyethylene glycol
PEI	polyetherimide
PEM	polymer electrolyte membrane
PEO	polyethylene oxide
PES	polyethersulfone
PET	polyethylene terephthalate
PEVE	perfluoroethylvinylether
PFA	perfluoroalkoxy
PFAA	perfluoroalkyl acid
PFAS	per- and polyfluoroalkyl substances
PFBA	perfluorobutanoic acid
PFBE	perfluorobutylethylene
PFBS	perfluorobutanesulfonic acid
PFCA	perfluoroalkylcarboxylic acid
PFECA	perfluoroether carboxylic acid
PFESA	perfluoroether sulfonic acid
PFH	perfluorohexane sulfonic acid
PFH _x A	perfluorohexanoic acid
PFH _x S	perfluorohexanesulfonic acid
PFIB	perfluoroisobutylene
PFNA	perfluorononanoic acid
PFOA	perfluorooctanoic acid
PFOS	perfluorooctane sulfonic acid
PFPE	perfluoropolyether
PFSA	perfluoroalkane sulfonic acid
PhD	Doctor of Philosophy
PMIA	poly m-phenylene isophthalamide
PMMA	polymethyl methacrylate
PMVE	perfluoromethylvinylether

PNNL	Pacific Northwest National Laboratory
POM	polyoxymethylene
PP	polypropylene
PPSU	polyphenylsulfone
PPVE	perfluoropropylvinylether
PSF	polysulfone
PTFE	polytetrafluoroethylene
PU	polyurethane
PVA	polyvinyl alcohol
PVAC	polyvinyl acetate
PVC	polyvinyl chloride
PVDF	polyvinylidene fluoride
PVDF-CTFE	poly(vinylidene fluoride-chlorotrifluoroethylene)
PVDF-HFP	poly(vinylidene fluoride-hexafluoropropylene)
PVDF-TrFE	poly(vinylidene fluoride-trifluoroethylene)
PVF	polyvinyl fluoride
R22	difluorochloromethane
RCRA	Resource Conservation and Recovery Act
RMOA	Regulatory Management Option Analysis
SBR	styrene butadiene rubber
SBS	polystyrene-b-butadiene-b-styrene
SETAC	Society of Environmental Toxicology and Chemistry
SF ₆	sulfur hexafluoride
SIP	spectral-induced polarization
SLCA	social life cycle assessment
SNUR	significant new use rule
SRNL	Savannah River National Laboratory
SRS	Savannah River Site
TCE	trichloroethylene
TFE	tetrafluoroethylene
THV	tetrafluoroethylene-hexafluoropropylene-vinylidene fluoride (TFE-HFP-VF2)
TPE	thermoplastic elastomer
TRACI	Tool for Reduction and Assessment of Chemicals and Other Environmental Impacts
TrFE	trifluoroethylene
TSCA	Toxic Substances Control Act
TTD	2,2,4-trifluoro-5-trifluoromethoxy-1,3-dioxole
UF ₆	uranium hexafluoride
UHMWPE	ultra-high molecular weight polyethylene
UNEP	United Nations Environment Program
U.S.	United States
USD	United States Dollar
USLCI	U.S. Life Cycle Inventory Database

UV	ultraviolet
VDF	vinylidene fluoride
VDF-HFP	vinylidene fluoride-hexafluoropropylene
VF	vinyl fluoride
VF-HFP	vinyl fluoride-hexafluoropropylene
VF2	vinylidene fluoride
VF2-HFP	vinylidene fluoride-hexafluoropropylene
XANES	X-ray absorption near-edge structure
XAS	X-ray absorption spectroscopy
XLPE	cross-linked polyethylene

LIST OF TRADEMARKS/BRAND NAMES

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Armylor: Registered trademark of Mersen, Courbevoie, France.

Chemraz: Registered trademark of Greene Tweed, Selma, Texas.

Cytop: Trademark of AGC Inc., Tokyo, Japan.

Dai-el: Registered trademark of Daikin Industries, Osaka, Japan.

Dyneon: Registered trademark of 3M Company, St. Paul, Minnesota.

Fluon: Registered trademark of AGC Chemicals, Exton, Pennsylvania.

Fluorel: Trademark of 3M Company, St. Paul, Minnesota.

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Hostaflon: Registered trademark of Hoechst Celanese, Irving, Texas.

Hyflon: Registered trademark of Solvay S.A., Brussels, Belgium.

Kalrez: Registered trademark of DuPont Performance Elastomers, Wilmington, Delaware.

Kel-F: Registered trademark of 3M Company, St. Paul, Minnesota (discontinued production in 1995).

Kynar: Registered trademark of Arkema S.A., Colombes, France.

Licity: Registered trademark of BASF, Ludwigshafen, Germany.

Lycra: Registered trademark of The LYCRA Company, Wilmington, Delaware.

Mylar: Registered trademark of the DuPont Teijin Corporation, Chester, Virginia.

Nafion: Trademark of The Chemours Company FC, LLC (formerly DuPont), Wilmington, Delaware.

Neoflon: Registered trademark of Daikin Industries, Ltd., Osaka, Japan.

Plaskon: Registered trademark of Panasonic Electric Works Electronic Materials Singapore Pte Ltd, Singapore.

Polyflon: Registered trademark of Daikin Industries, Ltd., Osaka, Japan.

SOLAR-THRU: Trademark of AI Technology Inc., Princeton Junction, New Jersey.

Solef: Registered trademark of Solvay S.A., Brussels, Belgium.

Tecnoflon: Registered trademark of Solvay S.A., Brussels, Belgium.

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Voltalef: Registered trademark of Arkema S.A., Colombes, France.

Xirallic: Registered trademark of Merck KGaA, Darmstadt, Germany.

1.0 INTRODUCTION

Fluoropolymers were first synthesized by DuPont in 1938 and in the decades since their initial creation have become tightly woven into the fabric of modern life. Fluoropolymers are used in a wide range of sectors such as infrastructure, aerospace, microelectronics, and green-energy solutions.

Concerns over the environmental and health impacts of the family of per- and polyfluoroalkyl substances (PFAS), which includes fluoropolymers, have grown significantly in recent decades. These substances tend to be highly persistent when released into the environment, prompting states and nations to consider further restrictions on the production and general use of PFAS. This report contains a qualitative life cycle assessment (Section 5.1) and cost-benefit analysis of common fluoropolymers currently in use (Section 5.2) and potential replacements of fluoropolymers in commerce. Due to limited availability of data on fluoropolymers, *de novo* quantitative life cycle assessments and cost-benefit analyses are not included in this report. In some cases, insufficient knowledge exists; while in other cases, the data are not publicly available to undertake the quantitative analyses.

1.1 What is a Fluoropolymer?

Fluoropolymers are a distinct subclass of PFAS, which are a large class of synthetic (or man-made) chemicals. The thousands of individual PFAS that have been developed divide into two classes: non-polymeric PFAS, consisting of a single unit (monomer), and polymeric PFAS, consisting of a chain of smaller repeating units. Non-polymeric PFAS consist of a single molecule of varying size (Figure 1-1A). Additional details on select, specific non-polymeric PFAS are provided in Sections 2.0 and 3.0. Non-polymeric PFAS (single molecule PFAS) are further divided into perfluoroalkyl and polyfluoroalkyl substances. These non-polymeric PFAS have a relatively small molecular weight and particle size. Non-polymeric PFAS are persistent and mobile in a variety of media, including water, air, soils, and sediments. This mobility increases the dispersion of non-polymeric PFAS in the environment and can lead to concerns about biological uptake and accumulation in plants and animals. Non-polymeric PFAS are often used in the production of polymeric PFAS, including fluoropolymers. The production of fluoropolymer plastics, defined herein and the focus of this report, is discussed in detail in Section 3.0.

There is no universally agreed on definition of the subcategories of polymeric PFAS, leading to confusion in the discussion and distinctions of different types of PFAS. For the purposes of this report, different subcategories of polymeric PFAS are distinguished as follows. The polymeric PFAS class comprises polymers and copolymers. Polymers are large molecules of smaller repeating units (called monomers) linked together in a chain-like or sheet-like form (Figure 1-1B). Copolymers consist of two or more different repeating monomers (Figure 1-1C).

PFAS, both polymers and copolymers, can also be divided into three main types: fluoropolymer plastics, oligomeric perfluoropolyether (PFPE) compounds, and side-chain fluorinated polymers. Polymeric

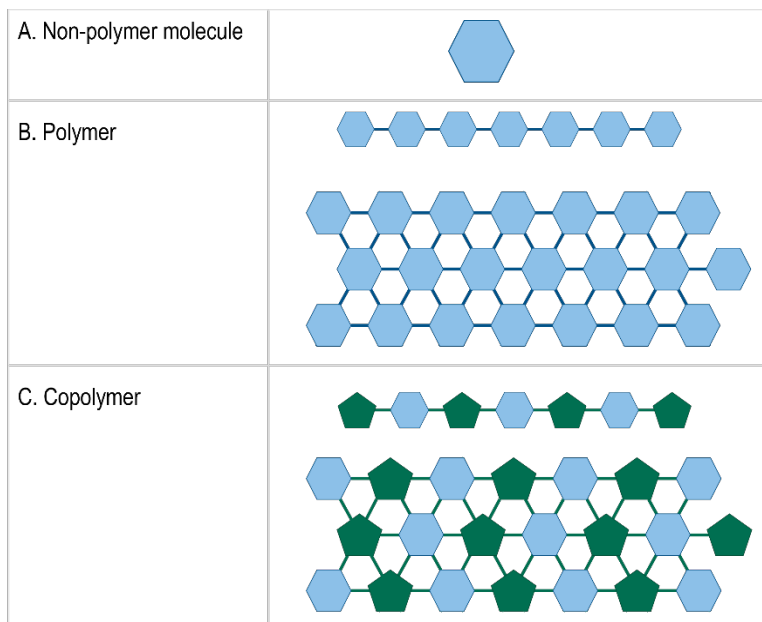


Figure 1-1. Non-polymer, Polymer, and Copolymer Molecules

PFAS are generally not soluble in water. Fluoropolymer plastics fall into this class. Fluoropolymer plastics are high molecular weight polymers and copolymers that consist of a carbon backbone with fluorine atoms directly bonded to the carbon atoms. Fluoropolymer plastics include both thermoplastic and elastomeric solid-state materials composed of fluoropolymers and are useful for fabrication of physical articles (which are distinct from fluorinated side-chain polymers mainly used for surface protection and coatings or oligomeric PFPEs used largely as chemically resistant lubricant oils and greases). Due to their molecular structure, fluoropolymer plastics have unique physical and chemical properties that have led to wide-spread integration into many sectors of modern commerce, including aerospace, automotive, chemical processes and storage, infrastructure, solar and wind energies, electronics, and many others. Selected applications are described in Section 4.0. Fluoropolymers can be chemically modified to optimize properties for specific applications, and many of these formulas are proprietary.

1.2 What Properties Make Fluoropolymers Desirable?

Fluoropolymers are thermally and chemically stable, lipophobic (i.e., reject oil/grease), and water-repellent, making them useful in a wide range of applications. Fluoropolymers can also be used in multiple forms, including surfactants, coatings, sheetings, and additives. As an example of their versatility, fluoropolymers can be found in the coating on electrical wiring, water and stain resistant fabrics, seals and gaskets, non-stick cookware, fuel lines, and anti-vandal paint. These unique forms make fluoropolymers long-lasting, stable, and resistant to chemical or biological breakdown, while still being light-weight and adaptable. Fluoropolymers enhance the durability, safety, and longevity of a wide range of products. Some applications rely on multiple fluoropolymer properties, with the most desired property being the primary determinant of the specific fluoropolymer used.

Fluoropolymers are used in thermally variable applications, including aerospace, automotive, and electronics, and are often used in electrical insulation, circuitry, and semiconductors for their thermal stability. Fluoropolymers add stability and safety to these applications due to their high melting points and insulation abilities; their flexibility is also a key property, allowing wiring to be run in corners and circuits to be printed. Their chemical-resistant properties add to their inclusion in applications where other materials breakdown quickly, including corrosive and acidic environments.

Fluoropolymers are used as tank and piping liners, seals and plugs, pumps and gaskets, fuel lines, and personal protective equipment; their non-stick nature and resistance to weathering are also desirable properties in these applications. The ability of fluoropolymers to repel water makes them ideal for applications such as outdoor and architectural fabric, cookware, and fiberglass coatings for construction and automotive applications. Additionally, their flame resistance, biostability, and durability increase their usefulness in these applications. These examples identify just a few of the industries and sectors where fluoropolymers have become integral components of various consumer products. A more detailed discussion is provided in Section 4.0.

1.3 Regulatory and Mitigation Efforts for Fluoropolymers

PFAS have been dubbed “forever chemicals” due to their stability and longevity in the environment. Researchers have noted many pathways through which PFAS enter the environment, including the use of aqueous film-forming foam (AFFF) for firefighting, runoff from fertilizer application, and discharges from the production of certain types of fluoropolymers. The polymer and copolymer fluoropolymers are typically not water-soluble and are resistant to breakdown by weathering. Fluoropolymers have not been identified as an environmental or human health hazard; however, their production may involve the use and release of PFAS of concern.

Importantly, fluoropolymers have not been singled out for significant regulatory efforts in the U.S. However, a number of compounds in the broader PFAS family have been the focus of both regulatory and industry mitigation efforts. In the U.S., states have taken the initiative to regulate PFAS. States are employing multiple approaches to mitigating the environmental effects of PFAS, including limiting PFAS as a source material, establishing guidelines or notification levels for PFAS in water, and eliminating the use of AFFF in training exercises.

Federal regulatory action has been directed primarily by the U.S. Environmental Protection Agency (EPA). Since 2000, these actions have followed two tracks. First, EPA began extensive data collection and information gathering efforts regarding PFAS under the *Toxic Substances Control Act of 1976* (TSCA) due to concerns about potential harmful effects to humans and the environment. This information gathering effort led to EPA's intended designation of two specific compounds – perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS) – as hazardous substances under Section 102 of the *Comprehensive Environmental Response, Compensation, and Liability Act of 1980* (CERCLA). In 2023, EPA proposed a significant new use rule (SNUR) under TSCA preventing the resumption of manufacturing or processing of phased-out PFAS without EPA review (EPA, 2023b). EPA has also made determinations for drinking water regulations for six PFAS (PFOS, PFOA, perfluorohexanesulfonic acid [PFH_xS], hexafluoropropylene oxide dimer acid [HFPO-DA], perfluorononanoic acid [PFNA], and perfluorobutanesulfonic acid [PFBS]).

Second, EPA worked with producers to implement voluntary phaseouts of the non-polymeric PFAS of concern. These efforts have resulted in the effective removal of non-polymeric PFAS from production and use in the U.S. 3M was the sole producer of PFOA and reported to EPA in 2000 that they had determined PFOA posed a significant risk to humans and the environment. 3M subsequently pledged to end all PFOA production, which they achieved by 2002. In 2006, PFOS was targeted for a similar voluntary program. In December 2022, 3M announced that manufacturing of all 3M fluoropolymers, fluorinated fluids, and PFAS-based additive products will be discontinued by the end of 2025.

EPA worked with eight of the major producers to implement the PFOS Stewardship Program. These companies achieved complete phaseouts of PFOS by 2017. Industry data submitted to EPA show over 90% reductions in PFOA emissions from 2000 to 2015 as part of an EPA-monitored voluntary control program (EPA, 2023b). The Centers for Disease Control and Prevention (CDC) confirm that the PFOA levels in the blood of the U.S. general population have declined 60% from 2000 to 2014. Even larger reductions – 80% – were reported for PFOS. However, CDC cautioned that as PFOS and PFOA are phased out and replaced, people may be exposed to other PFAS (ATSDR, 2017).

1.4 Discovery Methodology

To produce this report, a team of subject matter experts was convened from national laboratories and universities. The team gathered information through multiple sources, as described below, however, due to the lack of publicly available data, *de novo* data calculations could not be produced. Further, because this document is a public document, proprietary information, research, and data were not used in the completion of this report. Additional research and discovery efforts may be underway but not included in this document if the developer considers the efforts proprietary. The subject matter experts used the methods of discovery described below.

1.4.1 Existing Data and Literature

Existing literature was used in the development of the report. These sources included:

- Surveys and studies conducted by universities, government agencies, industries, and industry working groups

- Product documentation provided by manufacturers and industry working groups
- Market reports
- Industry, government, and non-government organization websites
- Peer-reviewed published literature and patents
- Documents generated by other government agencies.

1.4.2 Fluoropolymer Industry Survey

The subject matter expert team generated a survey (Appendix A), administered by Vanderbilt University (hereafter referred to as the Vanderbilt survey), directed toward fluoropolymer manufacturers, formulators, and end users. The survey was anonymous, and responses were only used in an aggregated manner to protect the companies' and product identities. Completion of the survey was entirely voluntary. The survey was used to gather additional available information directly from fluoropolymer manufacturers, formulators, and end users and to verify data and information gathered through existing data and literature sources.

Outreach Data	
26	Industry and trade organizations
22	Individual industries
32	Direct surveys sent
16	Surveys returned
10	Engagements with environmental advocacy organizations
	Coordination with federal agencies

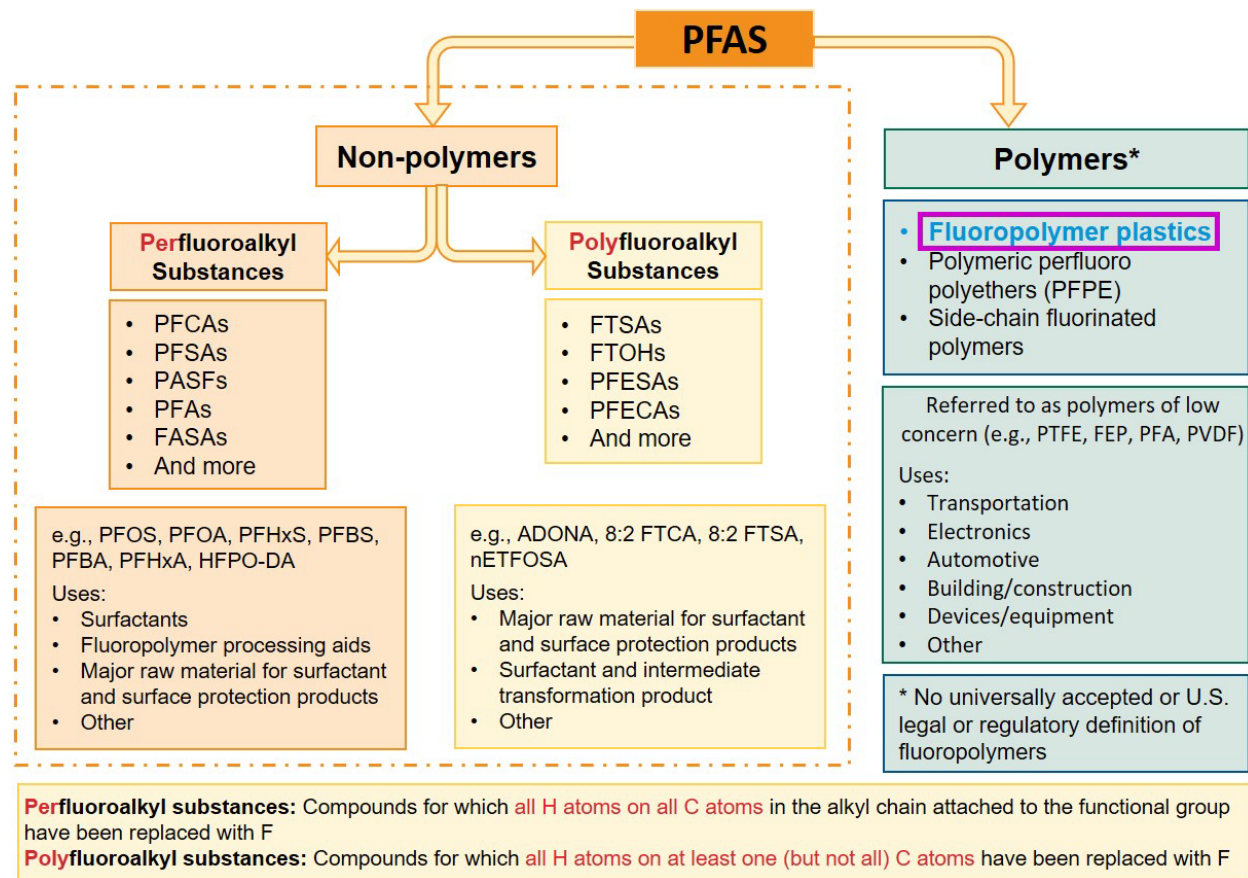
1.4.3 Interviews and Engagements

The team hosted and participated in engagements with industry partners, government agencies, and non-government organizations; several willingly participated in interviews with the subject matter expert team, providing valuable direct information and industry perspectives. Government interagency working groups, non-government organizations, and other government agencies were able to provide direct feedback to the team on methods employed and information gathered by the team.

2.0 FORMS, PROPERTIES, AND USES OF COMMON FLUOROPOLYMERS

Fluoropolymers are high molecular weight polymers consisting of a carbon (C) backbone and fluorine (F) atoms that are directly attached to the carbon atoms. These compounds are a distinct class of PFAS with a unique combination of attributes, such as chemical, biological, and thermal stability; low dielectric constant; and negligible solubility in water. These attributes, along with their high stability, help explain the extensive use of fluoropolymers in commerce and industry. Although stable, fluoropolymers may present environmental and human health challenges at certain points in their life cycle, including through low molecular weight PFAS by-products from manufacturing, degradation under certain conditions of use or disposal resulting in the generation of microplastics, and incomplete breakdown during thermal destruction.

PFAS constitute a large family of fluorinated chemicals, exceeding several thousand different chemicals, including high molecular weight fluoropolymers used in commercial (Section 4.0) and critical defense applications (Section 4.1.4), and low molecular weight non-polymeric PFAS and microplastics that have been emitted to the environment from production, misuse, or degradation of fluoropolymers. There is no universally accepted definition of PFAS nor the commercially important subcategory of fluoropolymers that is the subject of this report, which can result in confusion in identifying and attributing environmental impacts to specific groups of PFAS, including fluoropolymers (Buck et al., 2021). PFAS have been characterized as having carbon atoms linked to each other (i.e., a carbon “backbone”) and bonded to fluorine atoms at most or all of the available carbon bonding sites by which fluorination imparts properties to the molecule. As shown in Figure 2-1, fluoropolymers are an important subgroup of PFAS.



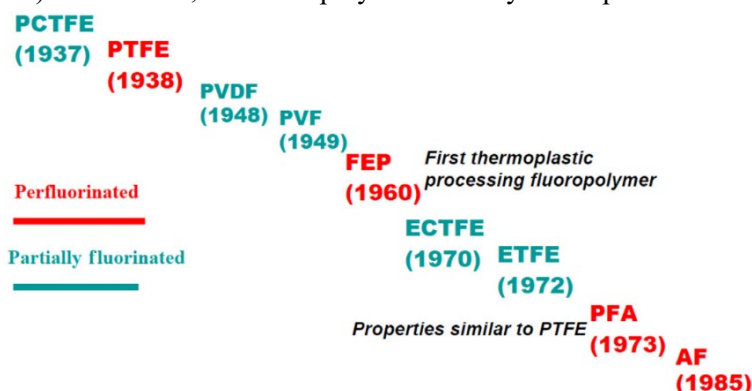
Source: ITRC, 2022, “PFAS — Per- and Polyfluoroalkyl Substances,” Report No. PFAS-1, Interstate Technology and Regulatory Council, Washington, D.C.

Figure 2-1. Per- and Polyfluoroalkyl Substances Family Tree and Classification

In addition, the term fluoropolymer may refer to any chemical substance formed by reaction of fluorinated monomeric precursors to form a macromolecular repeating structure. In the context of this report, the discussion is focused on fluoropolymer plastics (as defined herein), which are considered distinct from fluorinated side-chain polymers (used for surface protection and coatings) and oligomeric PFPE (used largely as chemically resistant lubricant oils and greases) because of differing structural properties and uses (Section 3.0). PFPEs contain a carbon and oxygen polymer backbone with fluorine atoms directly attached to the carbon atoms. Side-chain fluorinated polymers branch off of a non-fluorinated polymer backbone.

2.1 Development of the Fluoropolymer Industry

The fluoropolymer development industry began with the accidental discovery of polytetrafluoroethylene (PTFE) in 1938 by Dr. Roy J. Plunkett and his team at DuPont while conducting commercial experiments with chlorofluorocarbon refrigerants (Plunkett, 1986). However, the material did not initially gain much market attention because of its high cost. Later, during World War II, a scale-up in production was supported due to the need for handling extremely corrosive chemicals. The U.S. Army Corps of Engineers, and then the U.S. Atomic Energy Commission, controlled some production methods of the chemicals until the late 1940s (Okazoe, 2009). Since then, the fluoropolymer industry has expanded over the years to a wide range of products with applications in many industries, including aerospace, automotive, aviation, chemical processing, construction, electronics, medical, semiconductor manufacturing, and consumer products. An accidental discovery opened the door to the fluoropolymer industry, which many consider the most important in the field of applied chemistry, and has influenced the world for the last nine decades. Many new fluoropolymers were developed between the 1940s and 1970s; the timeline of the development of fluoropolymers and commercial application is presented in Figure 2-2.



Source: Ebnesajjad, S., 2021, "3 - Fluoropolymers—Discovery, History, Evolution, and Consumption," *Introduction to Fluoropolymers: Materials, Technology, and Applications*, Second Edition, pp 19-31.

Figure 2-2. Innovation Waves and Evolution of Fluoropolymers During its History

2.2 Per- and Polyfluoroalkyl Substances

PFAS are a large, complex group of synthetic fluorinated substances that have a wide variety of chemical and physical properties, as dictated by the chain length and degree of fluorination. PFAS are defined as a specific class of fluorinated organic substances that include solids, liquids, dispersions, and gases; polymers like fluoropolymers and non-polymers (e.g., low molecular weight PFAS); soluble and insoluble substances; reactive and inert substances; and volatile and non-volatile substances (Buck et al., 2011). An important distinction exists within the PFAS class (e.g., solids, liquids, and gases), as the state of matter affects the mobility of the PFAS. For example, the liquid-state PFAS-containing firefighting foams (e.g., AFFF, which is not a fluoropolymer) has greatly contributed to soil and water contamination (ITRC, 2022). Similarly, the gaseous-state PFAS (e.g., created from incineration at insufficiently low temperatures) contributes to air contamination. With their diverse properties, PFAS are organized in a family tree (taxonomy) of two primary classes, polymers (including fluoropolymer plastics) and non-polymers, where each class contains subclasses, groups, and subgroups. As shown in the classification of the PFAS family in Figure 2-1, fluoropolymer plastics, the subject of this study, are under the class of fluoropolymers with high molecular weights.

Significant differences exist between polymeric and non-polymeric PFAS.

- **Polymeric PFAS** (high molecular weight) consist of thousands of repeating molecular units with a carbon-only polymer backbone, with fluorine atoms directly attached to carbon atoms, thus making the polymers more stable and non-water soluble. The polymeric PFAS can be further divided into fluoropolymer plastics, oligomeric PFPE, and side-chain fluorinated polymers, as indicated in Figure 2-1.
- **Non-polymeric PFAS** (low molecular weight) consist of a single molecule (i.e., carbon atoms linked to each other and bonded to fluorine atoms at most or all of the available carbon bonding sites) with a relatively low molecular size/weight, which is more mobile and water-soluble, and therefore easy to spread in the environment (water/air/soil).

Per- and Polyfluoroalkyl Substances Classification

Fluoropolymers are a distinct class of synthetic polymeric PFAS with high molecular weights, with fluorine attached to the carbon atoms, forming their carbon-only backbone. The higher the content of fluorine atoms in the polymer chain, the stronger the specific properties of the molecule due to unique intermolecular and intramolecular interactions between the fluorinated polymer segments. This degree of fluorination imparts essential and important mechanical and physicochemical characteristics to the polymers that allow these materials to be used in demanding applications.

Selected Fluoropolymers and Trade or Brand Name(s)
Polytetrafluoroethylene (PTFE) – Teflon®
Ethylene copolymer of tetrafluoroethylene (ETFE) – Tefzel™, Fluon®, Neoflon®, Texlon®
Fluorinated ethylene propylene (FEP) – Teflon® FEP, Neoflon®, Dyneon® FEP
Perfluoroalkoxy (PFA) – Teflon® PFA
Polyvinylidene fluoride (PVDF) – Kynar®, Solef®, Dyneon® PVDF
Ethylene copolymer of chlorotrifluoroethylene (ECTFE) – Halar®
Polychlorotrifluoroethylene (PCTFE) – Voltalef®, Kel-F®, Neoflon®, Aclar®, Halon®, Fluon®, Hostafion®, Plaskon®
Fluorine Kautschuk material (FKM) – Viton®, Dyneon®, Tecnoflon®

Fluoropolymers can be classified into two types: homopolymers – repeatedly joined monomers, and copolymers – alternating monomers of different species (including terpolymers for this study). Fluoropolymers are a group of polymers within the class of PFAS, whereby monomers and oligomers (i.e., not polymers) can be emitted during the production, processing, use, or treatment of fluoropolymers. Because of their special chemical and physical characteristics, fluoropolymers are widely applied in the architectural, aerospace, automotive, chemical, construction, electrical, and electronic industries that are the focus of this report (defined in Section 1.0). Several commercially important fluoropolymers include PTFE (also known as Teflon¹²), polychlorotrifluoroethylene (PCTFE), fluorinated ethylene propylene (FEP), polyvinyl fluoride (PVF), perfluoroalkoxy (PFA), ethylene tetrafluoroethylene (ETFE), ethylene chlorotrifluoroethylene (ECTFE), Nafion,¹³ polyvinylidene fluoride (PVDF), and more.

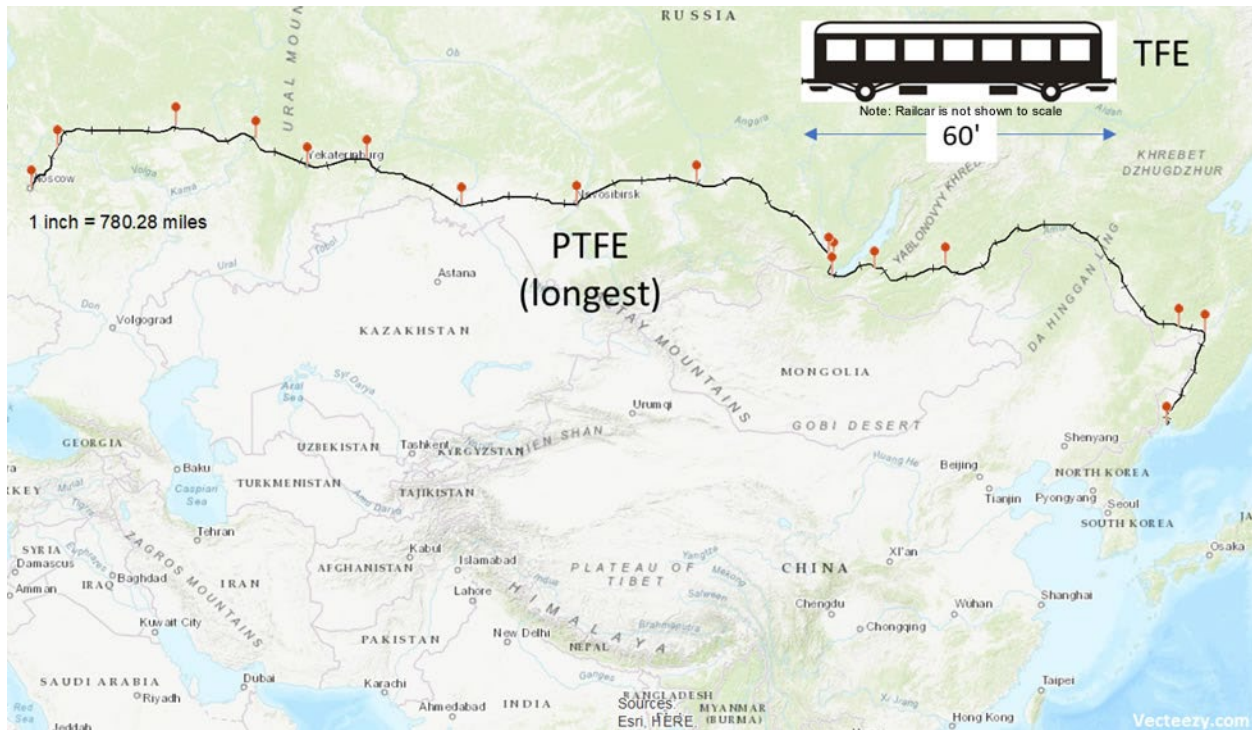
Non-polymeric PFAS are often divided into two sub-classes: perfluoroalkyl and polyfluoroalkyl substances, as shown previously in Figure 2-1. Perfluoroalkyl substances are alkyl chains with all hydrogen (H) atoms on all C atoms replaced with F atoms. Polyfluoroalkyl substances are alkyl chains where all H atoms on at least one C atom (but not all) have been replaced with F atoms.

A simple way to think of differences in scale between non-polymeric PFAS monomers like tetrafluoroethylene (TFE, with a molecular weight of 100.02 dalton [Da]) and PTFE (made from TFE with a molecular weight between 389,000 and 45,000,000 Da [Henry et al., 2018]) is the way that railcars are used to form a train. Assuming the length of a standard U.S. railcar (60 ft) represents the molecular weight of the TFE monomer, between 3,890 and almost 450,000 coupled railcars would represent the molecular weight range of the PTFE fluoropolymer.

¹² Teflon is a registered trademark of The Chemours Company FC, LLC (formally DuPont), Wilmington, Delaware.

¹³ Nafion is trademark of The Chemours Company FC, LLC (formerly DuPont), Wilmington, Delaware.

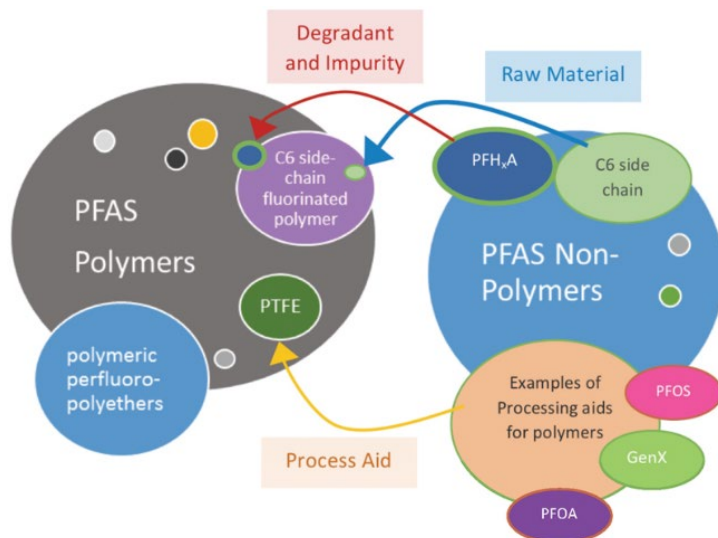
Another way to think of this is that the train comprising 3,890 railcars would stretch continuously for 45 miles (i.e., the lowest molecular weight for PTFE would be represented by a train 45 miles long), whereas the train with 450,000 railcars would stretch almost the length of the Trans-Siberian Railway (over 5,000 miles), the longest railway in the world (Figure 2-3 provides a graphical representation).



Note: • indicates major railway stations; railcar is not shown to scale.

Figure 2-3. Graphical Illustration of the Difference in Molecular Weights Between a Monomer (TFE) and a Fluoropolymer (PTFE)

A complex interdependence exists among some polymeric PFAS (including high molecular weight fluoropolymers) and non-polymeric PFAS. The low molecular weight non-polymeric PFAS can play a vital role as processing aids and raw materials for polymeric PFAS production. As a result, low molecular weight non-polymeric PFAS can be emitted during manufacturing or as unintentional by-products or impurities from polymeric PFAS. Non-polymeric PFAS may also be generated as combustion by-products during incineration, depending on conditions such as temperature, residence time, and physical state.



Source: Sullivan, H., 2021, "Dyeing, Printing & Finishing: PFAS – A Textile Perspective," *Textile World*.

Figure 2-4. The Interdependency of Per- and Polyfluoroalkyl Substances (Polymer and Non-polymer)

The interdependency and complexity of polymeric PFAS and non-polymeric PFAS are represented in Figure 2-4, where typical examples of low molecular weight PFAS materials like PFOA and HFPO-DA can be used as processing aids, and the C6 side-chain can be used as a raw material for polymeric PFAS production.

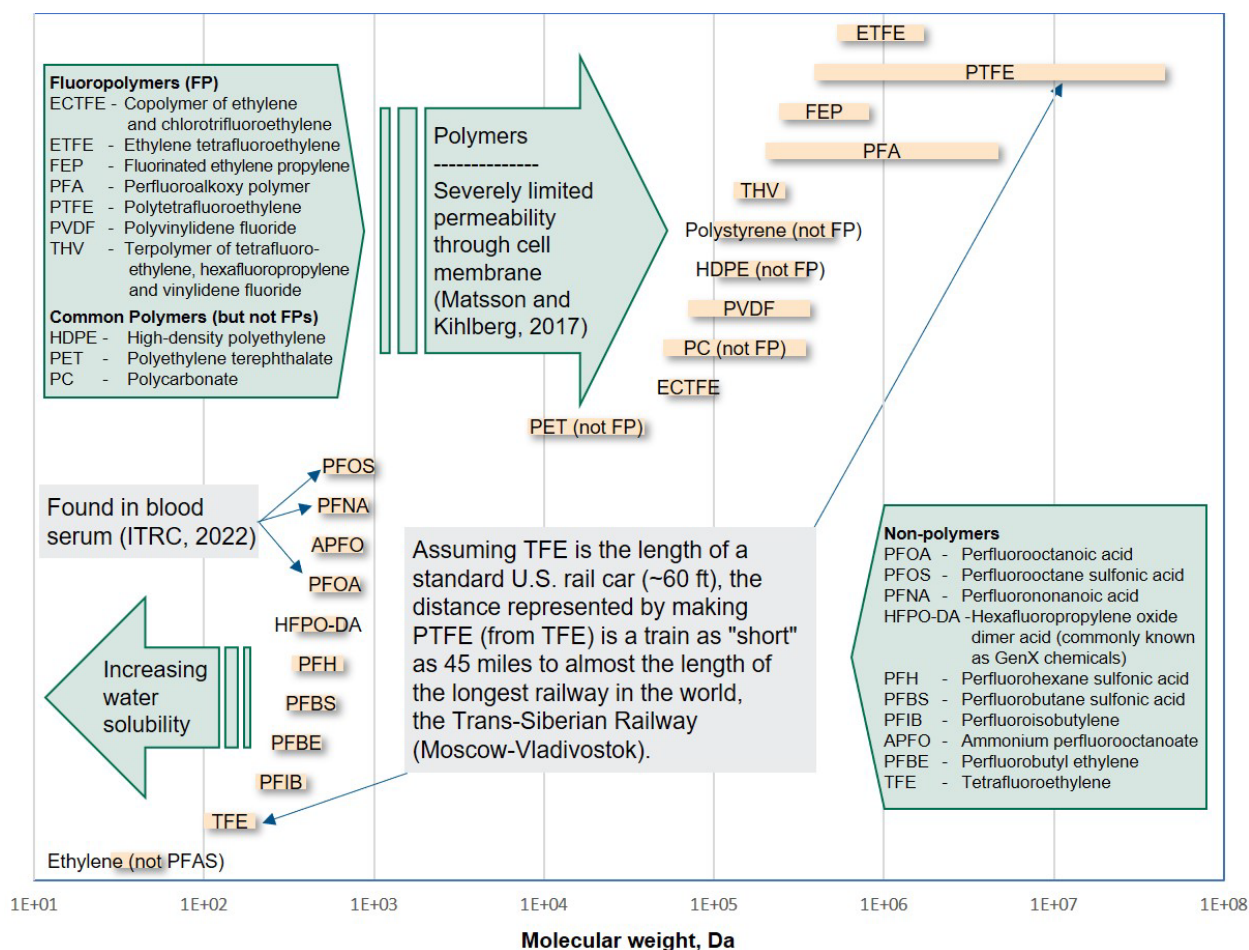


Figure 2-5. Properties of Polymeric and Non-Polymeric Per- and Polyfluoroalkyl Substances (PFAS) as a Function of Molecular Weight

Suggesting that all polymeric PFAS can be considered polymers of low concern is not straightforward because of their stability and water insolubility when compared to low molecular weight non-polymeric PFAS (Lohmann et al., 2020). The relatively small size and low molecular weight of non-polymeric PFAS make them highly mobile and easy to spread in water and air, as illustrated in Figure 2-5. Henry et al. (2018) suggest that polymers, including fluoropolymers, are too large to penetrate the cell membrane; however, Lohmann et al. (2020) disputes this assertion based on evidence for polymers other than fluoropolymers. With multiple pathways through a cell membrane, a more precise description is given by Matsson and Kihlberg (2017) for polymers in general, where the authors state that molecular sizes “severely limit[ed] permeability above 1000 Å³ [cubic angstrom], i.e., at a MW [molecular weight] of approximately 1000 Da.” Thus, when considering these compounds in general, fluoropolymers themselves may not present substantial risk – instead, the low molecular weight PFAS used to manufacture fluoropolymers, or degradation products from the fluoropolymers (including potentially from treatment), may dominate risks to human health and the environment associated with fluoropolymers.

The definition of PFAS has evolved to reflect the continued study of these compounds and may take different forms depending on the operational criteria used and the intended scope and application of the included list of chemicals (Buck et al., 2021). For example, the definition of PFAS used in a study by the Organisation for Economic Co-operation and Development (OECD) and the United Nations Environment Program (UNEP) expanded the Buck et al. (2011) definition to include chemicals that contain the C_nF_{2n} – moiety in addition to the C_nF_{2n+1} – moiety. This definition encompasses chemicals with both ends of the carbon-fluorine chain connected to hydrogen or a functional group, and the cyclic analogs of linear PFAS (OECD, 2018). The OECD (2018) study updated the report and identified 4,730 PFAS, including 267 fluoropolymers (by CAS¹⁴ numbers, not structures); other PFAS definitions have been proposed (Buck et al., 2021).

In general, PFAS can be classified as non-polymers (consisting of a single molecule) or polymers (consisting of thousands of repeating units). The 4,730 PFAS reviewed in the OECD (2018) report were assigned to structure categories, and eight such structure categories with assigned codes and subcodes were used to identify various subcategories. A summary of the 4,730 PFAS is provided in Table 2-1. The majority of relevant substances (~53%) of 4,730 PFAS (OECD, 2018) were in three categories: series 400, 500, and 800 (fluoropolymers).

Table 2-1. Per- and Polyfluoroalkyl Substances (PFAS) Assigned to Eight Structure Categories

Series	Structure Category	Total number of substances	Percentage (%)	Comments
100	Perfluoroalkyl carbonyl compounds	514	10.9	Non-polymer
200	Perfluoroalkane sulfonyl compounds	629	13.3	Non-polymer
300	Perfluoroalkyl phosphate compounds	23	0.5	Non-polymer
400	Fluorotelomer-related compounds	1872	39.6	Non-polymer and polymer
500	Per- and polyfluoroalkyl ether-based compounds	365	7.7	Non-polymer and polymer
600	Other PFAA precursors and related compounds—perfluoroalkyl ones	314	6.6	Non-polymer
700	Other PFAA precursors or related compounds—semifluorinated	746	15.8	Non-polymer
800	Fluoropolymers	267	5.6	Polymer
Total		4,730	100.0	

Source: OECD, 2018, “Toward a new comprehensive global database of per- polyfluoroalkyl substances (PFASs): Summary report on updating the OECD 2007 list of per- and polyfluoroalkyl substances (PFASs),” OECD Series on Risk Management, No. 39, Organisation for Economic Co-operation and Development, Paris, France.

PFAA = perfluoroalkyl acid.

Of the 267 fluoropolymers identified in the OECD (2018) study, which has been cited widely in scientific literature (e.g., Glüge et al., 2020; Buck et al., 2021), the following categories (by structure) were identified (where frequencies are indicated in []):

- Ethylene tetrafluoroethylene (ETFE) [2]
- Fluorinated ethylene propylene (FEP) [3]
- Polytetrafluoroethylene (PTFE) [2], functionalized PTFE [74], and non-functionalized PTFE [1]
- Polyvinylidene fluoride (PVDF) [1] and non-functionalized PVDF [1]
- (Fluorinated) oxitane polymer [3]
- Polychlorotrifluoroethylene (PCTFE) [1]
- Terpolymer of tetrafluoroethylene-hexafluoropropylene-vinylidene fluoride (THV) [1]

¹⁴ Unique registry number assigned to chemical compounds by the Chemical Abstracts Service (CAS).

- Vinylidene fluoride-hexafluoropropylene (VDF-HFP) [1] – survey
- Unspecified fluoropolymers [177].

The above fluoropolymers were also mentioned by the respondents to the Vanderbilt survey (Appendix A); however, PFA, fluorine Kautschuk material (FKM), and ECTFE were also indicated in these survey results. A search was performed (by CAS number) for the 177 unspecified fluoropolymers from the OECD (2018) study; the results indicated that 46 of the substances were identified as PTFE and another two as PVDF (i.e., categories already enumerated above). The above fluoropolymers, supplemented by the additional, important substances indicated by the Vanderbilt survey responses or from literature, form the foundation of this evaluation. Of further note, the set of fluoropolymers in this report is consistent with the fluoropolymers discussed in the Henry et al. (2018) and Korzeniowski et al. (2023) articles; these fluoropolymers dominate the world market for such materials (CEH, 2022).

Buck et al. (2021) indicated that less than 6% of the 4,730 PFAS (and 38 fluoropolymers) identified in the OECD (2018) study were “commercially viable globally,” suggesting that grouping and categorizing PFAS using criteria based on composition and structure could be used to identify appropriate groups of PFAS for risk assessment, “thereby dispelling assertions that there are too many PFAS chemistries to conduct proper regulatory risk assessments for the commercially relevant substances.” A group of 38 commercially viable fluoropolymers (not identified by name, CAS number, or structure because of the double-blind nature of the study) was indicated by Buck et al. (2021). Authors from Buck et al. (2021) suggested that considering the set of fluoropolymers in the Henry et al. (2018) and Korzeniowski et al. (2023) articles would also provide a reasonable basis for this study,¹⁵ which is consistent with the approach in this report, as described later in Sections 2.4 and 4.0.

With tens of thousands of chemicals in commerce and more introduced every year, the EPA, through its computational toxicology research, developed the web-based CompTox Chemistry Dashboard (EPA, 2023c). This dashboard is a publicly available application that provides access to a chemical’s toxicity, chemistry, and exposure information, with the focus being to support the mission to evaluate chemical safety and protect human health and the environment. As per the list released in August 2022 (EPA, 2022a), 15,000 PFAS are reported (where fluoropolymers are not indicated as such). This number was derived based on a threshold of a minimum of 30% fluorine (without hydrogens) in a molecular formula with sufficient fluorination levels to *potentially* impart PFAS-type properties. For example, a chemical structure with a molecular formula of $C_6HF_9O_6$ has 43% fluorine ($9F/(6C+9F+6O)$, without hydrogen). The EPA also added PFAS as a class to the list of unregulated contaminants that will be monitored in drinking water across the U.S. (87 FR 68060, “Drinking Water Contaminant Candidate List – Final”) and provided a list of 10,239 PFAS (EPA, 2022b) that meet the definition of PFAS used in this report. Note that EPA only proposed to regulate six PFAS (PFOS, PFOA, PFH_xS , HFPO-DA, PFNA, and PFBS) that have been demonstrated to have possible negative health effects (88 FR 18638, “PFAS National Primary Drinking Water Regulation Rulemaking”). The EPA studies address PFAS in general and not specifically fluoropolymers.

2.3 The Science of Fluoropolymers, Properties and Uses

Fluoropolymers possess a unique combination of characteristics, such as heat, chemical and electrical resistance, durability, and unique dielectric properties, which enables the material to perform under harsh operating conditions. This section provides information on (1) chemical types/groupings and physical forms (e.g., sheeting, coatings, solutions, thin films, fibers, additives), and (2) properties, including beneficial physical/chemical properties (e.g., non-stick, heat-resistant, hydrophobicity, chemically inert) and additional properties that may limit use such as expansive aspects, radiation degradation, and thermal.

¹⁵ Personal communication with the authors of Buck et al. (2021) on September 26, 2023.

Fluoropolymers can be classified into homopolymers – repeatedly joined monomers of the same chemical structure, and copolymers – alternating monomers, including those (e.g., terpolymers) consisting of different types of monomers. Fluoropolymers can be further classified based on the degree of fluorination as perfluoropolymers (e.g., FEP and PFA), where fluorine substitutes for hydrogen in *all* possible bonds to carbon, and polyfluoropolymers (e.g., PVF and ETFE), where hydrocarbon functional groups are incorporated into the backbone of the polymer.

Fluoropolymers are a group of polymers within the class of PFAS also including low molecular weight monomers and oligomers that can be emitted during the use, production, processing, or treatment of fluoropolymers (ITRC, 2022). Typical properties of fluoropolymers for the sectors pertinent to this report and specific requirements or functions of each industrial application are summarized in Table 2-2 and Table 2-3, respectively.

Table 2-2. Summary of Fluoropolymers and General Properties

Fluoro-polymer	Starting year	Melting temperature (°C)	Tensile modulus (MPa)	Break elongation (%)	Dielectric strength (kV/mm)	Appl. temp (°C)	Main Applications
PTFE	1947	317-337	550	300-550	19.7	260	Chemical processing, wire and cable
PCTFE	1953	210-215	60-100	100-250	19.7	200	Barrier film, packaging and sealing
FEP	1960	260-282	345	~300	19.7	200	Cable insulation
PVF	1961	190-200	2,000	90-250	12-14	110	Lamination, film, and coating
PVDF	1961	155-192	1,040-2,070	50-250	63-67	150	Coating, wire, cable, electronic
ECTFE	1970	235-245	240	250-300	80	150	Flame resistant insulation
PFA	1972	302-310	276	~300	19.7	260	Chemical resistant components
ETFE	1973	254-279	827	150-300	14.6	150	Wire and cable insulation
THV	1996	145-155	82-207	500-600	48-62	93	Barrier film and insulation

Source: Teng, H., 2012, "Overview of the Development of the Fluoropolymer Industry," *Applied Sciences*, 2(2), pp 496–512.

ECTFE	= ethylene chlorotrifluoroethylene.	PTFE	= polytetrafluoroethylene.
ETFE	= ethylene tetrafluoroethylene.	PVDF	= polyvinylidene fluoride.
FEP	= fluorinated ethylene propylene.	PVF	= polyvinyl fluoride.
PCTFE	= polychlorotrifluoroethylene.	THV	= tetrafluoroethylene-hexafluoropropylene-vinylidene fluoride (TFE-HFP-VF2).
PFA	= perfluoroalkoxy.		

Table 2-3. Typical Applications of Fluoropolymers for Different Industry Sectors (2 pages)

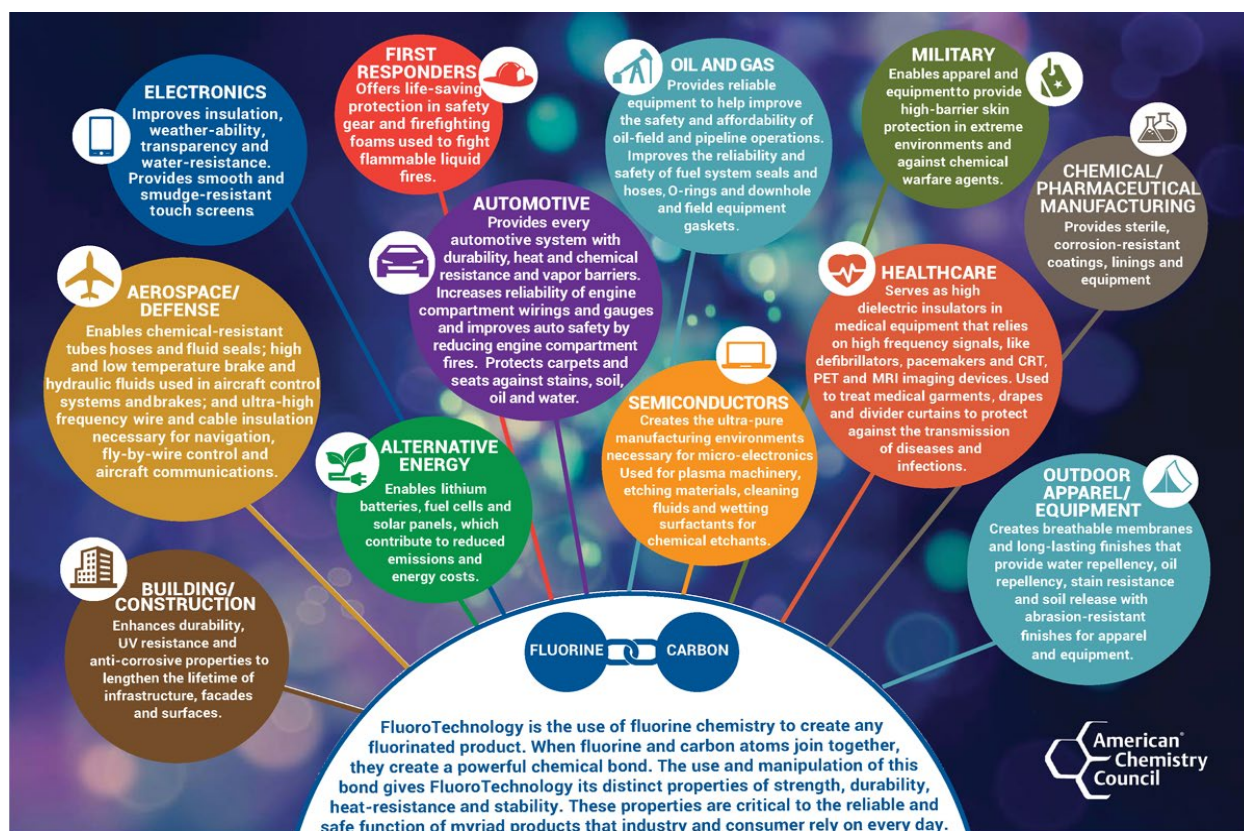
Industries	Functions	Forms
Automotive	Mechanical property, thermal property, chemical property, and friction property	O-rings, gaskets, valve stem seals, shaft seals, linings for fuel hoses, power steering, and transmission
Chemical	Chemical resistance, mechanical property, thermal property, and weather stability	Coatings for heat exchangers, pumps, diaphragms, impellers, tanks, reaction vessels, autoclaves, containers, flue duct expansion joints, and heavy-wall solid pipe and fittings
Electrical/electronic	Dielectric constant, flame resistance, and thermal stability	Electrical insulation, flexible printed circuits, ultrapure components for semiconductor manufacture
Architectural and domestic	Weatherability, flame retardancy, friction property, thermal stability	Water-repellent fabric, architectural fabric, non-stick coatings for cookware, and fiberglass composite for construction

Table 2-3. Typical Applications of Fluoropolymers for Different Industry Sectors (2 pages)

Industries	Functions	Forms
Engineering	Mechanical property, thermal stability, chemical stability, weatherability, and surface energy	Seats and plugs, bearings, non-stick surfaces, coatings for pipes, fittings, valve and pump parts, and gears
Medical	Surface energy, biological stability, mechanical property, chemical resistance	Cardiovascular grafts, ligament replacement, and heart patches

Source: Teng, H., 2012, "Overview of the Development of the Fluoropolymer Industry," *Applied Sciences*, 2(2), pp 496–512.

The unique characteristics of fluoropolymers can enhance product durability, sustainability, and safety. Products that are lighter and longer-lasting will generally have lower life cycle costs, embodied energy, transportation-related emissions, and safety risks. Fluoropolymers are found in many commercial and industrial applications, consumer products, and medical equipment. Examples include fuel tubes and hoses that significantly reduce fugitive emissions; release films in carbon-fiber-reinforced composite structural components for lightweight automotive and aerospace applications; gaskets and seals across many industries; and coatings, lining, piping, fuel tubes, batteries, semiconductor equipment, data transmission cables, cell phones, and wind turbines. Industry applications of fluoropolymers used in a wide range of products are summarized in Figure 2-6.



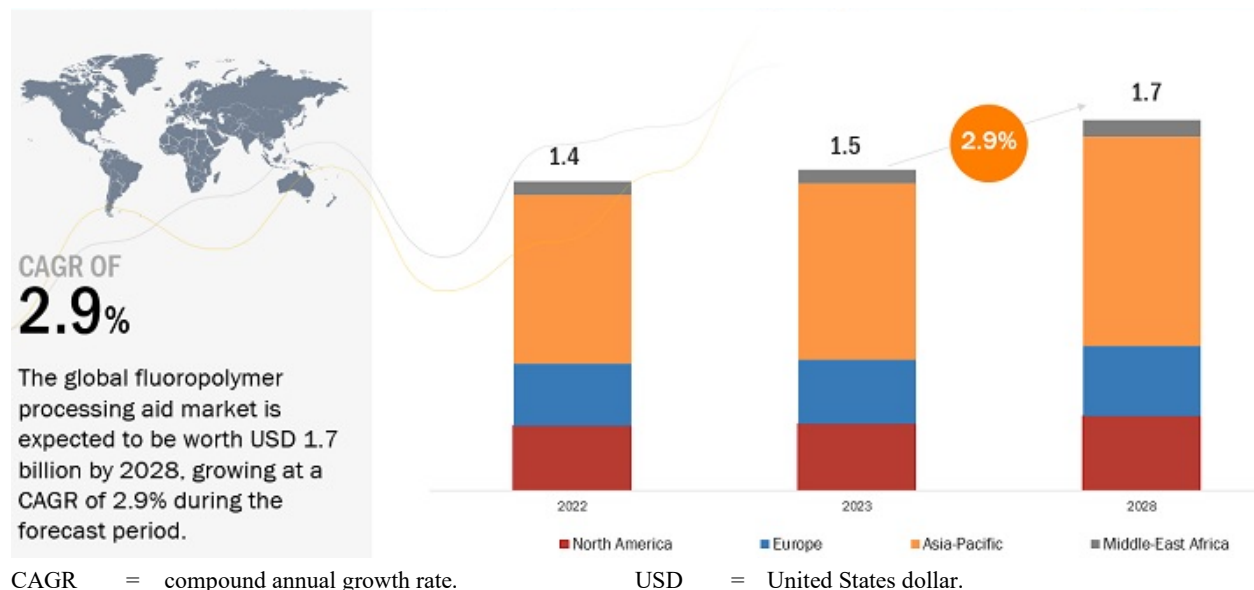
Source: Sullivan, H., 2021, "Dyeing, Printing & Finishing: PFAS – A Textile Perspective," *Textile World*.

Figure 2-6. Fluoropolymer and Fluorotechnology End Uses by Industry

2.3.1 Fluoropolymer Processing Aids Used in Polymer (Non-fluorinated Polymer) Processing

A well-known and economically significant use of selected fluoropolymers (FKM, PVDF, and PVDF copolymer) is as fluoropolymer processing aids (FPA), or synonymously fluorinated polymer processing aids, as an integral part of the processing of polyethylene (PE) products (Seiler et al., 2017), with lesser amounts of fluoropolymers also used for processing other polyolefins like polypropylene (PP) and polyethylene terephthalate (PET), where PE, PP, and PET are *not* fluoropolymers. FPAs act as lubricants, reducing friction, preventing melt fracture, improving surface finish, and facilitating processing. The most common FPAs are (1) vinylidene fluoride-hexafluoropropylene (VF2-HFP) copolymer and (2) vinyl fluoride-hexafluoropropylene (VF-HFP) copolymer with additives such as polyethylene oxide (PEO). FPAs are generally prepared using emulsion polymerization of VF2 and HFP in an aqueous reaction medium with an initiator and water-soluble fluorosurfactant¹⁶ capable of emulsifying both the initiator and reaction mass during the polymerization.

FPAs were originally developed to aid in the processing of linear low-density polyethylene (LLDPE) for blown films and tubing, where the addition of very small amounts of fluoropolymers (0.1 – 2.0 wt%) to polyolefins was discovered to provide processing benefits. The use of FPAs has expanded to many types of polyolefins and various types of melt processing because of (1) the effectiveness of FPAs as a melt processing/extrusion aid, and (2) growing demands for consumer goods and packaging and for plastics and composites in the automobile industry, even with the high cost of FPAs and potential regulatory concerns (MarketsandMarkets, 2023). As indicated in Figure 2-7, the FPA market was estimated at \$1.5B for 2023 and projected to increase to \$1.7B in 2028, driven largely by increased consumption of polymers such as PE, PP, and PET used in containers and packaging in the food and beverage industries.



Source: MarketsandMarkets, 2023, “Fluoropolymer Processing Aid Market by Polymer Type (PE, PP, PVC), Application (Blown & Cast Film, Wires & Cables, Pipes & Tubes, Fibers & Raffia), and Region (Europe, North America, Asia Pacific, MEA, South America) – Global Forecast to 2028,” CH 8634, MarketsandMarkets Research Pvt. Ltd, Pune, India.

Figure 2-7. Fluoropolymer Processing Aid Market – Global Forecast to 2028

¹⁶ Fluorosurfactants and fluorochemicals are forms of PFAS.

2.4 Properties of Fluoropolymers Used in the Sectors of this Study

This section outlines important properties for fluoropolymers used in the sectors of interest (as defined in Section 1.0) for this report, which include:

- Aerospace and automotive
- Battery, solar, and wind energy
- Building construction and infrastructure
- Chemical processing, storage, and disposal
- Electronics and semiconductors.

Because of the large quantity and ubiquity of fluoropolymers in the marketplace, the above list is not intended to be exhaustive but instead captures a high-level review of the breadth and depth of fluoropolymer activity.

2.4.1 Properties of Fluoropolymers Used in Aerospace and Automotive Applications

Exceptionally strong durability and resistance to extreme temperatures (from -200 °C to +200 °C), corrosion, oxidation, and ultraviolet (UV) radiation make fluoropolymers ideal for use in various environments in the aerospace and automotive sectors. Because of their resistance to heat, cold, smoke, fire, humidity, fluids, fuels, compression, and vibration, fluoropolymers prolong the useful life of various components and help improve reliability and engine efficiency. Compared to traditional steel and aluminum, fluoropolymers weigh significantly less and have superior strength and durability that help reduce payloads that ultimately provide added safety.

2.4.2 Properties of Fluoropolymers Used in Battery, Solar, and Wind Energy

Examples of fluoropolymer properties related to uses in the battery, solar, and wind energy sector (discussed further in Section 4.5) include:

- **Solar panels** – Fluoropolymers are used in both frontsheets for solar panels, as a result of their stability in UV light, low permeability, weather resistance, and ability to transmit light in the visible range, and in backsheets. A backsheet in a solar panel needs to be weather resistant, have mechanical strength, and provide electrical insulation over a wide range of operating temperatures. As with the frontsheet, the backsheet needs to maintain these properties over a wide range of operating temperatures.
- **Wind turbines** – Fluoropolymers are used in wind turbines for weather and corrosion-resistant properties.

2.4.3 Properties of Fluoropolymers Used in Building Construction and Infrastructure

Fluoropolymers, with their unique combination of properties, provide solutions for many challenging applications in building materials. Fluoropolymers are applied as coatings and are used in building materials that provide resistance to fire, water, and corrosive chemicals. Fluoropolymer coatings can also enable significant energy savings and can reduce building cooling costs and improve energy efficiency and use, up to 22% (Plastics Europe, 2023a). The non-wetting, non-stick properties and lightweight nature of fluoropolymers can extend the life of a building even in harsh/extreme environments and thus reduce maintenance. Fluoropolymers provide durable, thermally stable building materials that will enhance the overall stability of the structure. Such unique properties help in designing novel architectural designs that require flexibility and thin, lightweight materials that reduce energy use. Further, the very low surface energy provides dirt adhesion resistance that helps maintain solar reflective qualities, thereby preserving its energy efficiency and reducing maintenance costs (i.e., a high level of dirt adhesion resistance requires less frequent cleaning).

Fluoropolymer films and paints in the materials used for stadiums, domes, and glass fabric roofs provide enhanced stability. Fluoropolymer paints are used in bridge and offshore bearing pads for the lowest friction coefficient of all plastics (ACA, 2023).

2.4.4 Properties of Fluoropolymers Used in Chemical Processing, Storage, and Disposal

For chemical processing applications, important properties of fluoropolymers include stability, high continuous use temperature, weatherability, chemical resistance, fire resistant properties, release properties, biological inertness, low friction, cryogenic properties, flexibility, electrical properties, low dielectric constant, and low dissipation factor. The Vanderbilt survey responses indicate other critical properties of fluoropolymers, including specific gravity, melting point, tensile strength, elongation of break, compressive strength, and flex life. Other important chemical processing properties (e.g., mechanical strength, cryogenic, ultra-high purity) can be realized by choosing a specific fluoropolymer.

2.4.5 Properties of Fluoropolymers Used in Electronics and Semiconductor Processing and Components

Fluoropolymers are specialty materials that can be used to provide chemical and heat resistance, electrical insulation, strength, and durability to other materials. Depending on the selected fluoropolymer, the material can be used to extend the lifespan of components, improve fire safety, increase transmission speeds, and enable the creation of smaller, more powerful, and more integrated electronic products. For the semiconductor industry, fluoropolymers are used to enable pipes, vessels, valves, and pumps used in semiconductor manufacturing to withstand harsh etching and processing conditions, while maintaining purity requirements critical to this industry (West, 2020).

2.5 Fluoropolymer Distinctions

Research continues on whether or not fluoropolymers are polymers of low concern (Henry et al., 2018; Lohmann et al., 2020). To better explain fluoropolymer usage, scientists defined distinctions among three sets of fluoropolymers: (1) fluoropolymer substances, (2) fluoropolymer products, and (3) fluoropolymers in finished articles (Lohmann et al., 2020). The details of the definitions are provided in Table 2-4. The distinction is important mainly because fluoropolymers are diverse in their production (how they are produced), how they are transported or shipped, and how they are used; these distinctions are important to consider when assessing their potential ecological and human health hazards and risks.

Table 2-4. The Fluoropolymer Distinction

Fluoropolymer	Details	Examples
Fluoropolymer substance	Chemical structure of a fluoropolymer	PTFE: $(-\text{CF}_2-\text{CF}_2-)_n$, FEP: $(-\text{CF}_2-\text{CF}_2-)_n-(-\text{CF}_2-\text{CF}(\text{CF}_3)-)_m$, PFA: $(-\text{CF}_2-\text{CF}_2-)_n-(-\text{CF}_2-\text{CFOCF}_3-)_m$
Fluoropolymer product	Actual fluoropolymer material produced (solid or liquid) in different grades as granulates, fine powders, or aqueous dispersions	<ul style="list-style-type: none"> Teflon-granulate or Teflon-fine powder produced and sold by a chemical manufacturer May contain non-polymeric PFAS impurities from the production process (raw materials or processing aids)
Fluoropolymer in finished articles	Fluoropolymer products that are incorporated in their finished articles	PTFE tape, waterproof clothing with a PTFE membrane, PTFE-coated cookware, lubricant liquid

Source: Lohmann et al., 2020, "Are Fluoropolymers Really of Low Concern for Human and Environmental Health and Separate from Other PFAS?," *Environmental Science and Technology*, 54(20), pp 12820–12828.

FEP = fluorinated ethylene propylene.
PFA = perfluoroalkoxy.

PFAS = per- and polyfluoroalkyl substances.
PTFE = polytetrafluoroethylene.

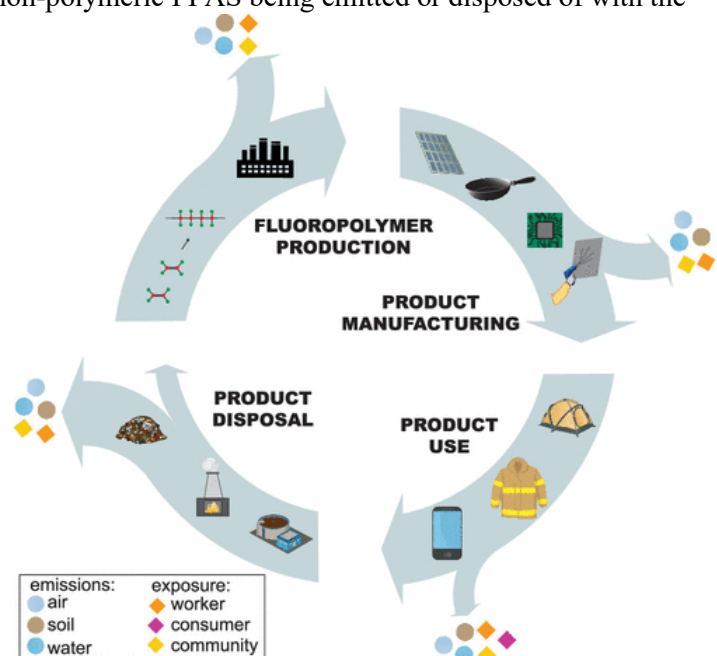
Increased attention on pollution caused by low molecular weight non-polymeric PFAS emissions is related to specific fluoropolymers during their life cycle (e.g., non-polymeric PFAS [low molecular weight] as processing aids in the production or emitted during product manufacture, usage, and disposal).

2.6 Fluoropolymers Production (Polymerization)

Synthesis of some fluoropolymers may require low molecular weight non-polymeric PFAS as polymerization aids, dispersion agents, or foaming agents. Specifically, in emulsion polymerization, non-polymeric PFAS act as surfactants or emulsifiers that help to improve the dispersion of monomers and enable polymerization in aqueous solution. Non-polymeric PFAS polymerization aids are important nonreactive additives that are used in fluoropolymer synthesis. In some fluoropolymers, the non-polymeric PFAS act as raw materials.

In either type of fluoropolymer synthesis, most of the polymerization aid is recycled or recovered from the solution, with the remaining fraction of non-polymeric PFAS being emitted or disposed of with the effluent wastewater or waste. Typical polymerization aids used in industry are PFOA, PFNA, and HFPO-DA. Significant fluorosurfactant polymerization aid is incorporated into the polymer during the polymerization process; however, much of this unbound polymerization aid is removed during heat treatment of the resulting powdered fluoropolymer.

Under typical manufacturing conditions (Lohmann et al., 2020), a low concentration of the processing aid may remain incorporated with the fluoropolymer and be released during use (Drohmann et al., 2021); the fluoropolymer itself may also be degraded (e.g., at high temperature but too low for complete destruction, aggressive conditions), with the resulting low molecular weight PFAS degradation products (potentially including microplastics) emitted into the environment during its life cycle (Lohmann et al., 2020). A conceptual diagram of low molecular weight PFAS emissions during the fluoropolymer life cycle is presented in Figure 2-8.



Source: Lohmann et al., 2020, "Are Fluoropolymers Really of Low Concern for Human and Environmental Health and Separate from Other PFAS?," *Environmental Science and Technology*, 54(20).

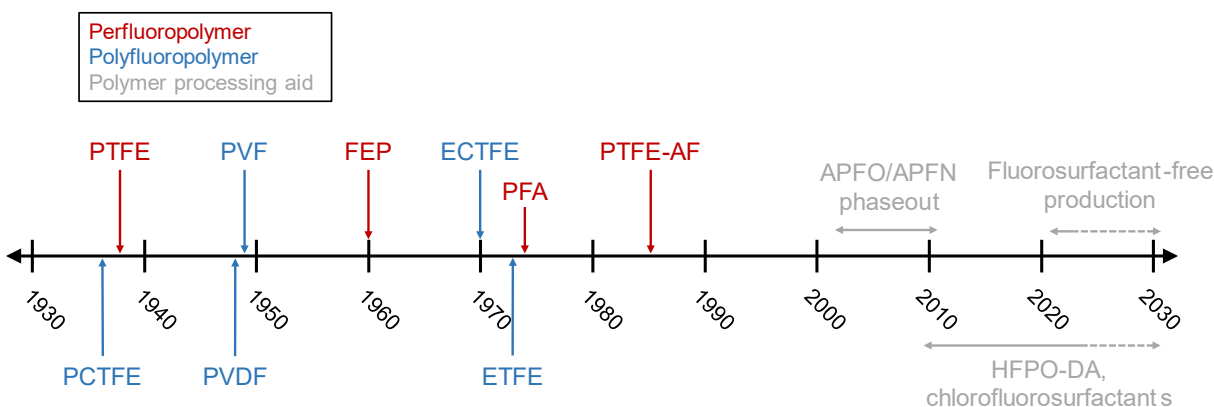
Figure 2-8. Conceptual Diagram Showing the Low Molecular Weight Per- and Polyfluoroalkyl Substances (Non-polymers) Emissions During Fluoropolymer Production, Manufacturing, Usage, and Disposal

In the production of flexible fluoropolymer products via radiation or electron beams, remaining non-polymeric PFAS could potentially be released. For example, fluoropolymers such as ETFE, PVDF, and ECTFE can be chemically etched via irradiation to induce reactive free-radical sites or functionalization directly on the polymer chains, which renders reactive sites on the polymer for linking to other polymers and typically results in improved mechanical and physicochemical properties (Gardiner, 2014; Teng, 2012). Such methods will improve performance of these fluoropolymers as engineering thermoplastics in demanding applications. As a result of radiation or electron-beam processing, non-polymeric PFAS (low molecular weight) may be formed as by-products of the etching process, with subsequent potential for release.

3.0 FLUOROPOLYMER MANUFACTURING

Fluoropolymers find use in many sectors of commercial and industrial applications and are manufactured in a wide variety of chemistries and physical forms to accommodate specific end uses. Although the term fluoropolymer may refer to any chemical substance formed by reaction of fluorinated monomeric precursors to form a macromolecular repeating structure, in the context of this report, the discussion in this section is constrained to treatment of fluoropolymer plastics, including both thermoplastic (rigid materials formed by heating or machining) and elastomeric (flexible material) forms. In this context, fluoropolymer plastics refer to water-insoluble, solid-state materials (either hard or soft), composed of fluoropolymers and useful for fabrication of physical articles. Many of these materials share similar synthetic production routes and chemical properties (discussed in Section 2.0). Fluoropolymer plastics are distinct from fluorinated side-chain polymers, which are formed through polymerization of non-fluorinated polymeric backbones with various perfluorocarbon side chains. Also distinct from fluoropolymer plastics are PFPEs, which are typically produced as oligomeric formulations for use in applications such as high-temperature, chemically resistant lubricant oils and greases (Glüge et al., 2020).¹⁷

The commercial production of fluoropolymer plastics began after the 1938 discovery of PTFE as an unintentional reaction product of the refrigerant candidate TFE (Plunkett, 1986). PTFE was found to be exceptionally resistant to chemical attack and highly thermally stable and was initially used for applications in the Manhattan Project because of these unique properties (i.e., the uranium hexafluoride used in the separation process is highly reactive). PTFE was marketed commercially as Teflon by DuPont starting in the late 1940s, and development and commercialization of additional fluoropolymer plastics continued through the 1980s, as shown in Figure 3-1.



Based on information from McKeen and Ebnesajjad (2023a).

Figure 3-1. Timeline of Fluoropolymer Development (Major Fluoropolymer Plastics and Polymer Processing Aids)

Many forms of fluoropolymer plastics required the use of fluorosurfactant emulsifiers as polymer processing aids during production. These low molecular weight fluorochemicals, including PFOA and PFNA, were eventually found to be of concern due to their exceptionally long half-lives in biological and environmental systems, water solubility, and toxicity at low levels (Prevedouros et al., 2006).

¹⁷ Fluorinated side-chain polymers and PFPEs are taxonomically distinguished in this report from fluoropolymers and may have different life cycle characteristics and environmental impacts than fluoropolymer plastics, which are the focus of this study. Fluorinated side-chain polymers and PFPEs, which are considered distinct categories, are thus not included as part of the evaluation in this report.

In recent years, the fluoropolymer industry has introduced low molecular weight fluorochemical replacements for PFOA and PFNA as polymer processing aids (Figure 3-1), although these replacements (including chlorofluorosurfactants and HFPO-DA) also have significant environmental implications (McCord et al., 2020; Sun et al., 2016). Most recently, several fluoropolymer manufacturers have introduced fluorosurfactant-free production methods to address environmental safety concerns (Reich, 2008; Solvay, 2022).

3.1 Fluoropolymer Plastic Forms

Fluoropolymer plastics are produced in several physical and chemical forms, depending on the polymer chemistry and the desired end-use (McKeen and Ebnesajjad, 2023; Gardiner, 2014). The four primary classes of fluoropolymer plastic production forms are:

- **Crystalline, non-melt-processable:** PTFE (Teflon) is the most important commercial example of this type of fluoropolymer. These fluoropolymers are produced in several physical forms, including granular, powdered, aqueous dispersion, or paste. The materials are highly crystalline and undergo thermal decomposition at temperatures below their flow transition and, therefore, cannot be processed into useful shapes via conventional thermoplastic extrusion and molding techniques. Fabrication of finished parts from non-melt-processable polymers, such as PTFE, typically requires techniques similar to those used in metal sintering and results in an opaque and somewhat porous material.
- **Crystalline, melt-processable:** Most of the major fluoropolymer plastics shown in Figure 3-1 fall into this category. These polymers can be processed into final shapes using conventional thermoplastic extrusion and molding techniques, making them more economical than the non-melt-processable polymers. These fluoropolymers can be further classified as perfluoropolymers, such as FEP and PFA, where fluorine substitutes for hydrogen in all possible bonds to carbon, and polyfluoropolymers such as PVF and ETFE, where hydrocarbon functional groups are incorporated into the backbone of the polymer. Typically, crystalline, melt-processable fluoropolymers are either opaque or translucent and cannot be produced in transparent form. These materials can be extruded or molded into practically any shape, including tubes and films.
- **Amorphous, melt-processable:** These fluoropolymers were introduced in the mid-1980s and include, most notably, Teflon amorphous fluoropolymer (AF) (Figure 3-1), which offers the chemical resistance of perfluoropolymers such as PTFE in a form that can be readily processed via thermoplastic extrusion and molding techniques. In addition, the amorphous, low-crystallinity nature of the macromolecular polymer structure makes these polymers more transparent than their crystalline analogs, with excellent optical properties. Semicrystalline materials, such as the terpolymer THV, bridge the gap in properties between amorphous and crystalline melt-processable polymers.
- **Fluoroelastomers:** Elastomeric forms of fluoropolymers are produced by a combination of multiple monomers, including those that form straight-chain segments and bulkier monomeric components that break up the crystallinity of the polymer at regular intervals. These polymers are engineered to exist below their glass transition temperatures in typical operating conditions, making them easily deformable and recoverable from strain (Drobny, 2016).

3.2 Overview of Fluoropolymer Production

Fluoropolymer production begins in all cases with the availability of precursor monomers. In nearly all cases, these monomers are based on a vinyl group substructure (Figure 3-2), wherein an ethylene functional group serves as the site for attack of free-radical-based initiators that induce polymerization.

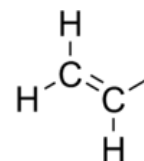
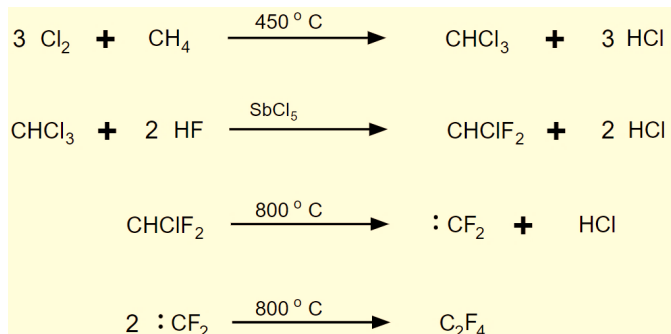


Figure 3-2. Vinyl Group Substructure

Variations on the chemical substituents bonded to the vinyl core structure lead to different polymer properties in fluoropolymers. The simplest monomer in fluoropolymer production is TFE (C_2F_4 in Figure 3-3), which is directly analogous to the hydrocarbon monomer ethylene used in production of low- and high-density polyethylene. While ethylene (and other hydrocarbon vinyl monomer feedstocks) are easily isolated from petrochemical feedstocks through cracking during refining, fluorochemical monomers such as TFE are considerably more difficult to prepare.



Source: Mierdel, K., A. Jess, T. Gerdes, A. Schmidt, and K. Hintzer, 2019, "Energy and Resource Efficient Production of Fluoroalkenes in High Temperature Microreactors," *ChemEngineering*, 3(4), 77.

Figure 3-3. Production of Tetrafluoroethylene (TFE | C_2F_4) Through the R22 Process

The complexity of monomer production contributes to the significantly higher cost of fluoropolymer production relative to the analogous hydrocarbon polymers (e.g., polyethylene and polypropylene). An example of this cost difference is production of TFE through the so-called R22 route (Mierdel et al., 2019), wherein multi-step synthesis of the final TFE monomer proceeds through synthetic routes, including chlorinated hydrocarbons and hydrofluoric acid, to produce the intermediate difluorochloromethane (R22), which was formerly used as a refrigerant before being recognized as a potent contributor to high global warming potential and ozone depletion in the upper atmosphere. Further treatment by pyrolysis yields TFE through an unstable difluorocarbene intermediate (Figure 3-3). Apart from the elaborate and resource-intensive synthetic route necessary to prepare it, production of TFE via the R22 route produces waste products that must be disposed of, including carbon tetrachloride and hydrochloric acid (Mierdel et al., 2019). As discussed in Section 3.3, TFE is required in nearly all fluoropolymer plastic production methods.

Production of fluoropolymer plastics proceeds at-scale through industrial processes appropriate to the particular formulation. In most cases, industrial synthesis of fluoropolymers is based on free-radical polymerization using peroxide-based catalysts such as ammonium persulfate or potassium permanganate (Gardiner, 2014). For some polymers, small quantities of crosslinkers or other additives are introduced at the polymerization stage to adjust final properties. In nearly all cases, polymerization of fluoropolymer plastics proceeds under aqueous conditions either (1) through suspension polymerization whereby monomers are directly added to an aqueous solution with catalysts, or (2) via emulsion polymerization whereby a fluorosurfactant such as ammonium perfluorooctanoate (APFO), ammonium perfluorononanoate (APFN) (Prevedouros et al., 2006), HFPO-DA, also known as GenX (Strynar et al., 2015), or chlorofluorosurfactants (McCord et al., 2020) are introduced along with the monomer to form a fine dispersion prior to polymerization. In both cases, the resulting polymers are insoluble in aqueous solution and are readily isolated by settling or filtration (Gardiner, 2014).

Many melt-processable fluoropolymer plastics are di-block or tri-block copolymers, requiring careful control of the various monomer ratios to obtain the desired physicochemical properties. In addition, additives and chain-transfer agents can be added to adjust the molecular weight of the produced resins (Gardiner, 2014) in an analogous manner to the production of hydrocarbon thermoplastics. Perfluoropolymers, such as PTFE, are typically recalcitrant to reactive crosslinking, due to their extraordinarily inert fluorine-carbon bond structure, and thus, these polymers often exhibit lower tensile strength and are subject to creep and flow under pressure.

Polyfluoropolymers such as ETFE can be crosslinked via introduction of chemically reactive crosslinking additives or via irradiation to induce reactive free-radical sites directly on the polymer chains (Gardiner, 2014). This introduction of sites typically results in improved mechanical and physicochemical properties such that these polyfluoropolymers are often used as engineering thermoplastics in demanding applications (Section 2.6).

Crystalline fluoropolymers are insoluble in nearly all known solvents and, therefore, must be processed into final form via either sintering (e.g., for PTFE) or thermal molding/extrusion (e.g., for thermoplastic fluoropolymers). Some amorphous fluoropolymers are soluble in select organic solvents, enabling such fluoropolymer plastics to be solvent-cast into thin (and optically transparent) films (Gardiner, 2014).

The primary manufacturers of fluoropolymer plastic resins as of 2014 were DuPont, Chemours, Asahi Glass/AGC, Solvay, 3M, Dyneon (a 3M and Hoechst joint venture), Honeywell, Arkema, and Daikin (Gardiner, 2014). Production and consumption of fluoropolymers reached approximately 270,000 tons per year by 2015, with most of this consumption accounted for by PTFE (140,000 tons/year) (Mierdel et al., 2019).

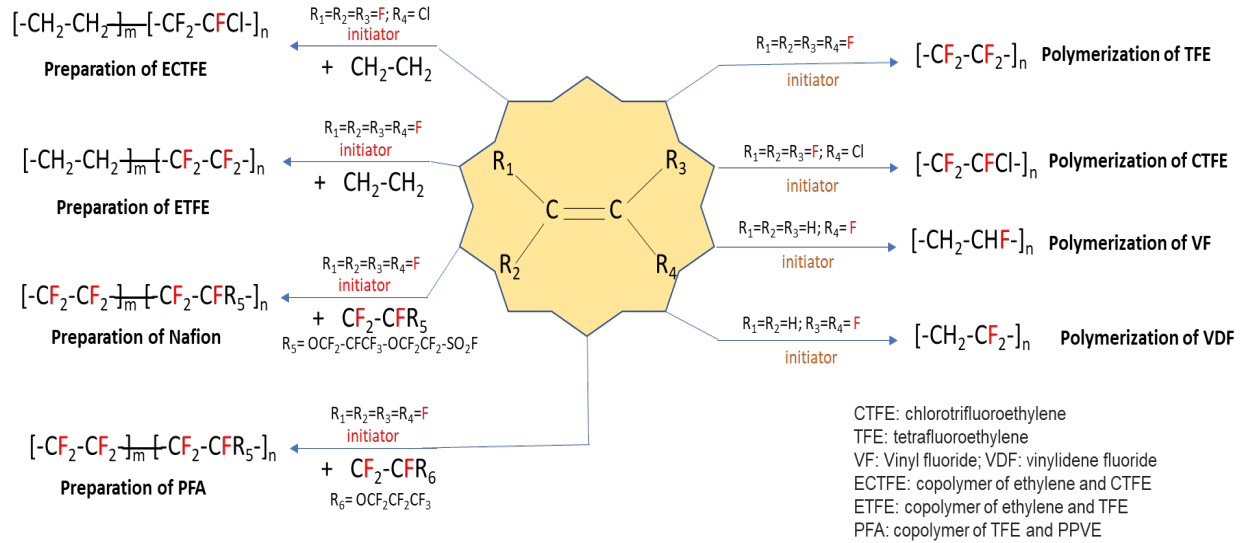
The market for fluoropolymers was expected to grow to 475,000 tons per year by 2022, with a compounding annual growth rate of 6.5% over the period 2016 – 2022. The largest consumer and user of PTFE in the world is China, accounting for 44% of consumption and 50–55% of production, respectively, in 2017. The U.S. is a net importer of PTFE, and several tens-to-thousands of tons of PTFE oversupply are typically in the global market, contributing to price depression worldwide. Melt-processable fluoropolymer plastic consumption worldwide is dominated by China and the U.S., with each accounting for approximately 30% of consumption, while western countries and Japan account for most of the corresponding production capacity (McKeen and Ebnesajjad, 2023a).

North America is the second largest fluoropolymers market (second to the Asia-Pacific region), which accounts for approximately 25% revenue share of global consumption in 2019. North American fluoropolymer consumption was estimated to be 92 kilotons (kt) and \$1.4B in 2019. Fluoropolymer consumption is forecast to grow during the 2020 to 2025 period at a compound annual growth rate (CAGR) of 4.8% kt. The North American fluoropolymer market is forecast to grow during 2020 to 2025 at a CAGR of 5.0% to reach approximately \$1.9B (PLS080B, *Fluoropolymer Materials: Technologies and Global Markets*).

PTFE accounted for the largest portion of the U.S. fluoropolymer market in 2020, where it was extensively used in chemical processing, cookware and bakeware, and medical applications. North American fluoropolymer consumption is also being affected by the growing use of fluoropolymers in wire and cable applications, where fluoropolymers are used as jacketing and primary insulation material and for fiber optic cables. FEP and PVDF are the fastest-growing product types with respect to these applications. PVDF is also expected to grow relatively quickly in North America, as the material is increasingly being used in lithium-ion batteries and architectural coating applications (PLS080B).

3.3 Overview of Fluoropolymer Chemistry

The chemistry of fluoropolymer production is based on free-radical initiated polymerization of vinyl-based monomers, including TFE and related compounds (Figure 3-4). Details of production and synthesis methods for the most important fluoropolymer plastics in use today are described as follows.



Note: Based on information from Teng (2012).

Figure 3-4. Fluoropolymer Plastic Synthesis Begins with Vinyl Monomer Precursors, Proceeding Through Free-Radical-Initiated Polymerization to Form Final Polymers

3.3.1 Polytetrafluoroethylene (PTFE)

PTFE was the first commercial fluoropolymer, accidentally discovered in 1938 (Figure 3-1) (Plunkett, 1986; Teng, 2012). This homopolymer is chemically analogous to polyethylene, with all hydrogen atoms replaced by fluorine atoms. PTFE differs structurally from polyethylene in its helical polymer chain configuration, leading to a very high crystallinity (Teng, 2012). The very high fluorine-to-carbon ratio of this material and its dense structure gives PTFE the highest density of any fluoropolymer (Sastri, 2014). The high density and the corresponding rigidity of the polymer chain result in an exceptionally high melting point (320 °C) and a corresponding high viscosity near the melting point (Teng, 2012; McKeen and Ebnesajjad, 2023b). PTFE thermally decomposes at a temperature below its flow-point, such that it cannot be melt-processed through conventional thermoplastic extrusion and molding techniques.

Synthesis of PTFE is accomplished via peroxide-initiated polymerization of TFE monomers in aqueous solutions (Figure 3-5) (Teng, 2012; McKeen and Ebnesajjad, 2023b). The initial physical form of the polymer is dictated by the use or absence of dispersion agents such as fluorosurfactants. When PTFE is produced using emulsion polymerization without a fluorosurfactant, PTFE forms granules that can be isolated from the synthesis liquor by settling. These granules are useful for fabrication of parts via compression molding and ram extrusion (Teng, 2012).

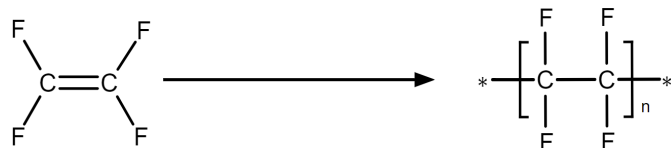


Figure 3-5. Production of Polytetrafluoroethylene from Tetrafluoroethylene Precursor

Emulsion polymerization of PTFE in the presence of a fluorosurfactant yields an aqueous dispersion of fine PTFE powders, which is then useful for fabrication of parts via paste extrusion or (in aqueous dispersion) to produce coatings or thin films by casting (Teng, 2012). For powdered PTFE, the fluorosurfactant is typically removed by heat-treating, while PTFE dispersions retain the fluorosurfactant as an impurity (Prevedouros et al., 2006).

The most commonly used fluorosurfactant for PTFE emulsion polymerization was APFO until the early 2000s, when this compound was replaced in the Chemours process by HFPO-DA (Figure 3-1). Discharge of fluorosurfactant from PTFE and other fluoropolymer production, and its presence as an impurity in fabricated products, has led to widespread environmental contamination and has motivated a move toward fluorosurfactant-free production methods. Representative commercial PTFE resins and manufacturers include Teflon (DuPont), Polyflon¹⁸ (Daikin), Dyneon¹⁹ PTFE (Dyneon), and Fluon²⁰ (Asahi Glass/AGC).

3.3.2 Polychlorotrifluoroethylene (PCTFE)

A close structural analog to PTFE, the homopolymer PCTFE, was the second fluoropolymer to be commercialized as Kel-F²¹ by the M. W. Kellogg Company in 1953 (Teng, 2012), although it was first reported in 1937, before PTFE (McKeen and Ebnesajjad, 2023a). This plastic is a polyfluoropolymer, wherein one of the fluorine atoms of TFE is replaced by a chlorine atom. Relative to PTFE, this substitution renders the resulting polymer less crystalline due to the incorporation of the bulkier chlorine atom and disruption of the tightly packed polymer chain (Teng, 2012; McKeen and Ebnesajjad, 2023f). This material was the first truly extrudable and thermoplastic fluoropolymer. PCTFE is produced by the same synthetic route as PTFE, with aqueous suspension or emulsion polymerization methods (Figure 3-6).

PCTFE is somewhat more expensive to produce than PTFE, due to the added expense of the chlorinated monomer, and is typically used in specialty applications. The material is not as solvent-resistant as PTFE but exhibits enhanced engineering properties such as less susceptibility to creep and cold-flow (Teng, 2012; McKeen and Ebnesajjad, 2023f).

Although 3M no longer manufactures PCTFE as Kel-F, it is currently in production by Daikin as Neoflon,²² by Honeywell as Aclar,²³ and by Arkema as Voltalef²⁴ (Teng, 2012).

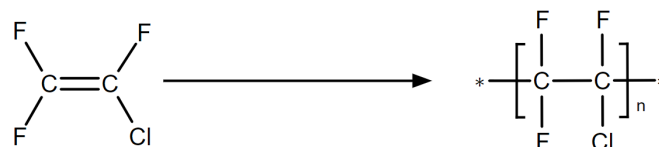


Figure 3-6. Production of Polychlorotrifluoroethylene from Chlorotrifluoroethylene

3.3.3 Polyvinyl Fluoride (PVF)

The hydrofluoropolymer PVF was introduced in 1961 by DuPont. This homopolymer is very similar in structure to polyethylene, with only a single substitution of hydrogen to fluorine in the monomer structure (Teng, 2012; McKeen and Ebnesajjad, 2023e). As with the other fluorinated homopolymers described above, PVF is synthesized in an aqueous solution by free-radical initiated polymerization (Figure 3-7).

However, the production of PVF requires higher pressure than, for example, PTFE (Teng, 2012). Because the vinyl fluoride precursor is asymmetric, PVF can polymerize in two orientations (head-to-tail and head-to-head), leading to irregularities and structural defects in the resulting polymer material (McKeen and Ebnesajjad, 2023e).

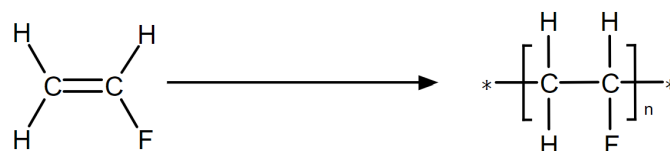


Figure 3-7. Production of Polyvinyl Fluoride from Vinyl Fluoride

¹⁸ Polyflon is a registered trademark of Daikin Industries, Ltd., Osaka, Japan.

¹⁹ Dyneon is a registered trademark of 3M Company, St. Paul, Minnesota.

²⁰ Fluon is a registered trademark of AGC Chemicals, Exton, Pennsylvania.

²¹ Kel-F is registered trademark of 3M Company, St. Paul, Minnesota.

²² Neoflon is a registered trademark of Daikin Industries, Osaka, Japan.

²³ Aclar is a registered trademark of Honeywell International Inc., Charlotte, North Carolina.

²⁴ Voltalef is a registered trademark of Arkema S.A., Colombes, France.

As with other homopolymer fluoropolymer plastics, PVF can be prepared via suspension or emulsion polymerization. PVF is not as chemically resistant as PTFE and PCTFE but exhibits good melt-processibility and can be cast into films that are easily functionalized by exposure to radiation and electron beams (Teng, 2012). Currently, the only commercial PVF is produced in film form by DuPont under the brand name Tedlar.²⁵

3.3.4 Polyvinylidene Fluoride (PVDF)

Polymerization of vinylidene fluoride (VDF) to form PVDF was first reported in 1948 by DuPont (McKeen and Ebnesajjad, 2023e). This homopolymer is prepared by aqueous free-radical initiated emulsion or suspension polymerization in a similar manner to that used for other vinylic homopolymer fluoropolymer plastics such as PTFE (Figure 3-8). The resulting polyfluoropolymer is easily melt-processable and moldable using conventional thermoplastic handling methods.

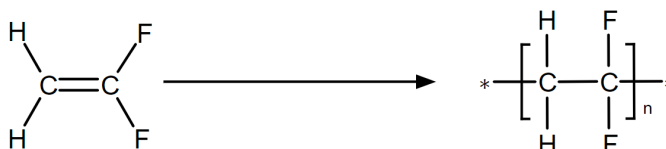


Figure 3-8. Production of Polyvinylidene-Fluoride from Vinylidene Fluoride

PVDF is less chemically resistant than PTFE but exhibits excellent mechanical properties and can be crosslinked by ionizing radiation (Teng, 2012), making it the second most highly produced fluoropolymer plastic after PTFE (McKeen and Ebnesajjad, 2023e). The largest producer of PVDF is Arkema, through their Kynar²⁶ product line (Teng, 2012; McKeen and Ebnesajjad, 2023e). Historically, Arkema used APFN as a surfactant in their production method; however, the use of fluorosurfactants in Kynar production has been phased out due to environmental concerns (Reich, 2008). Solvay produces PVDF as Solef²⁷ and also historically used APFN as a polymer processing aid. Solvay has recently announced their intention to move to a fully fluorosurfactant-free PVDF production process in 2026, while employing a perfluoroether surfactant in the interim period (Solvay, 2022). The third major producer of PVDF is Daikin, as Neoflon PVDF (Teng, 2012).

3.3.5 Ethylene-Chlorotrifluoroethylene (ECTFE) Copolymer

Copolymers between hydrocarbon-based and fluorochemical vinyl monomers were introduced as commercial products in the 1970s starting with the development of ECTFE and its subsequent production by Ausimont. This polymer has an alternating ethylene and chlorotrifluoroethylene (CTFE) structure, as shown in Figure 3-9.

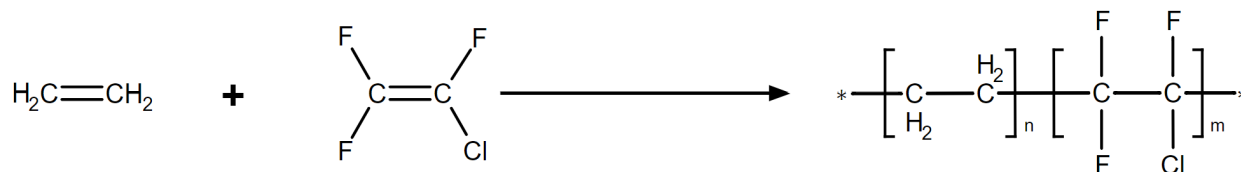


Figure 3-9. Production of Ethylene-Chlorotrifluoroethylene from Ethylene and Chlorotrifluoroethylene

Polymerization of this copolymer is performed under aqueous conditions using a peroxide-based free-radical catalyst together with a chain transfer agent (usually halogenated), which serves to control the resulting polymer molecular weight (Teng, 2012). No fluorosurfactants are reported to be used in this process.

²⁵ Tedlar is a registered trademark of DuPont, Wilmington, Delaware.

²⁶ Kynar is a registered trademark of Arkema S.A., Colombes, France.

²⁷ Solef is a registered trademark of Solvay S.A., Brussels, Belgium.

The polymeric production of ECTFE results in a zig-zag structure, which yields moderate crystallinity (50-60%) and stability over a wide range of temperature conditions. As a melt-processable thermoplastic, ECTFE can be extruded and molded into a variety of shapes, including sheets and filaments. ECTFE is more dimensionally stable than PTFE and other perfluoropolymers, exhibits high tensile strength (Teng, 2012), and can be chemically crosslinked using ionizing radiation (Gardiner, 2014). ECTFE is currently manufactured as Halar²⁸ by Solvay, primarily for use in cable and wiring insulation (Teng, 2012).

3.3.6 Ethylene-Tetrafluoroethylene (ETFE) Copolymer

Unlike many other fluoropolymers, the copolymer of ethylene and TFE (Figure 3-10) developed by DuPont in 1973 and marketed as ETFE is not typically produced under aqueous conditions.

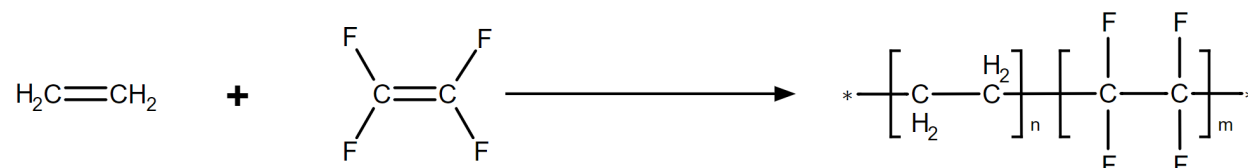


Figure 3-10. Production of Ethylene Tetrafluoroethylene from Ethylene and Tetrafluoroethylene

This copolymer is typically prepared in a solvent (usually a chlorofluorocarbon liquid) with a fluorinated peroxide initiator (Teng, 2012) but without an emulsifier. Like ECTFE, ETFE forms a zig-zag polymer structure, yielding a crystallinity below 60% and a variable melting temperature depending on the ratio of ethylene to TFE.

Among all copolymers of TFE, ETFE exhibits some of the best engineering properties, as it can be fabricated into finished products using the full range of thermoplastic processing techniques. For example, ETFE can be blow molded, extruded, injection molded, or compression molded (Teng, 2012). This copolymer is moderately chemically resistant and like many ethylene copolymers can be crosslinked by ionizing radiation (Gardiner, 2014; Teng, 2012). ETFE is marketed commercially by DuPont as Tefzel,²⁹ by Asahi Glass/AGC as Fluon, by Solvay as Halon³⁰ ETFE, by Daikin as Neoflon ETFE, and by Dyneon as Dyneon ETFE.

3.3.7 Fluorinated Ethylene Propylene (FEP) Copolymer

The need to create a perfluoropolymer with the chemical resistance of PTFE but with the melt-processability of conventional hydrocarbon-based thermoplastics led to development of a FEP copolymer by DuPont in 1960. This copolymer of TFE and hexafluoropropylene (HFP) yields a perfluorinated structure that is very similar to PTFE but with a trifluoromethyl functional side-group on the polymeric chain (Figure 3-11) (Gardiner, 2014; Teng, 2012).

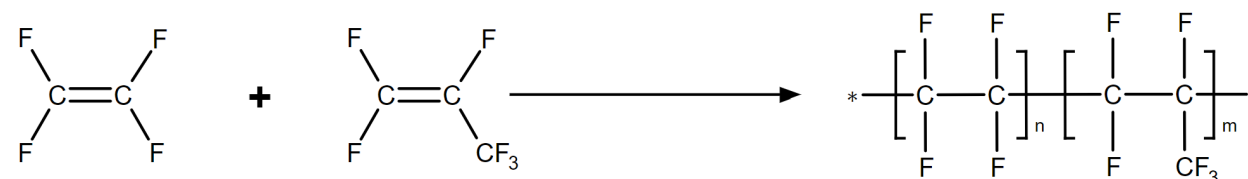


Figure 3-11. Production of Fluorinated Ethylene Propylene from Tetrafluoroethylene and Hexafluoropropylene

²⁸ Halar is a registered trademark of Solvay S.A., Brussels, Belgium.

²⁹ Tefzel is a trademark of Chemours, Wilmington, Delaware, for its brand of ETFE fluoropolymer resins.

³⁰ Halon is a registered trademark of Allied Corporation, Morristown, New Jersey.

This polymer is a structural analog of the hydrocarbon plastic polypropylene. As with PTFE, the synthesis of FEP typically involves free-radical polymerization in an aqueous medium, usually in the presence of a fluorosurfactant dispersing agent – commonly HFPO-DA (McKeen and Ebnesajjad, 2023c). As a copolymer, careful control of the monomer ratio and reaction conditions is necessary to generate a polymer with acceptable use properties. FEP typically contains approximately 5 mol% HFP, which is sufficient to disrupt the regular crystal structure of pure PTFE and yield a crystallinity below 70% (Teng, 2012; McKeen and Ebnesajjad, 2023c). The resulting copolymer is somewhat more translucent than PTFE and can be melt-processed but retains its exceptional chemical inertness and insolubility with superior mechanical properties relative to PTFE (Teng, 2012). Some specific FEP commercial products include Teflon FEP (Dupont), Neoflon FEP (Daikin), and Dyneon FEP (Dyneon).

3.3.8 Perfluoroalkoxy (PFA) Polymer

Additional work by DuPont to generate melt-processable analogs of PTFE resulted in development of a PFA polymer, which is a perfluorinated copolymer of TFE and a fluorinated vinyl ether such as perfluoropropylvinylether (PPVE) (Figure 3-12).

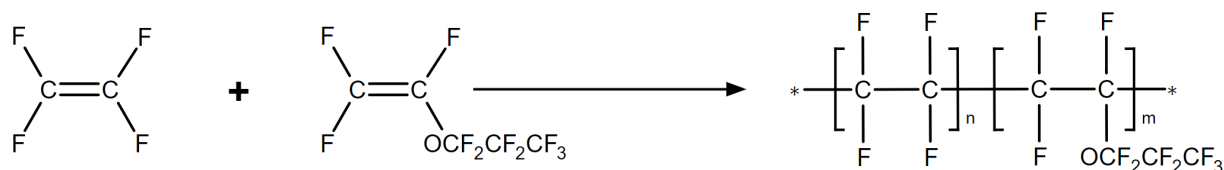


Figure 3-12. Production of Perfluoroalkoxy from Tetrafluoroethylene and Perfluoropropylvinylether

The incorporation of PPVE into PFA represents the first incorporation of oxygen-containing ether functional groups into perfluoropolymers and yields a fluoropolymer plastic with exceptional chemical resistance and processability (Teng, 2012; McKeen and Ebnesajjad, 2023d). As with most other fluoropolymer plastics, the dominant method used to prepare PFA is dispersion or suspension polymerization with fluorosurfactants such as HFPO-DA. Commercial PFA formulations typically have approximately 3.5–4% vinyl ether monomer incorporated into the structure. As with FEP, this branched monomer incorporation is sufficient to lower the crystallinity of the polymer sufficiently to allow ready-melt processibility (McKeen and Ebnesajjad, 2023d).

In addition to PPVE, additional vinyl ether monomers such as perfluoroethylvinylether (PEVE, Chemours) and perfluoromethylvinylether (PMVE, Solvay) have been produced and marketed (McKeen and Ebnesajjad, 2023d). PFA polymers can be made in exceptional purity for sensitive applications requiring low levels of impurities and additives (e.g., semiconductors). Commercial PFA formulations include Teflon PFA (DuPont), Aflon³¹ PFA (Asahi Glass/AGC), Dyneon PFA (Dyneon), Neoflon PFA (Daikin), and Hyflon³² PFA (Solvay) (Teng, 2012).

3.3.9 Amorphous Perfluoropolymer

The limited solubility in solvents, poor optical clarity, and relatively high deformability under stress inherent to crystalline or semicrystalline perfluoro- and polyfluoropolymers described above limited their applications in specialized scenarios (Teng, 2012). The first amorphous perfluoropolymer was developed by DuPont in 1985 by copolymerization of TFE and perfluoro-2,2-dimethyl-1,3-dioxole (PDD) (Figure 3-13). Consistent with other fluoropolymer production methods, the synthesis is carried out in aqueous media with a peroxide-based initiator.

³¹ Aflon is a registered trademark of AGC Inc. (formerly Asahi Glass Co., Ltd.), Tokyo, Japan.

³² Hyflon is a registered trademark of Solvay S.A., Brussels, Belgium.

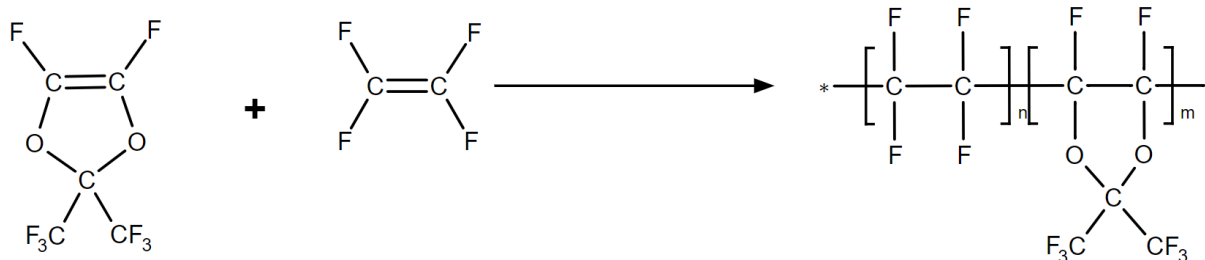


Figure 3-13. Production of Teflon Amorphous Fluoropolymer from Tetrafluoroethylene and Perfluoro-2,2-Dimethyl-1,3-Dioxole

Once polymerized, these materials have very low refractive indices, making them suitable for use in optical applications such as spectrometer windows and transparent tubing and fiber cladding. Amorphous fluoropolymers are also soluble in several organic solvents, rendering them viable for thin-film casting and use in dip-coating of circuits and other specialized applications. The DuPont product is branded as Teflon AF, while Solvay markets an analogous copolymer of TFE and 2,2,4-trifluoro-5-trifluoromethoxy-1,3-dioxole (TTD) as Hyflon AD. Asahi Glass/AGC produces an amorphous homopolymer of perfluoro-3-butenylvinylether (PBVE) as Cytop.³³

3.3.10 Sulfonated Perfluorinated Ionomer (Nafion)

The fluoropolymer plastics discussed previously are neutral polymers, carrying no net charge. The development of the copolymer Nafion by DuPont in the 1960s yielded the first ionic fluoropolymer, or ionomer (Teng, 2012). This polymer is synthesized by copolymerization of TFE and the ionogenic monomer based on perfluoroalkylvinylethersulfonyl fluoride chemistry (Figure 3-14).

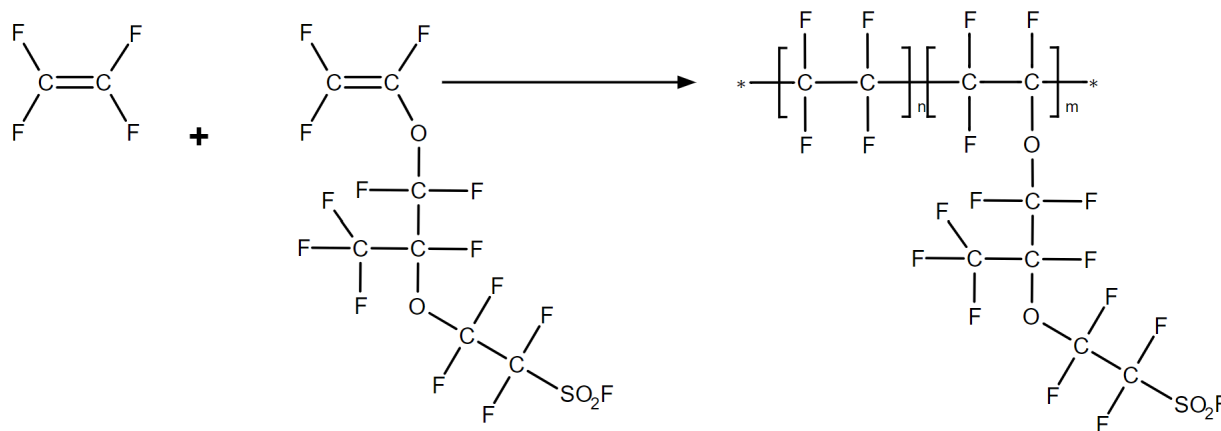


Figure 3-14. Production of Nafion from Tetrafluoroethylene and Perfluoroalkylvinylethersulfonyl Fluoride

Polymerization of this material under aqueous conditions, with the addition of concentrated sodium hydroxide, yields sulfonic acid functional groups from hydrolysis of the sulfonyl fluoride (Teng, 2012). The resulting polymer is soluble in hot aqueous alcohol and such preparations are suitable for the production of thin films.

The primary form of sulfonated perfluorinated ionomers is used to make ion-conductive membranes, which exhibit chemical resistance while offering high ion-conductivity (Teng, 2012). These materials are not typically melt-processed or extruded due to their intended uses in membrane technology. To date, the primary producer of these perfluoroionomer materials is DuPont, as Nafion.

³³ Cytop is a trademark of AGC Inc., Tokyo, Japan.

4.0 COMMERCIAL USES OF FLUOROPOLYMERS AND COMPETING TECHNOLOGIES

Throughout various industries, fluoropolymers are often essential to maintaining the effectiveness, safety, and robustness of a wide range of products across many industry sectors. A consistent theme throughout this section is that no industrially scaled materials are currently available and viable to fill the role of fluoropolymer plastics if required for multiple performance characteristics, as described in Section 2.0. While other polymers and non-polymers can resist chemical attack, be used at temperatures exceeding 260 °C, resist UV radiation, have low weight, and have considerable strength and durability, finding alternative materials that can meet multiple or all these requirements for the intended application is difficult. This section outlines various potential options for individual needs in the following industrial sectors:

- Chemical processing, including applications critical to DOE waste storage and processing
- Microelectronics and semiconductors
- Building construction and infrastructure
- Aerospace and automotive
- Battery, solar, and wind energy.

The fluoropolymers listed in Table 4-1 (Korzeniowski et al., 2023) are those that tend to dominate the fluoropolymer marketplace, especially for the sectors of interest in this report, and are specifically mentioned in the Vanderbilt survey results. Because there is no strict or regulatory definition of PFAS (and thus of fluoropolymers) and the definition is still evolving (Buck et al., 2021), this report captures what the subject matter expert team considered the most significant set of fluoropolymers based on literature and the survey results. For example, 267 fluoropolymers (by CAS numbers) were identified in the OECD (2018) study, which has been cited widely in scientific literature (e.g., Glüge et al., 2020; Buck et al., 2021). Of those fluoropolymers of economic significance identified in OECD (2018),³⁴ the fluoropolymers listed in Table 4-1 are in agreement with OECD (2018), where most of the fluoropolymers that could be identified were PTFE (although more than a hundred could not be identified – OECD [2018] indicated there was more work to do). Of further note, the set of fluoropolymers listed in Table 4-1 is consistent with the fluoropolymers discussed in Henry et al. (2018) and Korzeniowski et al. (2023); authors from the Buck et al. (2021) report who looked at commercial viability indicated that the fluoropolymers in Table 4-1 dominate the world market for such materials.³⁵

Table 4-1. Selected Fluoropolymers and Example Uses for Sectors of Interest in the Vanderbilt Study (2 pages)

Industries and uses	Transportation		Chemical		Telecommunications		Infrastructure construction and architecture	Renewable energy		
	Auto-motive	Aero-space	Oil and gas	Chemical process industry (CPI)	Electronics and semiconductors	Internet and wireless communications		Energy production	Hydrogen production	Energy storage
Fluoropolymer Thermoplastics										
PTFE	•	•	•	•	•	•	•	•	•	•
ETFE	•	•	•	•	•	•	•	•		•
FEP	•	•	•	•	•			•		
PFA	•	•	•	•	•			•		
PVDF homopolymer	•	•	•	•	•	•	•	•	•	•
PVDF copolymer	•	•		•	•	•	•		•	•
ECTFE copolymer		•	•	•	•	•	•			
ECTFE terpolymer			•	•						
PCTFE		•			•					
FEVE	•	•			•		•			

³⁴ OECD (2018) did not consider global commercial viability according to Buck et al. (2021).

³⁵ Personal communication with the authors of Buck et al. (2021) on September 26, 2023.

Table 4-1. Selected Fluoropolymers and Example Uses for Sectors of Interest in the Vanderbilt Study (2 pages)

Industries and uses	Transportation		Chemical		Telecommunications		Infrastructure construction and architecture	Renewable energy		
	Auto-motive	Aero-space	Oil and gas	Chemical process industry (CPI)	Electronics and semiconductors	Internet and wireless communications		Energy production	Hydrogen production	Energy storage
EFEP	•			•	•					
CPT	•				•					
THV	•	•		•	•		•	•		•
Fluoropolymer Elastomers										
FEPM	•	•	•	•	•		•	•		
FKM	•	•	•	•	•		•	•	•	•
FFKM		•	•	•	•					
Specialty Fluoropolymers										
Amorphous		•		•	•	•			•	•
Ionomer	•			•	•			•	•	•

Source: Based on Henry et al., 2018, “A critical review of the application of polymer of low concern and regulatory criteria to fluoropolymers,” and Korzeniowski et al., 2023, “A critical review of the application of polymer of low concern regulatory criteria to fluoropolymers II: Fluoroplastics and fluoroelastomers,” *Integrated Environmental Assessment and Management*.

CPT	=	chlorotrifluoroethylene-perfluoroalkoxy-tetrafluoroethylene.	FEVE	=	fluoroethylene-vinyl ether.
ECTFE	=	ethylene chlorotrifluoroethylene.	FFKM	=	TFE-PMVE perfluoroelastomer.
EFEP	=	ethylene-tetrafluoroethylene-hexafluoropropylene.	FKM	=	fluorine Kautschuk material.
ETFE	=	ethylene tetrafluoroethylene.	PCTFE	=	polychlorotrifluoroethylene.
FEP	=	fluorinated ethylene propylene.	PFA	=	perfluoroalkoxy polymer.
FEPM	=	trifluoroethylene-propylene copolymer.	PTFE	=	polytetrafluoroethylene.
			PVDF	=	polyvinylidene fluoride.
			THV	=	TFE-HFP-VF2.

4.1 Chemical Processing

This section describes fluoropolymers used in chemical processing, storage, and disposal. For example, chemical processing industries often handle corrosive chemicals during the manufacturing of diverse products. Fluoropolymers often replace stainless steel and exotic alloys in processes that involve highly reactive chemicals, where fluoropolymers also meet purity requirements, which are essential in semiconductor, food, and biopharmaceutical production. Examples of industries using fluoropolymers include chemical manufacturing, plastics manufacturing and processing, semiconductor manufacturing, pharmaceutical and biopharmaceutical industries, and food processing (Ebnesajjad and Khaladkar, 2018, p. 1). Their unique characteristics also make replacing fluoropolymers difficult and often cost prohibitive, as fluoropolymers are typically used if alternate polymers or other materials cannot tolerate the stringent conditions required.

4.1.1 Forms of Fluoropolymers Used in Chemical Processing, Storage, and Disposal

Fluoropolymers can generally be found in several forms (Biering, 2023):

- Granulates are the most common form of fluoropolymers and are available commercially as solid granules or pellets, which can be processed using various techniques (e.g., extrusion or compression molding) to create a wide variety of parts and components.
- Some fluoropolymers are melt-processable materials; these fluoropolymers can be melted and processed using techniques like extrusion and injection or blow molding, which offer more versatility in terms of design and manufacturing because these materials can be easily shaped into complex geometries.

- Thin, flexible, and strong fluoropolymer films, which can be produced by various methods (e.g., casting, extrusion, or skiving), are suitable for use in applications such as electrical insulation, gaskets, and seals.
- Fluoropolymer emulsion-modified paste is a viscous, semi-solid material that can be made into films, thin wall heat-shrink, or industrial tubing, pipe seal tape, and membranes where product materials can be sintered or non-sintered depending on end-use.
- Dispersions are liquid suspensions of fluoropolymer particles in a solvent or aqueous medium; these dispersions can be applied as coatings or used to impregnate other materials and are typically used in applications that require a thin, uniform layer of the resulting material.

Examples of the forms (typically rods, tubes, and sheets) of fluoropolymers used in chemical processing that tend to dominate in the fluoropolymer marketplace (Vincent, 2023) or are specifically mentioned in the Vanderbilt survey results include:

- **Polytetrafluoroethylene (PTFE)**/Teflon is offered commercially primarily in three forms – granular resins, fine powders, and aqueous dispersions (Drobny, 2009) – that can be processed into rods, tubes, sheets, heat shrink, O-rings to produce gaskets, seals, and linings that are suitable for chemical applications due to the material’s inertness; high resistance to corrosion, solvents, and chemicals; and ability to withstand operating temperatures up to 260 °C.
- **Ethylene tetrafluoroethylene (ETFE)**/Tefzel/Texlon³⁶/Fluon is a thermoplastic copolymer offered commercially in the form of powders that can be processed into rods, tubes, and sheets where ETFE coatings supply chemical inertness similar to fluoropolymers like PTFE but also provide mechanical strength and resistance to abrasion. Because of its resistance to petroleum, ETFE is increasingly being used for fuel tubing in the automotive industry and for gaskets, O-rings, and hose linings.
- **Fluorinated ethylene propylene (FEP)**/Teflon FEP/Neoflon/Dyneon FEP materials are offered commercially in the form of varying melt viscosity resins and aqueous dispersions (Drobny, 2009) that can be processed into rods, tubes, and sheets that are used to line chemical processing equipment and tubing.
- **Perfluoroalkoxy fluorocarbon (PFA)**/Teflon PFA is offered commercially in the form of an aqueous dispersion or copolymer resin (Drobny, 2009) that can be extruded into rods, tubes, sheets, and foams and to coat components and tubes that are suitable for chemical processing due to its high resistance to most chemicals and its anti-stick properties.
- **Polyvinylidene fluoride (PVDF)**/Kynar is offered commercially in the form of aqueous dispersions or resins (Drobny, 2009) that can be processed into rods, tubes, and sheets that are used to produce flexible, heat-shrinkable tubing and components like pumps and sensors for chemical processing.
- **Ethylene chlorotrifluoroethylene (ECTFE)**/Halar is offered commercially as resin or hot cut pellets (Drobny, 2009) that can be processed into rods, tubes, sheets, and films. The oil, gas, and chemical industries use ECTFE to line vessels, tanks, and other components.
- **Ethylene-tetrafluoroethylene-hexafluoropropylene (EFEP)**/Neoflon is a melt-processable fluoropolymer derived from ETFE that is typically supplied in pellet form. EFEP has good chemical resistance and high clarity for applications in which transparency is important, for example, in the chemical processing industry in which liquid levels must be viewed through valves or pipes.

³⁶ Texlon is a registered trademark of Vector Foiltec GmbH, Siegsdorf, Germany.

- **A terpolymer of tetrafluoroethylene, hexafluoropropylene, and vinylidene fluoride (THV)**/Dyneon THV is a melt-processable fluoropolymer that is available in nine commercial grades (five dry grades in pellet or agglomerate form and four aqueous dispersions) that differ in monomer ratios and consequently in melting points, chemical resistance, optical properties, and flexibility (Drobny, 2009). The chemical resistance and low permeation of THV make it suited for chemical processing particularly where tight radius bends of the tubing require high flexibility without cracking.
- **Trifluoroethylene-propylene copolymer (FEPM)** originally designated copolymers of **tetrafluoroethylene (TFE) and propylene (P)**/Alfas³⁷/Viton Extreme,³⁸ where the primary form TFE/P (commercially available in the form of pellets) provides a unique combination of chemical, heat, and electrical properties resisting both acids and bases, along with steam, amine-based corrosion inhibitors, hydraulic fluids, alcohol, and petroleum fluids. TFE/P typically retains its chemical resistance even in high temperatures.
- **Fluorine Kautschuk material (FKM)**/Viton³⁸/Fluorel³⁹ /Dai-el⁴⁰/Tecnoflon⁴¹ is commercially available in latex form or as sheets, ribbons, and pellets and can be fabricated into O-rings, expansion joints, diaphragms, blow-out preventers, valve seats, gaskets, hoses, safety clothing and gloves, stack and duct coatings, tank linings, drill bit seals, and V-ring packers for typical chemical and petrochemical applications (McKeen, 2013, pp 195-196).
- **Perfluoroelastomer (FFKM)**/Kalrez⁴²/Tecnoflon⁴¹/Chemraz⁴³ is available in the form of pellets, fine powder, granules, and sheets for uses in chemical processing, including O-ring agitator shaft and pump seals, mechanical pump seals at elevated temperatures and high pressures, pipeline seals, and outlet valve seals (McKeen, 2013, p. 197).

4.1.2 Critical Properties for Fluoropolymers Used in Chemical Processing, Storage, and Disposal

The properties important for use of fluoropolymers in chemical processing, storage, and disposal applications include (Ebnesajjad and Khaladkar, 2018; Korzeniowski et al., 2023):

- Low coefficient of friction (non-stick properties)
- Chemically stable, inert, and nontoxic
- Biocompatible for medical applications and bioinert
- High resistance to solvents, chemicals, and corrosion (i.e., nonleachable/good release properties)
- Stable at low and high operating temperatures (i.e., high temperature resistance and high continuous use temperature) and cryogenic properties
- Electrical properties, low dielectric constant, and low dissipation factor
- Flame resistant
- Recyclable
- Weather resistance/weatherability; UV, radiation, and arc resistant
- Low deformation under stress and remains flexible at low temperatures.

³⁷ Alfas is a registered trademark of Asahi Glass Company, Tokyo, Japan.

³⁸ Viton/Viton Extreme are trademarks of The Chemours Company FC, LLC (formerly DuPont), Wilmington, Delaware.

³⁹ Fluorel is a trademark of 3M Company, St. Paul, Minnesota.

⁴⁰ Dai-el is a registered trademark of Daikin Industries, Osaka, Japan.

⁴¹ Tecnoflon is a registered trademark of Solvay S.A., Brussels, Belgium.

⁴² Kalrez is a registered trademark of DuPont Performance Elastomers, Wilmington, Delaware.

⁴³ Chemraz is a registered trademark of Greene Tweed, Selma, Texas.

The Vanderbilt survey responses indicate other critical properties of fluoropolymers, including specific gravity, melting point, tensile strength, elongation of break, compressive strength, and flex life.

A summary of important properties related to chemical processing for selected fluoropolymers (Korzeniowski et al., 2023) is provided in Table 4-2. The fluoropolymers in Table 4-2 (that correspond to those that tend to dominate the marketplace as indicated in Section 2.0) provide resistance to chemicals—providing a barrier material for lining process vessels and lines in aggressive environments; most can also be used over a broad range of operating temperatures. Other important chemical processing properties (e.g., mechanical strength, cryogenic, ultra-high purity) can be realized by choosing a specific fluoropolymer.

Table 4-2. Selected Fluoropolymers and Properties of Interest Related to Chemical Processing

Properties and functionality	Durable			Inert – Stable					Functional						
	Mechanical strength	Wear resistance	Flexibility	Resistance to chemicals	Weatherability	Cryogenic properties (lower than -50 °C)	High operating temperature range	High limiting oxygen index	Electrical insulator	Ionic conductivity	Piezo-electrical properties	Barrier properties	Non-stick properties	Ultra-high purity grades for clean applications	Polymer processing additives
Fluoropolymer Thermoplastics															
PTFE		•		•	•		•	•	•			•	•	•	•
ETFE	•			•			•		•			•	•		
FEP				•	•		•	•	•			•	•	•	
PFA			•	•			•	•	•			•	•	•	
PVDF homopolymer	•	•		•	•		•	•			•	•		•	•
PVDF copolymer	•	•		•	•		•	•			•	•			•
ECTFE copolymer	•	•		•	•	•	•	•	•			•			
ECTFE terpolymer		•		•	•		•	•				•			
PCTFE	•	•		•	•	•	•	•				•	•	•	
FEVE	•	•	•	•	•		•	•				•			
EFEP	•	•		•	•	•	•	•				•	•		•
CPT				•	•	•	•	•				•	•	•	
THV			•	•	•		•	•				•			•
Fluoropolymer Elastomers															
FEPM	•	•	•	•	•		•	•	•			•			
FKM	•	•	•	•	•		•	•				•	•		•
FFKM	•	•	•	•			•	•	•			•		•	
Specialty Fluoropolymers															
Amorphous			•	•			•	•	•	•		•		•	
Ionomer			•	•				•	•	•		•	•		

Source: Based on Korzeniowski et al., 2023, “A critical review of the application of polymer of low concern regulatory criteria to fluoropolymers II: Fluoroplastics and fluoroelastomers,” *Integrated Environmental Assessment and Management*.

- | | | | |
|-------|--|-------|--------------------------------|
| CPT | = chlorotrifluoroethylene-perfluoroalkoxy-tetrafluoroethylene. | FEVE | = fluoroethylene-vinyl ether. |
| ECTFE | = ethylene chlorotrifluoroethylene. | FFKM | = TFE-PMVE perfluoroelastomer. |
| EFEP | = ethylene-tetrafluoroethylene-hexafluoropropylene. | FKM | = fluorine Kautschuk material. |
| ETFE | = ethylene tetrafluoroethylene. | PCTFE | = polychlorotrifluoroethylene. |
| FEP | = fluorinated ethylene propylene. | PFA | = perfluoroalkoxy polymer. |
| FEPM | = trifluoroethylene-propylene copolymer. | PTFE | = polytetrafluoroethylene. |
| | | PVDF | = polyvinylidene fluoride. |
| | | THV | = TFE-HFP-VF2. |

4.1.3 Fluoropolymer Applications Used in Chemical Processing, Storage, and Disposal

Typical fluoropolymer applications tend to exploit one or a combination of important fluoropolymer properties (e.g., chemical resistance, good mechanical properties, thermal stability, and cryogenic properties) that differentiate them from other plastics, polymers, metal alloys, and other alternative materials. Typical chemical processing uses include gaskets, T's, bellows, spacers, high-pressure hoses and tubing, coatings, fluid handling systems, vessel liners, and valve, pipe, and fitting liners (Ebnesajjad and Khaladkar, 2018, p. 5).

In chemical processing, fluoropolymers have exceptional resistance to chemical attack and are often used as barrier materials. These materials are often used to fabricate linings for carbon steel vessels and for piping and other fluid handling components (where construction of whole vessels, pipe, or components would often be cost prohibitive). Fluoropolymers provide durable, low maintenance, and economical alternatives to exotic metal alloys and may also offer thermal stability for use at high temperatures. As they do not react with process streams, fluoropolymers help prevent contamination during chemical processing (Ebnesajjad and Khaladkar, 2018, pp 5-6).

Applications for corrosion control are typically classified as follows (McKeen, 2013, p. 271):

- Barrier (linings)
- Self-supporting structures
- Others (e.g., seals, gaskets, column internals⁴⁴).

Fluoropolymers, which have the highest chemical resistance and maximum-use temperature range among polymers, are often used for barriers (linings) and other applications such as column internals, seals, gaskets, and occasionally to construct self-supporting structures (Ebnesajjad and Khaladkar, 2018, p. 15). Corrosion resistance is a function of the level of fluorine; thus, fully fluorinated fluoropolymers (e.g., PTFE, FEP, PFA, and methyl fluoroacetate [MFA]) that are resistant to solvents, esters, and ketones are preferred for more challenging applications. Of the partially fluorinated materials, ETFE is also resistant to solvents, esters, and ketones, although others (PVDF and PCTFE) may show mild effects or even degradation to solvents, esters, and ketones (Ebnesajjad and Khaladkar, 2018, p. 12).

Examples of general uses of fluoropolymers in chemical processing include (McKeen, 2013, pp. 271-273):

- **Chemical reactors** – Vessels, mixers, and pipes are frequently coated (via liquid or powder) with thick fluoropolymer films (40+ mils) where the most chemically resistant and highest-temperature-rated material is PFA.
- **Ducts for corrosive fumes and fire resistance (semiconductor industry)** – Ductworks in a semiconductor fabrication plant carry corrosive and flammable materials, and fluoropolymer-coated metal (using ETFE or ECTFE) has replaced fiber-reinforced plastic (FRP) (resin-impregnated fiberglass that is not sufficiently fire resistant) in many of these applications.

Specific examples of chemical applications of the fluoropolymers (Table 4-1 and Table 4-2) that dominate the marketplace for fluoropolymers, are mentioned in the Vanderbilt survey responses, and cover those in widely cited articles (OECD, 2018; Henry et al., 2018; Korzeniowski et al., 2023; and Buck et al., 2021) include:

- **PTFE** – Non-stick properties and heat resistance make PTFE appropriate for bearings, insulators, surface coatings, and conveyor belt rollers in the food processing and service industry. PTFE gaskets and linings are suitable for chemical applications due to the material's chemical resistance; its high temperature resistance also makes PTFE useful for insulating external aircraft fittings and jet engines in the aerospace industry.

⁴⁴ "Column internals" refers to packings and internal structures in petroleum and chemical processing reactors and separations columns to provide increased surface area and regulate internal flows.

- **ETFE** – Resistance to corrosive chemicals and high temperatures make ETFE appropriate for the construction of chemical processing equipment, storage tanks, and piping systems; ETFE is also used to make chemical pumps, valves, and gaskets. Because of its resistance to petroleum, ETFE is increasingly being used for fuel tubing in the automotive industry and for gaskets, O-rings, and hose linings. The electrical industry uses the material for insulating wires and components like connectors.
- **FEP** – Used to line chemical processing and storage equipment, tubing, pipes, and fittings, FEP coatings are one of the important coating materials in the chemical industry because they can store and transport harsh chemicals.
- **PFA** – The main applications of PFA are chemical-resistant components for valves, pumps, and pipes due to its high resistance to most chemicals and its anti-stick properties. PFA is also widely used in the semiconductor manufacturing industries for high purity and chemical-resistant moldings. Its purity and U.S. Food and Drug Administration approval also make PFA ideal for sensitive applications like pharmaceutical and semiconductor handling processes.
- **PVDF** – Offered commercially in a broad range of melt flow rates (in the forms of latex and fine powders from emulsion processes and as granules), PVDF can be compounded with a variety of additives to improve either processing or end-use performance properties (McKeen, 2013, pp 145-147). PVDF components are used extensively in the following:
 - **Nuclear waste processing** (radiation and hot-acid resistant) (Section 4.1.4 discusses related DOE fluoropolymer applications)
 - **General chemical processing industry** (extreme chemical and temperature applications)
 - **PVDF resins** used in a wide range of components, including pipes, fittings, and valves; pump assemblies; tubing (flexible and rigid); tanks and vessels; nozzles; membranes and filter housing; and polymer processing aids
 - **PVDF powder-coating systems**, which allow formation of a thick spray coating of the resin to be applied to metals for optimum corrosion resistance; PVDF powder coatings can be applied without primer.
- **ECTFE** – In the semiconductor industry, ECTFE is suitable for coating ductwork to prevent contamination and corrosion. The oil and gas and chemical industries use ECTFE to line vessels, tanks, and other components.
- **EFEP** – A melt-processable fluoropolymer derived from ETFE, EFEP has good chemical resistance and high clarity for applications in which transparency is important; for example, in the chemical processing industry in which liquid levels must be viewed through valves or pipes.
- **THV** – A melt-processable fluoropolymer, THV comprises three different monomers: tetrafluoroethylene, hexafluoropropylene, and vinylidene fluoride. Chemical resistance and low permeation make THV suited for chemical processing particularly where tight radius bends of the tubing require high flexibility without cracking.
- **FEPM** – FEPM originally designated copolymers of TFE and P, where the primary form TFE/P provides a unique combination of chemical, heat, and electrical properties resisting both acids and bases, along with steam, amine-based corrosion inhibitors, hydraulic fluids, alcohol, and petroleum fluids. TFE/P typically retains its chemical resistance even in high temperatures.
- **FKM** – Typical chemical and petrochemical applications of FKM, a family of fluoropolymer rubbers, include O-rings, expansion joints, diaphragms, blow-out preventers, valve seats, gaskets, hoses, safety clothing and gloves, stack and duct coatings, tank linings, drill bit seals, and V-ring packers (McKeen, 2013, pp 195-196).

Other industrial applications of fluorocarbon elastomers include valve seals, hose (rubber-lined or rubber-covered), wire and cable covers (in steel mills and nuclear power plants), diaphragms, valve and pump linings, reed valves, rubber-covered rolls (100% fluorocarbon elastomer or laminated to other elastomers), electrical connectors, pump lining and seals, and seals in food-handling processes approved by the U.S. Food and Drug Administration (McKeen, 2013, p. 196).

- **FFKM** – Perfluoroelastomer FFKM compounds contain higher amounts of fluorine than standard FKM. Examples of FFKM applications in the chemical industry include O-ring agitator shaft seals in an oxidation reactor operating at high temperatures and in contact with 70% acetic acid; mechanical process pump seals pumping alternately acetone, dichloromethane, and methyl isocyanate at elevated temperatures; pipeline seals exposed to chloromethyl ether or dichlorophenyl isocyanate at elevated temperatures; outlet valve seals exposed to a 50/50 mixture of methylene chloride/ethanol; mechanical pump seals handling a mixture of ethylene oxide and strong acids at high temperature and pressure; O-rings in a pump handling 99% propylene at low temperatures; and O-ring pumps for pumping chromate-inhibited water at high temperature (McKeen, 2013, p. 197).

4.1.4 Fluoropolymer Applications Critical to U.S. Department of Energy Waste Storage and Processing

Within DOE, the wide usage of polymer products includes fluoropolymers. Similar to other chemical processing organizations, the need for fluoropolymers within the DOE complex is driven by the unique properties of the materials described in Sections 2.0 and 3.0. Sealing components are a major use of fluoropolymers in radioactive waste processing systems. Metal or ceramic seals may be used for some seals; however, polymers are frequently used due to common design, low cost, compliance, and lower sealing stresses. The most used fluoropolymer sealing component is PTFE; however, ethylene propylene diene monomer (EPDM) is used when the heat and chemical resistance of PTFE is not required, or additional elasticity is required.

Valve seats, which are where valves contact the containing vessel and maintain the seal around the valve, are often made of stiffer polymers based on the needs of the valve. Common polymer components of seat valves include ETFE (a fluoropolymer), ultra-high molecular weight polyethylene (UHMWPE), and polyetheretherketone (PEEK). An important limitation of PTFE is that it is unsuitable for high-level waste processing due to the considerable degradation of PTFE when exposed to those conditions, and ETFE is only suitable for short-term processing. PEEK has shown significantly higher resistance to degradation and may provide an alternative to current technologies.

Elastomers are often used to seal containment vessels in radioactive material packages. For example, O-rings of fluoroelastomer are used to seal the stainless-steel containment vessels in Model 9975 shipping packages designed to transport plutonium-bearing materials. New liquid processing equipment and transfer systems have been developed using chlorinated and fluoropolymer-based plastics, such as chlorinated polyvinyl chloride (CPVC) end plates, commercial-grade plastic piping and valves for internal glovebox transfer systems, and PVDF slab tanks for process storage.

Fluoropolymers are widely used in DOE national laboratories, and an exhaustive list would encompass dozens of specific uses. Examples include:

- PFA fluoropolymer (Teflon) resin vessels used for product consistency tests (PNL-10497, *Product Consistency Testing of Three Reference Glasses in Stainless Steel and Perfluoroalkoxy Resin Vessels*)
- Fluoropolymer distillate receiver vials for Hanford waste tank mercury analyses (PNNL-29555, *Mercury Speciation and Quantification of Hanford 241-AP-107 Tank Waste Feed and Treated Samples*)

- Fluoropolymer bottles for preservation and storage of mercury and methylmercury (MeHg) tank waste samples (PNNL-32726, *Measurement of Total, Elemental, and Methyl Mercury in Hanford Tank Waste*; SRNL-STI-2019-00056, *Total Mercury Analysis Comparison: Deployment of Analytical Method for the Savannah River Site Liquid Waste System*)
- Hanford tank waste corrosion testing of fluoropolymer-lined kettles (PNNL-11064, *Hanford Waste Vitrification Plant Technical Manual*)
- Teflon fluoropolymer vessel used for hydrogen generation rate flow-system measurements (SRNL-STI-2019-00411, *Investigation of Thermolytic Hydrogen Generation Rate in Tank 28 and Tank 39 Samples*)
- PVDF membrane disc filter for measurement of sulfur solubility from glass samples (PNNL-28838, *Enhanced Hanford Low-Activity Waste Glass Property Data Development: Phase 2*)
- PVDF filter for crystalline silicotitanate (CST) equilibrium batch contact testing (SRNL-STI-2020-00128, *Characterization and CST Batch Contact Equilibrium Testing of Modified Tank 9H Process Supernate Samples in Support of TCCR*).

The historical significance of the precursor of DOE is also important to understanding the legacy of fluoropolymer use within the DOE complex. During the Manhattan Project, under the direction of the U.S. Army Corps of Engineers (transferred to the Atomic Energy Commission in 1946, which later became DOE), the first atomic bomb was produced. PFAS (including fluoropolymers) were first produced on an industrial scale for use in uranium separation activities during the Manhattan Project. PTFE was used for valves and gaskets due its resistance to chemical attack from highly reactive uranium hexafluoride (UF₆) at the Oak Ridge K-25 Gaseous Diffusion Plant, which was the largest industrial facility ever constructed at the time.

4.1.5 Potential Competing Technologies and Alternatives for Fluoropolymers in Chemical Processing, Storage, and Disposal

The Fluoropolymer Group of Plastics Europe requested Chemservice to develop a Regulatory Management Option Analysis (RMOA) for fluoropolymers to evaluate possible regulatory management options that could address concerns related to a chemical substance or group of substances (Drohmann et al., 2021). Under an RMOA, the expected impacts of relevant regulatory management options are analyzed against a selection of criteria and factors based on the following guidance (Drohmann et al., 2021, p. 125):

- *Guidance for the preparation of an Annex XV dossier for restrictions* (ECHA, 2007)
- *Guidelines for an Industry Risk Management Option Analysis* (Eurometaux, 2017)
- *Integrated Regulatory Strategy Annual Report* (ECHA, 2019).

In terms of alternatives to fluoropolymers, Drohmann et al. (2021, p. 84) states:

The information on alternatives is based on general feedback on alternatives and on specific examples provided by the supply chain of [fluoropolymers] FPs. As a result, it does not necessarily cover all applications and/or all products. The alternatives mentioned as part of the consultation include steel and other metals; high nickel alloys, polypropylene, polyvinyl chloride (PVC), glass, ceramics, mica, polyether sulfone, polyimide, ethylene propylene diene monomer (M-class) rubber (known as EPDM rubber), nitrile [butadiene] rubber (NBR), hydrogenated nitrile [butadiene] rubber (HNBR), acrylic rubber (ACM), ethylene-acrylic rubber (AEM rubber), fluorosilicone (FVMQ), graphite, aramid, slip agents. Each would only be a possible alternative for some of the applications of FPs.

In sectors such as chemical, power, pharmaceuticals or transport, FPs provide resistance to a wide range of low and high temperatures and universal chemical resistance. This “universal” resistance to chemicals is a crucial characteristic of FPs that is not present in any of the alternatives, according to consultation feedback. There are alternatives that are more or less resistant to specific chemicals, but there is not one that is universally suitable.

A high-level alternatives analysis was performed as part of the RMOA for sectors related to this report (as defined in Section 1.0) and considered the following (Drohmann et al., 2021, p. 84-85):

- Technical implications (e.g., lower performance, increased weight and associated impacts, and reduced durability and reliability)
- Economic implications (e.g., regression of advanced technologies, reduced ability of Europe to compete and attract high and medium technology manufacturing, efficiency losses, higher initial [investment] costs, and higher maintenance costs)
- Environmental/health implications (e.g., potential for higher risk of staff exposure to hazardous substances, higher safety risks, and increases in emissions).

Some of the above criteria (e.g., economic impact on Europe) would only loosely be considered relevant to this report; however, the results begin to depict the types of alternatives that have been considered for fluoropolymers. Table 4-3 provides an overview of the results of the RMOA (Drohmann et al., 2021, Table 40) focused on the chemical industry sector.

Table 4-3. Overview of Chemical Industry Alternatives (2 pages)

Alternative/s	Example potential application	Overview of likely technical economic and environmental implications
Stainless steel, copper	Pipes, liners, tubing	<p>Fluoropolymers are commonly used as liners in stainless-steel pipes and valves. Stainless steel is not corrosion resistant as a replacement for these applications; possible for certain very specific components. However, metals are likely to result in:</p> <ul style="list-style-type: none"> • Increased weight and size/design of components • Inferior resistance to corrosion and/or abrasion • Inferior non-stick and non-friction properties • Lack of flexibility. <p>Rapid corrosion and abrasion (on metal dynamic applications) would be the consequence. Other implications include costly redesigns, higher maintenance costs, higher design costs, and higher safety and environmental risks.</p>
High-performance nickel alloys	Pipes, desulfurization heat exchangers, and filters	<p>Various grades are available for specific applications, which are often quoted as highly resistant to corrosion. Fluoropolymers are generally more resistant to chemicals and at higher temperatures. Alloys are likely to be more costly, especially nickel-chromium-molybdenum alloys. This “universal” resistance to chemicals is a crucial characteristic of fluoropolymers that is not present in any of the alternatives. There are alternatives that are more or less resistant to specific chemicals but not one that is universally suitable. If there were no fluoropolymers, not only would the alternatives have inferior performance, a specific alternative would have to be developed for each manufacturing process, with potential differences across the industry. Only titanium and tantalum could have similar resistance, but their cost is very high, and they do not have the other required properties. Therefore, they are not considered as alternatives by industry.</p>

Table 4-3. Overview of Chemical Industry Alternatives (2 pages)

Alternative/s	Example potential application	Overview of likely technical economic and environmental implications
Polypropylene and PVC	Commonly used in pipes and liners	Low resistance to chemical attack and temperature hence lower corrosion prevention. Unsuitable for demanding applications, unless coated or reinforced (for instance with fluoropolymers).
Glass and ceramics	Historically used in several applications	Brittle, considerably heavier and more difficult to transport. Lack of chemical resistance to strong bases and hydrofluoric acid.
Polyethersulfone and polyimide	Seals	Their thermal resistance is similar to that of some fluoropolymers. It is understood that chemical resistance may be inferior. They are also rigid, posing design difficulties.
Rubbers and silicones such as NBR, HNBR, ACM, AEM rubber, or FVMQ	Seals, O-rings, and other applications	Suitable for other applications and resistant to specific chemicals. They have generally lower resistance to temperature changes, abrasion, and chemicals compared to fluoropolymers.
Graphite and aramid	Gaskets	Aramid is sensitive to acids (i.e., cannot prevent corrosion) and ultraviolet light. Graphite, while chemically resistant, is brittle.
Zinc stearate, calcium stearate	Polymerization additives	While the stearates can be used as processing additives in polymers, their effect is limited both on melt fracture elimination and pressure reduction. High loadings are required, which in turn impacts other film properties, rendering the alternatives not acceptable in the packaging sector.
Polysulfone (PSF) and polyethersulfone (PES)	Water filtration membranes	These materials can be used in certain applications, but they are less resistant to chemicals resulting in shorter membrane life. They are too stiff to be used as submersible membranes in bioreactors, where they are clearly not an alternative.
Boron nitride and other inorganic solids	Lubricants	Reduced chemical stability (e.g., hydrolysis), downgraded lubricity, expensive.

Source: Extracted from Table 40 of Drohmann et al., 2021, *Regulatory Management Option Analysis for Fluoropolymers*, Plastics Europe, Association of Plastics Manufacturing, Brussels, Belgium.

ACM	= acrylic rubber.	NBR	= nitrile butadiene rubber.
AEM	= ethylene acrylic elastomer.	PES	= polyethersulfone.
FVMQ	= fluorosilicone.	PSF	= polysulfone.
HNBR	= hydrogenated nitrile butadiene rubber.	PVC	= polyvinyl chloride.

The replies from direct uses of fluoropolymers (Drohmann et al., 2021) indicated that one case out of the 42 analyzed would provide a viable alternative (i.e., evaluated against the criteria of technical feasibility, economic feasibility, availability, and hazards and risks of the alternative [Drohmann et al., 2021, p. 84]) for one minor and very specific use of fluoropolymers in the manufacture of leather products to provide anti-soiling properties, although resulting in certain performance decrease. However, this alternative for leather manufacturing is not part of the sectors of interest for this report. Information from Table 4-3 does suggest that there may be specific or even niche chemical industry applications where alternatives may exist:

- Stainless steel or copper may provide possible alternatives for certain, very specific applications although with inferior properties, redesigns, and higher maintenance and design costs.
- High performance nickel alloys are alternatives for specific applications needing resistance to corrosion; however, at higher costs and inferior corrosion resistance at higher temperatures.
- Polypropylene and polyvinyl chloride (PVC) may present alternatives for less demanding applications.

- Polyethersulfone (PES) and polyimide may provide comparable thermal resistance at the cost of inferior chemical resistance and potential design difficulties.
- Polysulfone (PSF) and PES can be alternatives for water filtration membranes but are less resistant to chemicals, resulting in shorter membrane life and higher maintenance and replacement costs.

In the cases evaluated in the RMOA (Drohmann et al., 2021, p. 85), 16 replies from the direct users indicated that alternatives are not available “that would meet the technical conditions required for the specific application and which render the specific [fluoropolymers] FPs of interest unique.” In addition, three direct users indicated that alternatives had not been tested, and as many as 12 did not provide information on alternatives.

In the Vanderbilt survey results, of the 16 responses, five provided no information related to alternatives. The responses pertaining to fluoropolymer alternatives ranged from “none” to “We have been researching for the last 20 years and have not found alternatives yet.” However, the two following responses to the Vanderbilt survey are of interest considering the results from the RMOA (Drohmann et al., 2021):

- No alternative chemicals have been found to replace PTFE powder as additives in critical applications requiring high temperature and chemical stability.
- No alternatives have been found, even with the intense development actions, for polymeric PFPE and PTFE. For PTFE only, some options might be available, but no real alternatives are currently being evaluated. However, these options might fall under other regulations (e.g., microplastics).

These results suggest that alternatives may exist for specific applications in less challenging temperature and corrosion environments but possibly at the cost of lower performance and higher design, maintenance, and replacement costs.

4.2 Microelectronics and Semiconductor Processing and Components

Microelectronics and semiconductor components are found in a variety of products that are used daily, from common consumer goods to complex machinery. Fluoropolymers find extensive use in the fabrication and production of microelectronics and semiconductors. The use of fluoropolymers in this industry is primarily due to two specific requirements: (1) physical and electronic properties of the polymers make them uniquely suited for incorporation into electronic and semiconductor devices, and (2) the high purity and chemical inertness of many fluoropolymer plastics render them useful for handling solutions necessary within semiconductor manufacturing processes (Drohmann et al., 2021; Glüge et al., 2020). As noted below, few if any viable alternatives for fluoropolymers are used in microelectronics and semiconductor processing.

4.2.1 Forms of Fluoropolymers Used in Microelectronics and Semiconductor Processing and Components

As shown in Table 4-1, nearly all fluoropolymers are used to some degree in the fabrication and manufacturing of electronics and semiconductors. Several of the most important applications, and the specific fluoropolymers used in those contexts, are described below.

Electrical Wiring

The primary use of fluoropolymer plastics in the electronics industry is for insulation of wiring and cabling in scenarios where resistance to high temperatures, chemical corrosion, and mechanical stress is paramount (Drohmann et al., 2021). The primary fluoropolymers used as insulation in wire insulation for electronics include PVDF, FEP, ETFE, ECTFE, and PCTFE (Glüge et al., 2020). The following applications are notable:

- **PVDF** – Used in heat-shrinkable cable splice insulation and in wiring within computers and industrial process controls in cases where low-frequency signals are carried (Gardiner, 2014)
- **FEP** – Fire resistance and physical durability make FEP well-suited for insulation of cables routed within a plenum or other electronic device component exposed to vibration, movement, or heat stress (Gardiner, 2014)
- **ECTFE and ETFE** – Used in specialty applications for electronics within the aerospace and automotive industries due to their high flexibility and flame-retardant nature (Gardiner, 2014).

Printed Circuit Boards

Fabrication of printed circuit boards requires layering of typically copper conductor paths on an electrically resistive polymeric layer atop a fiberglass substrate. Many circuit boards use fluoropolymers as the dielectric layer for this application. Specifically, PTFE and an ETFE copolymer with 1,1'-oxybis(ethene) are reportedly used for this application (Glüge et al., 2020).

Piezoelectric Devices

Electronic devices designed for measuring electromagnetic radiation or for producing or detecting sound (e.g., speakers and microphones) make use of piezoelectric materials, which change their electrical properties (i.e., resistance) as a function of mechanical or thermal stress. Films of PVDF and copolymers of PVDF and trifluoroethylene (TrFE) are particularly useful as piezoelectric elements in sensors and transducers (Drohmann et al., 2021; Glüge et al., 2020).

Semiconductor Photoresist

Production of semiconductors on silicon wafers using photolithography require the application of a photoresist or light-sensitive polymer. Functionally, exposure to light via the application of a mask renders the photoresist layer either more (positive photoresist) or less (negative photoresist) soluble in the developer solution that is subsequently applied in the process. Two novel fluoropolymer photoresists are known to be used in semiconductor fabrication – both of these are copolymers with TFE (Glüge et al., 2020):

- 2-Propenoic acid, 1,1-dimethylethyl ester, polymer with 4,5-difluoro-2,2-bis(trifluoromethyl)-1,3-dioxole and tetrafluoro ethene: $-(C_7H_{12}O_2)_x-(C_5F_8O_2)_y-(C_2F_4)_m-$, CAS #851389-08-7
- Propanoic acid, 3-[1-[difluoro[(1,2,2-trifluoro ethenyl)oxy]methyl]-1,2,2,2-tetrafluoroethoxy]-2,2,3,3-tetrafluoro-, methyl ester, polymer with 4,5-difluoro-2,2-bis(trifluoromethyl)-1,3-dioxole and 1,1,2,2-tetrafluoroethene: $-(C_9H_3F_{13}O_4)_x-(C_5F_8O_2)_y-(C_2F_4)_m-$, CAS #86179-28-4.

Semiconductor Antireflective Coatings

Artifacts of internal and external reflection of light during the photolithography process in semiconductor manufacturing can be reduced by the inclusion of antireflective coatings either as a topcoat above a reflective substrate or as an undercoat below the photoresist. These coatings are typically polymers with very low refractive indices and good liquid barrier properties (Ober et al., 2022).

Several fluoropolymers are used for these applications. Unlike many other fluoropolymer uses described for electronics and semiconductors, these are functional ionomers with either carboxylic acid or sulfonic acid functional groups (Glüge et al., 2020; Ober et al., 2022):

- **Topcoat:** 2-Propenoic acid, polymer with 2-ethylnaphthalene and 4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoro-2-hydroxyundecyl 2-propenoate: $-(C_{14}H_9F_{17}O_3)_x-(C_{12}H_{10})_y-(C_3H_4O_2)_m-$, CAS #934505-67-6
- **Undercoat:** 2-Propenoic acid, 4,4,5,5,6,6,7,7,7-nonafluoro-2-hydroxyheptyl ester, polymer with 2-propene-1-sulfonic acid: $-(C_{10}H_9F_9O_3)_x-(C_3H_6O_3S)_y-$, CAS #910114-99-7
- **Undercoat:** 2-Propenoic acid, 4,4,5,5,6,6,7,7,7-nonafluoro-2-hydroxyheptyl ester, polymer with 2-methyl-2-[(1-oxo-2-propen-1-yl)amino]-1-propane sulfonic acid: $-(C_{10}H_9F_9O_3)_x-(C_7H_{13}NO_4S)_y-$, CAS #910114-98-6
- **Undercoat:** 2-Propenoic acid, 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl ester, polymer with 2-methyl-2-[(1-oxo-2-propen-1-yl)amino]-1-propane sulfonic acid and 2,2,2-trifluoroethyl 2-propenoate: $-(C_{10}H_9F_9O_3)_x-(C_7H_{13}NO_4S)_y-(C_5H_5F_3O_2)_m-$, CAS #172083-53-3.

Semiconductor Manufacturing Process Equipment

The photolithographic process for semiconductor manufacturing requires extremely high purity of all chemical reagents used in the process, along with the use of highly aggressive and corrosive chemicals, including organic solvents and strong acids (Drohmann et al., 2021; Korzeniowski et al., 2023; Glüge et al., 2020). Few materials are available that can withstand these aggressive conditions without releasing leachable or extractable constituents into the process solutions, thereby introducing contaminants. Because of this, fluoropolymers find essential use in semiconductor manufacturing equipment and facilities.

- **PTFE, PVDF, PFA, FEP, and ETFE** are used as molds, reaction vessels, and piping within semiconductor manufacturing facilities to handle aggressive process fluids (Glüge et al., 2020, Drohmann et al., 2021).
- **ECTFE and PCTFE** are used as liners for high-purity water systems within the semiconductor manufacturing process to avoid contamination from corrosion of water piping by ultrapure water (Korzeniowski et al., 2023).
- A unique terpolymer of chlorotrifluoroethylene, perfluoroalkoxy-vinyl-ether, and tetrafluoroethylene, known as **CPT**, is of particular use in fabricating multi-layer tubes with **PFA** – used to increase the liquid barrier performance of tubing for transporting strong acids – relative to use of PFA alone (Korzeniowski et al., 2023).
- Fluoroelastomers such as **FKM** and **FFKM** are used for valve seats and O-rings within liquid handling systems delivering high-purity or corrosive chemicals in semiconductor manufacturing processes (Korzeniowski et al., 2023).

4.2.2 Potential Competing Technologies and Alternatives for Fluoropolymers in Electronics

Because of the very stringent chemical, physical, and in some cases electrical requirements of materials used to fabricate microelectronics and semiconductors, very few viable replacement materials can be identified for fluoropolymers within such applications. Table 4-4 provides an overview of the results of the RMOA (Drohmann et al., 2021, Table 40) focused on the electronics sector, describing some possible alternatives in specific applications and the trade-offs inherent in such alternatives.

Table 4-4. Overview of Electronics Alternatives

Alternative/s	Example potential application	Overview of likely technical economic and environmental implications
Polyolefin with flame retardant	Cable insulation	These materials do not offer the same resistance to temperature range as fluoropolymers (maximum limits differ but the minimum working temperature of polyolefins is higher than that of fluoropolymers, reducing their performance in cases where coolants are used to decrease the temperature of data processing systems). Polyolefins also have inferior fire resistance, often requiring a flame retardant. Flame retardants commonly increase dielectric constant and dielectric loss, which reduce data communication rates. The use of polyolefins would likely result in weaker data processing and slower signal return, reflecting inferior purity, friction properties, and stability compared to fluoropolymers. If an alternative is found at some point, the industry states at least 10 years may be required to replace equipment and adapt manufacturing methods and processes.
Non-conductive plastics	Historically used in semiconductor manufacture	Unviable. The modern semiconductor industry has stringent requirements, and fluoropolymers are the only material that can currently protect the processing equipment in which semiconductors are etched and cleaned from the chemicals used in the manufacturing process while at the same time offering the highest purity. Microprocessors and chips need to be increasingly small, yet powerful, preventing metallic contamination and corrosion to maximize chip yields.

Source: Extracted from Table 40 of Drohmann et al., 2021, *Regulatory Management Option Analysis for Fluoropolymers*, Plastics Europe, Association of Plastics Manufacturing, Brussels, Belgium.

4.3 Building Construction and Infrastructure

The resistance of fluoropolymer compounds to environmental degradation makes these compounds desirable in construction applications as weatherproofing materials, insulation materials for wire and cables, and liners for corrosion-resistant pipes, and in many other applications. While fluoropolymer compounds are generally more expensive than alternative materials, the extended lifetime and superior performance of these compounds make them desirable for applications in construction and infrastructure.

4.3.1 Forms of Fluoropolymers for Use in Construction and Infrastructure

Fluoropolymers are used in a wide variety of applications across construction and infrastructure. This section describes critical uses of fluoropolymers across these industries.

Fluoropolymer materials are used extensively for enhanced durability and extended lifetime of materials. Due to the strength of the carbon-fluoride bond of the fluoropolymers, these materials are resistant to UV degradation, have exceptional weatherability and durability, and in many applications, are expected to have functional lifetimes exceeding 50 years (Darden and Takayanagi, 2007).

Weatherproofing

Environmental exposure of structures leads to rapid corrosion, degradation, and deterioration (Sirojiddin and Yulchiyeva, 2023). This destructive impact can lead to financial losses, decreased lifespan of structures, and compromising safety. Fluoropolymer coatings provide a lightweight barrier to prevent degradation of structural materials. Specific examples of fluoropolymers used as weatherproofing materials include:

- **Fluoroethylene-vinyl ether (FEVE)** – FEVE fluoropolymer resins are used to manufacture bridge, architectural, and other industrial weatherproof coatings (Korzeniowski et al., 2023).

- **PVDF** – PVDF dispersions and coatings are applied to architectural structures to provide weather resistance (Dallaev et al., 2022). The long lifetime of PVDF coatings (50+ years) is also desirable for building facades to maintain color and gloss, and its chemical resistance makes PVDF suitable as an anti-graffiti coating for building exteriors (Korzeniowski et al., 2023).
- **ETFE** – ETFE has high corrosion resistance, high tensile strength, high impact strength, and is resistant to degradation through exposure to UV radiation. ETFE is used as a transparent structural material – owing to its resistance to discolor when exposed to UV radiation (Lamnatou et al., 2018).

Pipes and Insulation

Fluoropolymers are crucial components in cable insulation and piping applications. In cable insulation, fluoropolymers provide electrical insulation, have high dielectric strength, and are resistant to chemicals. In pipes, these materials offer exceptional chemical resistance, temperature stability, and non-stick properties, making them ideal for transporting corrosive chemicals and maintaining high purity in industrial processes.

- **PVDF** – The weather and temperature (up to 120 °C) resistance of PVDF, coupled with its chemical inertness and high flexibility, make it useful as a pipe liner for a wide range of applications, including ultrapure water pipelines, nuclear power, chemical production and synthesis, and boiler service pipes (Dallaev et al., 2022). The low mass and high coefficient of resistance to heat transfer of PVDF also make it useful for insulation of electrical wires.
- **ECTFE** – A copolymer of ethylene and chlorotrifluoroethylene, ECTFE is a thermoplastic fluoropolymer often used for manufacturing corrosion-resistant pipes (Dallaev et al., 2022).
- **FEPM** – Used in a range of applications, including wire and cable applications as insulating materials, FEPM exhibits heat resistance, chemical resistance, and high electrical resistivity (Dallaev et al., 2022).

Sealants and Adhesives

Fluoropolymers offer superior chemical resistance, ensuring the longevity and reliability of seals and bonds in various industries.

- **PTFE** – The resistance of PTFE to wear, extreme temperatures, and chemical resistance make it desirable as sealant materials (Sui et al., 1999).
- **FFKM** – Perfluoroelastomers have high chemical and temperature resistance and are impermeable to gas and liquid permeation. FFKM is widely used as sealing materials in oilfield applications (Korzeniowski et al., 2023).

Other Specific Applications

- **Anti-vandal coatings** – PVDF is used as an anti-graffiti coating, offering protection by forming a durable and chemically resistant barrier. The chemical and UV resistance of PVDF make it effective for preserving the aesthetics of public buildings, transportation vehicles, and signs (Silagy et al., 2000).
- **Wastewater systems** – Fluoropolymers are used for lining pipes, tanks, and treatment facility structures to prevent corrosion due to wastewater and industrial chemicals. PTFE gaskets, seals, and pump components ensure watertight and chemical-resistant connections. Tanks and vessels lined with PTFE, PVDF, or ETFE are used for storage and treatment of corrosive wastewater (Korzeniowski et al., 2023).

- **Drinking water and water treatment** – The corrosion resistance and temperature stability of fluoropolymers make them useful in drinking water infrastructure applications. PTFE and PFA gaskets, coatings, and fittings prevent corrosion of infrastructure and contamination of drinking water. The long lifetime of fluoropolymers minimizes the need for maintenance and upkeep of drinking water infrastructure. The low friction properties of fluoropolymers make them useful in pumps, minimizing wear and tear and extending the lifetime of the pump equipment. Fluoropolymer membranes and filters are also used for treatment of water; PTFE, for example, has been used for oil/water separation due to its low surface free energy, chemical resistance, and its intrinsic hydrophobicity (Bongiovanni et al., 2020).
- **Electrical grid** – Fluoropolymers are used for insulation for wires, cables, and high-voltage components. PTFE, ETFE, PVDF, and ECTFE are often used to insulate wires and cables due to their insulation properties and high-temperature resistance.

4.3.2 Fluoropolymer Replacement Materials for Use in Construction and Infrastructure

Table 4-5 provides an overview of the results of the RMOA (Drohmann et al., 2021, Table 40) and other sources (as noted) focused on the architecture sector.

Table 4-5. Overview of Architecture Alternatives (2 pages)

Alternative/s	Example potential application	Overview of likely technical economic and environmental implications
Steel or glass	Insulation materials, pipes, and tubes	Steel and glass alternatives are heavier and more inflexible than fluoropolymers. Steel is not resistant to corrosion, leading to higher maintenance costs. Glass is more fragile to hail or other impact. These alternatives are not able to meet the design requirements of fluoropolymers. ^a
Polycarbonate sheets	Weatherproofing, architectural material	Polycarbonates are resistant to temperature and can withstand force; they tend to yellow in external applications in contrast to fluoropolymers. PVC/PES membranes for architectural applications are common; however, the membranes are often coated with a protective layer (often made of PVDF, a fluoropolymer) providing UV-resistance and weatherability. Without this coating, they offer lower performance due to not being resistant to denting or certain chemicals. ^a
Mica	Insulation material, cables	Rigid and brittle, mica has lower chemical resistance than fluoropolymers. Performance could be improved with additional insulation (additional weight, similar brittleness). ^a
EPDM rubber reinforced with lead	Underground cables and submersible pumps	This alternative has higher weight and lower chemical and temperature resistance compared to fluoropolymers. Due to inaccessibility of these cables/pumps, durability is essential, implying increased downtime and higher maintenance costs. ^a
Slip agents	Cable applications	These additives are designed to reduce friction and provide appropriate lubrication during polymer processing (e.g., adhering a film to a metallic surface). While these slip agents perform well for the elimination of melt fractures, die build-up and higher energy consumption may be problematic in some applications. ^a
Silicone	Weatherproof coatings, seals	Silicone-based coatings offer good adhesion, durability, and water repellence. Silicone maintains its flexibility and elasticity over a wide range of temperatures (-60 °F to 230 °F) and is highly resistant to many chemicals; therefore, it is a suitable material for use in sealants in pipelines and wastewater systems. ^b While silicone is a useful replacement, fluoropolymers exhibit superior resistance, durability, and performance; therefore, fluoropolymers are generally a preferred material in many applications.

Table 4-5. Overview of Architecture Alternatives (2 pages)

Alternative/s	Example potential application	Overview of likely technical economic and environmental implications
Polyurethane	Weatherproofing, coating, seals	Polyurethane can be used as an alternative for waterproofing or for sealants and gaskets; however, compared to fluoropolymers, it offers poor chemical, temperature, and UV resistance. ^c

^a Extracted from Table 40 of Drohmann et al., 2021, *Regulatory Management Option Analysis for Fluoropolymers*, Plastics Europe, Association of Plastics Manufacturing, Brussels, Belgium.

^b Aibada et al., 2017, “Review on Various Gaskets Based on the Materials, their Characteristics and Applications,” *International Journal on Textile Engineering and Processes*, 3(1), pp 12–18.

^c Somarathna et al., 2018, “The use of polyurethane for structural and infrastructural engineering applications: A state-of-the-art review,” *Construction and Building Materials*, 190, pp 995–1014.

EPDM = ethylene propylene diene monomer.

PVDF = polyvinylidene fluoride.

PES = polyethersulfone.

UV = ultraviolet.

PVC = polyvinyl chloride.

4.4 Automobiles and Aerospace

Fluoropolymers play a vital role in the automotive and aerospace industries, possessing several essential characteristics such as high heat and chemical resistance, low permeability, a low coefficient of friction, and excellent mechanical properties. These attributes are instrumental in ensuring safety, enhancing fuel efficiency, and reducing carbon emissions within these sectors. Consequently, the pursuit of alternative or competing technologies necessitates a delicate balance. Safety features and technological performance must be maintained, while considering potential toxicity concerns associated with fluoropolymer manufacturing and end-of-life disposal. The challenge lies in the complexity of achieving real substitutions on a large scale. The deep-rooted reliance on fluoropolymers in the traditional automotive and aviation industries has somewhat hindered their exploration of novel materials and technologies. Additionally, finding equivalent products to replace fluoropolymers in each specific field proves to be a formidable task. Section 4.4.4 provides a summary of alternative materials and competing technologies for fluoropolymer applications in various automotive and aerospace contexts. Note that based on available information, none of these alternatives have been implemented on a large scale.

4.4.1 Forms of Fluoropolymers Used in Automotive and Aerospace

Fluoropolymers come in both plastic and elastomeric forms in diverse formats, including powders, granules, pellets, aqueous dispersions, and lattices (Drobny, 2007). In the transportation sector, PTFE and fluoroelastomer are the two major types of resins, constituting 27.9% and 43.8% of the fluoropolymer volume in 2020, respectively (PLS080B). PTFE comes in three primary forms: granular, fine powder or coagulated dispersion PTFE, and aqueous dispersion PTFE (Ramboll, 2023; Drobny, 2007).

In the transportation sector, PTFE granules are used in seals, gaskets, valves, protective linings, expansion joints, pipes, and fittings due to their exceptional resistance to extreme temperatures and chemicals. PTFE powder is used for various purposes in transportation, including coating for fuselages and wings, gaskets, O-rings, shaft seals, drive belts, window/door seals, window wipers, pump heads, gears, valves, bushings, bearings, slides, and other wear components.

PTFE aqueous dispersions can also be formulated into a range of coatings that are easily applicable to different components, such as weld nuts/pierce nuts, air conditioning pistons, intake valves, and more (Drobny, 2007). PTFE micropowders, available in dry form or as aqueous dispersions, serve as additives to oils and greases, enhancing their lubricating properties.

4.4.2 Critical Properties of Fluoropolymers Used in Transportation

Fluoropolymers offer a set of critical properties for their role in transportation applications:

- **Chemical and thermal resistance** – Fluoropolymers are resistant to a wide variety of lubricants and fuels at elevated temperatures over the vehicle’s lifetime, therefore guaranteeing the highest possible safety (PLS080B).
- **Low permeation rate** – Fluoropolymers serve as highly effective barrier materials against evaporative emissions. This capability contributes significantly to improved fuel efficiency and reduced greenhouse gas emissions.
- **Low surface energy** – Fluoropolymers used in coatings possess a unique resistance to the adhesion of foreign substances. This property effectively reduces friction and prevents the buildup of contaminants.
- **Low coefficient of friction** – Fluoropolymers enhance lubrication and facilitate low friction between surfaces. This property is pivotal for minimizing wear and enhancing efficiency.
- **Extreme condition resistance** – Fluoropolymers are used for insulation of electrical and data transmission cables in the aerospace industry due to their predictable operational life, ability to operate from cryogenic temperature (extremely low temperature) to 226 °C, and relative resistance to oxygen and humidity. Additionally, solid lubricants like PTFE are frequently used in aerospace applications under extreme conditions, including both high and low temperatures, and in vacuum environments (McCook et al., 2005).
- **Dielectric property** – Fluoropolymers are useful in preventing electrical fires in cables due to their dielectric properties.

4.4.3 Fluoropolymer Applications Used in Automotive and Aerospace

Due to the various applications in the automotive industry, fluoropolymer applications are categorized into three sectors: conventional vehicles, emerging energy (low-emission and zero-emission) vehicles, and agricultural machinery.

Applications of Fluoropolymers in the Automotive Industry

Conventional Vehicles (Drohmann et al., 2021; Henry et al., 2018; PLS080B; Wang et al., 2013)

- **Engine components**
 - Fluoropolymers are known for their thermal and chemical resistance, which has led to their application in parts like fuel lines, hoses, and turbocharger hoses made from PTFE, FEP, and PFA. These hoses are integral for fuel transport, and their multi-layered structure infused with fluoroelastomers ensures durability. Innovations involve the integration of PTFE liners with fiberglass braids to withstand high temperatures.
 - Seals, rings, and packings, typically made from fluoropolymers like FKM, FEP, and FFKM, serve vital functions – from protecting engine parts from contaminants to ensuring valve lubrication and durability.
 - Cylinder head gaskets and air intake manifold gaskets, both comprising fluoroelastomers, are used to seal cylinders and direct air to engines respectively, emphasizing their importance in ensuring engine efficiency.

- **Electrical, electronics, and sensors**
 - Fluoropolymers, particularly in lambda, NO_x, or oxygen sensors, are instrumental in reducing greenhouse gas emissions. Their unique properties make them ideal for sensor cables exposed to high temperatures.
 - PTFE is used in switches, ensuring structural integrity while offering waterproof and dustproof protection. The role of PTFE in millimeter wave radar antennas emphasizes its importance in high-frequency transmission systems.
 - Display device coatings benefit from the use of fluoropolymers to offer resistance to surface contamination and environmental factors.
- **Materials and adhesives** – PTFE adhesive tapes are applied to multiple vehicle components, owing to their superior resistance properties. Processes like nickel-phosphorus plating also incorporate PTFE to enhance material hardness, while treatments like the Geomet method employ a PTFE-containing film for adjusted friction.
- **Brake system** – In hydraulic systems, PTFE is fundamental in ensuring leak-free and durable hoses. Its role extends to anti-lock braking system brake lines, optimizing brake efficiency.
- **Venting products** – Crucial for lighting, electronic systems, and other components, vents employ fluoropolymers to offer protection against contaminants and to maintain optimal functioning amidst temperature and pressure fluctuations.
- **Vehicle parts and lubrication** – Door hinges, seat adjusters, and various car parts rely on PTFE and ETFE for reliability and minimized friction. Greases and lubricants use fluoropolymers like PTFE and PFPE as base oils due to their superior resistance and lubricity properties.

Low-Emission and Zero-Emission Vehicles

Fluoropolymers are used in low-emission and zero-emission energy vehicles. PVDF is used in lithium-ion battery binder, providing mechanical strength, flexibility, and thermal stability features over its operational life (Zhong et al., 2021). In fuel cells, fluoropolymer membranes are used to enable the movement of protons from the anode to the cathode side of the fuel cell and facilitate the electrochemical reactions that produce electricity (Sales et al., 2023; Améduri, 2018).

Agricultural Machinery

In agricultural equipment, fluoropolymers serve as protective coatings and linings, effectively preventing material buildup and clogging in critical components like hoppers and chutes. These durable coatings play a similar role in the automotive industry, where they are used for seals, gaskets, electrical insulation, high-temperature components, and bearing and bushing applications, enhancing the performance and longevity of these vital automotive parts.

Applications of Fluoropolymers in Aerospace Industry

Wires and cables insulated with fluoropolymers are used in data transmission in aircraft and spacecraft. Fluoropolymers like PTFE, ETFE, and PVDF are also used in in-flight connectivity. These materials enable multiple protocols to run through a single antenna, reducing the need for multiple antennas. In addition, fluoropolymers are important in aircraft interiors because of their broad temperature and UV resistance, flexibility, durability, chemical resistance to solvents and hydraulic fluids, and low smoke generation and flame resistance (Drohmann et al., 2021).

4.4.4 Competing Technologies

Table 4-6 provides a list of potential substitutes for fluoropolymers; however, each of these alternatives may only be suitable in specific applications where fluoropolymers are traditionally employed. No one-size-fits-all replacement exists that universally covers all fluoropolymer applications. Note that these replacements also often come with limitations, as fluoropolymers offer a range of critical properties essential for the automotive and aerospace industries.

Table 4-6. Overview of Automotive and Aerospace Alternatives (3 pages)

Alternative	Example potential applications	Overview of likely technical, economic, and environmental implications
Automotives		
General mineral oils or non-fluoropolymer-based thickener	Grease and lubricant	<ul style="list-style-type: none"> Mineral oils – lower heat and low-temperature resistance compared to fluorinated oils and may not coexist well with rubber and resins Thickeners (e.g., calcium, lithium, aluminum, and barium soaps) and non-soap materials (e.g., bentonite and urea) – inadequate heat resistance, water resistance, and shear stability^a
Mica-insulation sensor cables	Sensor cables for oxygen and nitrogen sensors	Not able to resist extreme conditions; less accurate measurement ^b
PA or EVOH	Hoses, cables, tubes, and wire solutions	Increased elastic modulus by a factor of 2 with EVOH and fuel permeability by a factor of 140 with PA ^a
PEEK	Fuel hoses, lines, gaskets, seals, cables, cable liners, wire insulation (both in automotive and aerospace)	<ul style="list-style-type: none"> Similar temperature resistance (260 °C), lower chemical resistance, rigid, and inferior electrical and data transmission properties Cost concerns when compared to fluoropolymers such as ETFE and PTFE or a fluoroelastomer (FKM)^{b,c}
Polysilazanes, Xirallic, ^d epoxy-based e-coats, aliphatic diisocyanate-based polyurethane coating	Coating	Comparable performance, including being “marketed as providing excellent weather resistance and can resist yellowing or paint degradation due to sunlight, gloss retention, resistance to water, oil and chemicals such as salt which adds to vehicle corrosion and scratch resistance” ^a
PU and PAN	Internal pressure regulator	<ul style="list-style-type: none"> Limited water resistance compared to fluoropolymer materials due to high surface tension Potential water-related issues in specific applications^a
Silicone rubbers	Gaskets, cables, and hoses	<ul style="list-style-type: none"> Offer a range of properties suitable for other applications (e.g., used in various applications in modern vehicles such as paint additives, air bag coatings, and radiator seals) While offering a range of properties suitable for these applications, silicone materials do not have the specific combination of properties required in fluoropolymer applications^b
Silicone, EPR, or EPDM rubber	Greenhouse gas emission control; lambda sensor cables	Reduced extreme heat resistivity and mechanical conditions ^c

Table 4-6. Overview of Automotive and Aerospace Alternatives (3 pages)

Alternative	Example potential applications	Overview of likely technical, economic, and environmental implications
Stainless steel, aluminum, or copper	Fuel lines in antique cars that do not need to meet modern standards; protection for plastic fuel lines	<ul style="list-style-type: none"> Used in metal fuel lines for antique cars that do not have to meet modern standards (these fuel lines are prone to leakage during crash tests) Difficult for other polymeric alternatives to meet fuel permeation standards, thus have limited application scope^b
Steel, high-temperature polymers, or UHMWPE	Door hinges and seat height adjustment bearing	Alternative materials pose challenges, including frequent regreasing, assembly issues, rigidity, and low temperature resistance ^c
Various elastomeric materials, including NBR, ACM, AEM, HNBR, UHMWPE, POM, PU, PEEK, and EPDM	Seals, rings, and packing	<ul style="list-style-type: none"> Limitations in friction, heat resistance, temperature ranges, or chemical resistance for alternatives Lower performance compared to fluoroelastomer-based systems (FKM, FEPM, FFKM)^{a,c}
XLPE or TPE	Cold air intake systems; control elements in car interiors	Limited chemical resistance when compared to fluoropolymers ^b
Low-Emission and Zero-Emission Vehicles		
Aluminized Mylar; ^e low-density PE; rubber or rubber composites; non-woven materials, elastic fibers such as spandex, nylon, Lycra, ^f or elastane	Facing layer for battery management system	Comparable performance to fluoropolymers, including durability, ease of handling, favorable insulation properties and reaction to fire, combustion, and flame-resistance properties ^g
Binder-free lithium-ion batteries	Facing layer material in components and systems to manage thermal runaway issues in electric vehicle batteries	Comparable performance in producing lithium-ion cells, including cost, energy density, safety, and reliability compared to cells manufactured using fluoropolymers as binders ^h
EVOH	Hose barrier layer for ethanol and methanol-containing fuels	Comparable performance to fluoroelastomers and/or fluoropolymer plastics such as FKM ⁱ
White latex containing PVAC, CMC, PVA, polyacrylic acid and polyacrylate modifier	Electrodes for lithium-ion batteries	<ul style="list-style-type: none"> Used as an alternative aqueous binder (for PVDF) in fabricating lithium-ion anodes Comparable or better performance for this application when considering cost, environment, decomposition, initial coulombic efficiency, and stability^j
Aerospace		
PVC and PE combined with HFFR; ceramics	Electric cables	<ul style="list-style-type: none"> Polymeric materials lack necessary temperature range performance Ceramics offer partial chemical protection but are inflexible and heavier^c

^a ECHA, 2023, "Submitted restrictions under consideration," European Chemicals Agency, Helsinki, Finland.

^b Drohmann et al., 2021, *Regulatory Management Option Analysis for Fluoropolymers*, Plastics Europe, Association of Plastics Manufacturing, Brussels, Belgium.

^c Chemservice, 2022, "Analysis of Alternatives to Fluoropolymers and Potential Impacts Related to Substitution in Different Sectors of Use," Version 1, Chemservice, Chicago, Illinois.

^d Xirallic is a registered trademark of Merck KGaA, Darmstadt, Germany.

^e Mylar is a registered trademark of the DuPont Teijin Corporation, Chester, Virginia.

^f Lycra is a registered trademark of The LYCRA Company, Wilmington, Delaware.

^g Evans et al., 2020, "Components and systems to manage thermal runaway issues in electric vehicle batteries," U.S. Patent US20210167438A1, Aspen Aerogels Inc., Northborough, Massachusetts.

^h 24M, 2023, "A Better Way to Work With Lithium-Ion: Simpler, Safer, More Reliable Cell Manufacturing," 24M Technologies, Inc., Cambridge, Massachusetts.

Table 4-6. Overview of Automotive and Aerospace Alternatives (3 pages)

Alternative	Example potential applications	Overview of likely technical, economic, and environmental implications
	ⁱ Miller et al., 2009, “Low-Permeation Flexible Fuel Hose,” U.S. Patent US20090123683A1, Gates Corporation, Denver, Colorado.	
	^j Lahiru Sandaruwan et al., 2022, “White Latex: Appealing “Green” Alternative for PVdF in Electrode Manufacturing for Sustainable Li-Ion Batteries,” <i>Langmuir</i> , 38(29), pp 8934-8942.	
ACM	= acrylic rubber.	PA = polyamide.
AEM	= ethylene acrylic elastomer.	PAN = polyacrylonitrile.
CMC	= carboxymethyl cellulose.	PE = polyethylene.
ECHA	= European Chemicals Agency.	PEEK = polyetheretherketone.
EPDM	= ethylene propylene diene monomer.	POM = polyoxymethylene.
EPR	= ethylene propylene rubber.	PTFE = polytetrafluoroethylene.
ETFE	= ethylene tetrafluoroethylene.	PU = polyurethane.
EVOH	= ethylene vinyl alcohol resin.	PVA = polyvinyl alcohol.
FEPM	= trifluoroethylene-propylene copolymer.	PVAC = polyvinyl acetate.
FFKM	= TFE-PMVE perfluoroelastomer.	PVC = polyvinyl chloride.
FKM	= fluorine Kautschuk material.	PVDF = polyvinylidene fluoride.
HFFR	= halogen-free flame retardant.	TPE = thermoplastic elastomer.
HNBR	= hydrogenated nitrile butadiene rubber.	UHMWPE = ultra-high molecular weight polyethylene.
NBR	= nitrile butadiene rubber.	XLPE = cross-linked polyethylene.

4.5 Lithium-Ion Batteries, Wind Turbines, and Solar Panels

Fluoropolymers have multiple uses in the clean energy sector, which includes lithium-ion batteries, wind turbines, and solar panels. These uses include ECTFE (wind turbines, solar panels); ETFE (solar); FEP (wind turbines); PTFE (lithium-ion batteries, wind turbines); PVF (solar); and PVDF and PVDF copolymers (lithium-ion batteries, wind turbines, solar panels).

4.5.1 Lithium-Ion Batteries: Fluoropolymer Uses and Properties

Lithium-ion battery components include electrodes, membrane separators, and electrolytes. In some cases, the separator and electrolyte are combined into an integrated, solid-state polymer electrolyte. Collectively, PTFE, PVDF, PVDF-HFP, PVDF-CTFE, and PVDF-TrFE are used in lithium-ion battery electrode binders, membrane separators, gel polymer electrolytes, and the battery pack. These components are described in more detail below.

Electrodes – Battery electrodes include a metal current collector (e.g., aluminum for cathode, copper for anode), and a porous composite that includes an active material in which lithium ions can be intercalated. The electrodes also use binders for cohesion of particles of the active material and to help the composite adhere to the current collector (Lingappan et al., 2021; Bicy et al., 2022). To be effective, binders need to have high mechanical strength, thermal resistance, chemical and electrochemical stability, and excellent binding to the active material (Arcella et al., 2014; Lingappan et al., 2021).

For these reasons, early lithium-ion batteries (e.g., 1980s) used PTFE as a binder in both cathodes and anodes. However, electrode manufacturing involves deposition of binder materials onto the current collector, as a slurry and homogeneous distribution of the binder is essential. This even distribution was difficult to achieve with PTFE (Lingappan et al., 2021). In the 1990s, PVDF battery binders were developed that offered the same advantageous properties as PTFE and could be evenly distributed in the slurry during electrode fabrication (Lingappan et al., 2021), although studies continue to investigate use of PTFE. Some studies also report use of a PVDF copolymer known as PVDF-HFP as a binder material; this binder material is reported to have greater mechanical strength relative to PVDF (Wang et al., 2018). Arkema products Kynar and Kynar-FLEX are examples of PVDF and PVDF-HFP, respectively, that are currently on the market (Stephan et al., 2006; Amin-Sanayei and He, 2015).

Separators – The separator is a membrane between the cathode and anode that prevents electrical shorting, while still allowing transfer of lithium ions between electrodes (Costa et al., 2013; Arcella et al., 2014). The separator is critical for lithium-ion batteries since short-circuiting of the separator inside the battery can lead to combustion of flammable lithium-ion battery electrolytes (Costa et al., 2013). To prevent electrical shorting and maximize the operation of the lithium-ion batteries, separators should be electrochemically stable, thermally stable, wettable, chemically stable in the battery electrolyte, and have high ionic conductivity and mechanical strength (Costa et al., 2013; Arcella et al., 2014). PVDF and copolymers PVDF-HFP, PVDF-CTFE, and PVDF-TrFE have all been reported for use in lithium-ion batteries (Costa et al., 2013).

Gel polymer electrolytes – Safety problems associated with lithium-ion batteries can be addressed through use of solid-state electrolytes that integrate the separator and electrolyte. In essence, polymers are used to gel the electrolytes yielding a solid-state “gel polymer electrolyte” that provides ionic conductivity, electrochemical stability, and thermal stability, while preventing the liquid electrolyte from leaking and decreasing safety concerns (Zhang et al., 2014). Notably, incorporation of the electrolyte or ionic liquid into the polymer provides the needed ionic conductivity, and in some cases, these ionic liquids are low molecular weight PFAS. Gel polymer electrolytes are prepared via multiple techniques, including polymerization in the presence of the ionic liquid and by soaking a polymer (post-polymerization) in ionic liquid. Different methods may lead to different gel polymer electrolyte morphologies. The latter is a key consideration for gel polymer electrolytes since they are solid-state systems that need to have porosity that will facilitate transport of ions through the matrix without leading to leakage of ionic liquids, which may short-circuit the lithium-ion battery (Stepniak et al., 2014). PVDF and PVDF-HFP are both reported for use in gel polymer electrolytes (Zhang et al., 2014; Liang et al., 2018; Liu et al., 2021).

4.5.2 Lithium-Ion Batteries: Non-fluorinated Alternatives

Electrodes – Alternative, non-fluorinated materials are currently on the market for use as electrode binders. Polymeric electrode binders are broadly subdivided into aqueous and nonaqueous binders, which is indicative of the solvents used during binder manufacturing. As noted above, slurry processing of binders is used during construction of electrodes, so aqueous binders use water as the solvent during processing, whereas nonaqueous binders use solvents such as *n*-methyl-2-pyrrolidone (NMP). Fluoropolymers are typically processed using NMP or other organic solvents, so they are considered nonaqueous binders (Lingappan et al., 2021). Examples of non-fluorinated, aqueous binders include carboxymethyl cellulose (CMC), PVC, polyacrylic acid (PAA), chitosan, and alginates (Lingappan et al., 2021). Binders such as CMC and PAA often also incorporate styrene butadiene rubber (SBR) to improve structural integrity and adhesion to the collector (Lingappan et al., 2021). For example, BASF markets a series of Licity⁴⁵ electrode binders that are reported as aqueous SBR co-polymers (BASF, 2023).

Separators – Similar to electrode binders, non-fluorinated polymers reported for use as lithium-ion battery separators include polyethylene, polypropylene, PEO, polyacrylonitrile (PAN), and polymethyl methacrylate (PMMA) (Costa et al., 2013; Costa et al., 2019). Separators also incorporate non-fluorinated fillers that increase the strength and conductivity of the membrane. Examples of fillers include ceramics (Al_2O_3 , SiO_2 , TiO_2), zeolites, carbon-based materials, and ferroelectric materials (BaTiO_3) (Costa et al., 2013). The above-mentioned polymers are well-referenced in the literature for use as separators, as evidenced by their inclusion in multiple review studies. Several additional materials are also being explored for use as separators as they reportedly offer more thermal stability and/or are more environmentally friendly (Costa et al., 2019). These materials include polyimide, poly *m*-phenylene isophthalamide (PMIA), PEEK, polybenzimidazole (PBI), polyetherimide (PEI), polystyrene-*b*-butadiene-*b*-styrene (SBS), cellulose, chitin, silk fibroin, and polyvinyl alcohol (PVA) (Costa et al., 2019).

⁴⁵ Licity is a registered trademark of BASF, Ludwigshafen, Germany.

Gel polymer electrolytes – Non-fluorinated polymers are documented for use as gel polymer electrolytes, including PEO and polyethylene glycol (PEG). However, use of non-fluorinated polymers does not mean that the overall gel polymer electrolyte is PFAS-free, because low molecular weight PFAS are still used as ionic liquids to increase the electrical conductivity (Costa et al., 2019).

4.5.3 Wind Turbines: Fluoropolymer Uses and Properties

As a result of their use in outdoor environments, wind turbines need to be resistant to weathering and corrosion. For example, icing of wind turbines can cause uneven weight distribution between wind turbines and change aerodynamic performance, which leads to mechanical vibrations and reduced efficiency of the turbine (Peng et al., 2012; Qin et al., 2020). One way to mitigate icing is the use of a hydrophobic coating (Peng et al., 2012; Qin et al., 2020). Rain can lead to corrosion, erosion, and scouring of the blades, which can also impact aerodynamics, reduce turbine efficiency, and eventually lead to loss in lift (Chen et al., 2019). To reduce the impacts of both precipitation and icing, “superhydrophobic” coatings are used on turbines. ECTFE, PTFE, PVDF, and FEP are reported to be used in wind turbines for weather and corrosion-resistant properties (Arcella et al., 2014; Améduri, 2018). PVDF, PTFE, and FEP are also reported in the literature for use as superhydrophobic coatings (Peng et al., 2012; Qin et al., 2020; Ellinas and Gogolides, 2022).

4.5.4 Wind Turbines: Non-fluorinated Alternatives

An extensive body of literature exists related to the development of superhydrophobic coatings; however, the field is much broader than its application to wind energy because superhydrophobic coatings have extensive applications in other areas such as automotive and solar. Studies have been published related to engineering of superhydrophobic surfaces that mimic the “lotus leaf effect”, which is known as a natural superhydrophobic surface (Ensikat et al., 2011). These coatings rely on a combination of water-repelling chemical characteristics and a surface roughness that is optimized to reduce nucleation of water molecules, which is beneficial for reducing ice formation and adhesion to surfaces (Liu et al., 2023). Several non-fluorinated materials have been explored to achieve the lotus effect, including silica nanoparticles (Karmouch and Ross, 2010) and biochar-based materials that offer thermal benefits for deicing scenarios (Liu et al., 2023). At this stage, whether such non-fluorinated alternatives are commercially available and/or used in the wind energy sector is unclear.

4.5.5 Solar Panels: Fluoropolymer Uses and Properties

Solar, or photovoltaic, cells generally consist of a metal frame that holds a series of layers, including a frontsheet, encapsulant, active layer, and backsheet (Arcella et al., 2014). Uses of fluoropolymers in the frontsheet and backsheet collectively include ECTFE, ETFE, PVF, and PVDF (Arcella et al., 2014). Uses in the frontsheet and backsheet are described in more detail below.

Frontsheet – The frontsheet of a solar panel is a transparent layer that allows light to pass through while protecting the underlying layers. As a result, a frontsheet needs to be transparent, weather resistant, and impact resistant; provide electrical insulation; and must maintain these properties over a wide range of operating temperatures. Frontsheets are often made of glass, but there is an increasing demand for solar panels that are more flexible and lighter. ECTFE (e.g., Halar manufactured by Solvay) and ETFE (e.g., Tefzel manufactured by The Chemours Company FC, LLC) are both documented for use in frontsheets as a result of stability in UV light, low permeability, weather resistance (i.e., superhydrophobic properties; described in Section 4.5.3), and ability to transmit light in the visible range (Arcella et al., 2014; Chemours, 2023; Singh et al., 2023; Solvay, 2023). Although studies have reported that PVDF is less suitable for lamination than ETFE and ECTFE (Singh et al., 2023), PVDF products are marketed for use as frontsheets in solar panels (e.g., SOLAR-THRU⁴⁶) (AiT, 2021). Additionally, FEP (e.g., Teflon FEP) is intermittently reported as a frontsheet on some solar cells (e.g., DuPont, 2013; Ross et al., 2014).

⁴⁶ SOLAR-THRU is a trademark of AI Technology Inc., Princeton Junction, New Jersey.

Backsheet – The role of the backsheet in a solar cell is like that of the frontsheet except that transparency is not needed in conventional (i.e., non-transparent) solar cells. As a result, the backsheet needs to be weather resistant, have mechanical strength, and provide electrical insulation. As with the frontsheet, the backsheet needs to maintain these properties over a wide range of operating temperatures. PVF (e.g., Tedlar), PVDF, and ECTFE are all reportedly used in solar cell backsheets (DeBergalis, 2004; Arcella et al., 2014; DuPont, 2023).

4.5.6 Solar Panels: Non-fluorinated Alternatives

Section 4.5.4 addressed non-fluorinated alternatives for superhydrophobic coatings used in wind turbines, and because superhydrophobic coatings are also used in the frontsheets and backsheets of solar cells, this information also applies to the solar industry. However, development of non-fluorinated alternatives for use in solar cells will need to address the additional requirements of transparency (i.e., for the frontsheet) and minimizing dust retention (Luo et al., 2023).

As noted in Section 4.5.4, superhydrophobicity depends in part on optimization of surface roughness to minimize nucleation of water droplets. However, such roughness can increase retention of dust, which in turn reduces transparency, a key property needed for solar cells (Luo et al., 2023). Similar to superhydrophobic coatings for wind turbines, studies in peer-reviewed literature document development of non-fluorinated alternatives for use in solar cells (Allahdini et al., 2022; Luo et al., 2023). For example, Allahdini et al. (2022) published a study using alkoysilane binder, silica nanoparticles, and methyltriethoxysilane to collectively yield a hydrophobic (including icephobic) and self-cleaning surface for use in solar cells. Also similar to wind turbines, if such non-fluorinated alternatives are primarily at the research and development stage or are available commercially for use in solar cells is unclear.

Table 4-7 provides an overview of the results of the RMOA (Drohmann et al., 2021, Table 40) focused on the renewable energy sector.

Table 4-7. Overview of Renewable Energy Alternatives

Alternative/s	Example potential application	Overview of likely technical economic and environmental implications
Pb (lead acid) battery	Batteries	Lead batteries are about one-third heavier than lithium-ion batteries in which fluoropolymers are used.
High-temperature fuel cells	Fuel cells (stationary applications)	The key disadvantage, compared to PEM fuel cells, is that the high-temperature fuel cells can only be used in stationary applications.

Source: Extracted from Table 40 of Drohmann et al., 2021, *Regulatory Management Option Analysis for Fluoropolymers*, Plastics Europe, Association of Plastics Manufacturing, Brussels, Belgium.

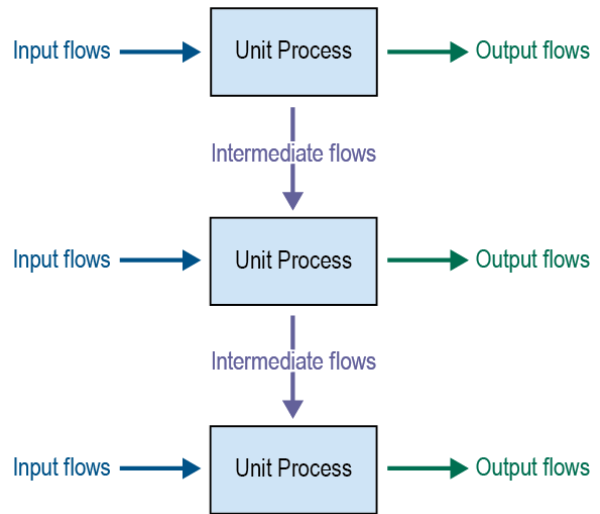
Pb = lead.

PEM = polymer electrolyte membrane.

5.0 FLUOROPOLYMER LIFE CYCLE ASSESSMENT AND COST BENEFIT ANALYSIS

5.1 Life Cycle Assessment

Life cycle assessment (LCA) is a framework and tool that is increasingly used in decision-making and regulatory measures as the U.S. continues to identify sustainable products and energy solutions. The International Organization for Standardization (ISO) defines LCA as the “compilation and evaluation of the inputs, outputs and the potential environmental impacts of a product system throughout its life cycle” (ISO 14040:2006, ISO 14044:2006). LCA enhances the understanding of environmental impacts from the production and use of a product and can be used to identify environmental hotspots in a product’s life cycle or to compare two product systems to identify which one is less detrimental to the environment. A product system comprises unit processes, each with its own input and output flows, that are linked via intermediate flows (Figure 5-1). Unit processes within a product system are often referred to as life cycle stages, such as raw material acquisition, manufacturing, use, recycling, and waste or end of life.

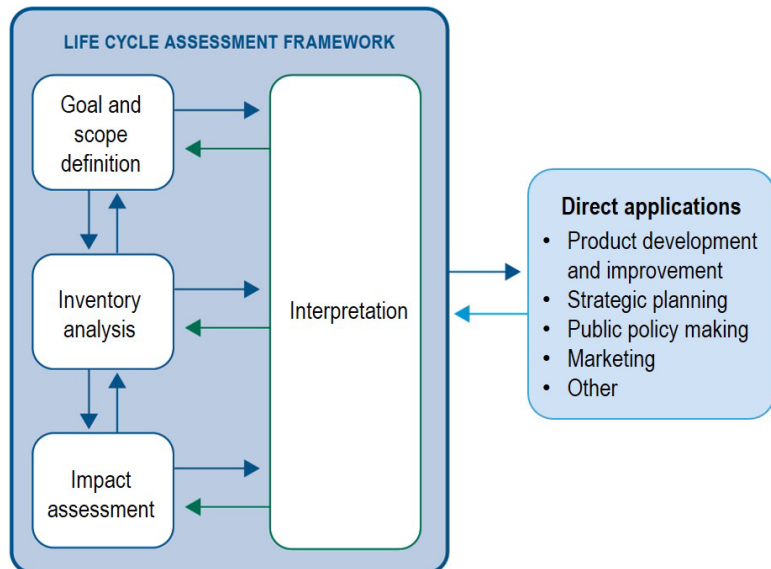


Source: ISO 14040:2006, “Environmental management — Life cycle assessment — Principles and framework.”

Figure 5-1. Unit Processes within a Product System

ISO 14040 outlines the principles and defines the framework of an LCA, whereas ISO 14044 defines the requirements and guidelines (i.e., how to carry out an LCA study). The two standards represent the foundation that LCAs are built on and reviewed based on the provided guidance. Both ISO standards, though separate, are not mutually exclusive and the requirements of one are closely linked with the requirements of the other.

ISO 14040 outlines the four phases of completing an LCA as follows: (1) goal and scope definition, (2) inventory analysis, (3) impact assessment, and (4) interpretation. Figure 5-2 shows the iterative nature of LCA, where the interpretation phase can inform the scope of the study or the inventory included for analysis. The “goal and scope definition” phase is a critical step in LCA studies. During goal setting, the LCA practitioner identifies what the study is for, why the study is being done, who will see the study results, and how the study results will be used.



Source: ISO 14040:2006, “Environmental management – Life cycle assessment – Principles and framework.”

Figure 5-2. Four Phases of Life Cycle Assessment

The scope of an LCA study defines the system being analyzed, the functional unit and system boundary of the study, and the impact categories and methodology selected for the study. The scope should also include information regarding the data being used in the study and any key limitations or assumptions. Notable steps in the goal and scope phase are defining the functional unit and setting a system boundary. A system will often have multiple functions; thus, defining the function of the system in the context of a particular study is critical. According to ISO 14040, “[t]he primary purpose of a functional unit is to provide a reference to which the inputs and outputs are related.” As a result, the functional unit and system boundary are closely linked.

Setting the system boundary may change what functional unit is selected and can significantly influence the results of the impact assessment. A system boundary can include the entire life cycle of a product, which is referred to as cradle-to-grave, or the boundary can be truncated to only include specific sections of the life cycle, referred to as cradle-to-gate. For example, an LCA study of a chemical with a cradle-to-grave system boundary would include all life cycle stages from raw materials extraction through production, use, and disposal. Whereas a cradle-to-gate system boundary for the same study would end after production (i.e., the plant gate) and would not consider the use or disposal of that product. Clearly defining the system boundary provides context for the interpretation of a study’s impact assessment results. Without this context, results may be misinterpreted, misleading, and can lead to misinformed decisions.

The life cycle inventory (LCI) phase of LCA includes “...data collection and calculation procedures to quantify relevant inputs and outputs of a product system” (ISO 14040). Inventory analysis can often result in refinement of the goal and scope, either as more data are discovered or as data gaps are identified. Data collected for LCA include raw material and energy inputs, product and waste outputs, and emissions to air, water, and soil. LCI data can be collected in several repositories, including both private and public options. Most notably, the Federal LCA Commons provides publicly available LCI data from several different organizations and institutions (FLCAC, 2023). Other notable databases include licensed options such as ecoinvent (Wernet et al., 2016) and GaBi (Sphera, 2023). The calculation component of inventory analysis includes both normalizing the data to a specific unit process and normalizing the data to the functional unit for the study. Dealing with unit processes and systems that produce more than one product is not uncommon. These additional products, referred to as co-products, are addressed during inventory analysis using a procedure called allocation. The allocation procedure in ISO 14044, Section 4.3.4.2, provides further detail on how to manage co-products within a system.

The third phase of LCA is the life cycle impact assessment (LCIA). Impact assessment “...involves associating inventory data with specific environmental impact categories and category indicators, thereby attempting to understand these impacts” (ISO 14040). LCIA can be performed using a variety of methods. EPA released and maintains its own impact assessment method called the Tool for Reduction and Assessment of Chemicals and Other Environmental Impacts (TRACI) (Bare, 2012). Impact assessment methods, like TRACI, comprise characterization factors (CF) that translate emissions into impacts. CFs characterize emissions using common equivalence units. For example, for the global warming potential (GWP) impact category, carbon dioxide (CO₂) has a CF of 1 kg CO₂ equivalents per kg (kg CO₂e/kg). Conversely, fossil methane (CH₄) has a CF of 29.8 kg CO₂e/kg. Therefore, CH₄ has a higher impact than CO₂, per unit of mass, in terms of GWP. The CFs are used to aggregate emissions into one category with a common equivalence unit, like CO₂ equivalents. CFs represent the potency of a specific emission, and that potency varies depending on the impact category and sometimes depending on the environmental compartment to which it is emitted (air, water, soil). Impact assessment methods rely heavily on modeling with varying levels of uncertainty to generate CFs.

Among the various impact assessment methods, there are two types of categories or indicators: midpoint and endpoint. Midpoint indicators represent individual environmental concerns, like GWP. Conversely, endpoint indicators represent aggregated environmental concerns like damage to human health.

A result of the aggregation that happens to reach endpoint indicators is increased uncertainty. This uncertainty is a result of the complexity associated with issues such as human health; various factors can impact human health, and the emission of one chemical cannot accurately indicate a health outcome. Thus, while providing a result that may have more meaning and connection to an audience, endpoint results have considerable uncertainty and should be presented with the associated limitations.

Optional components of the LCIA phase include sensitivity and uncertainty analysis. Uncertainty analysis is a way to determine the impact of assumptions, data gaps, and general uncertainties in the data. Sensitivity analysis can be used to determine the impact of specific changes to the data or the sensitivity of the data and results to changes. Additional details on how to perform impact assessments are provided in ISO 14044, Section 4.4.

Finally, the last phase of LCA, life cycle interpretation, includes completeness, sensitivity, and consistency checks, using the LCIA results to identify any limitations and provide conclusions. The interpretation phase connects the results of the LCI and LCIA back to the goal and scope of the study. This final phase of the LCA provides the practitioner an opportunity to interpret the results in the context of the defined goal and scope. This phase also affords an opportunity to refine the goal and scope, revisit the LCI, and recalculate the LCIA results as necessary.

In addition to this introduction to LCA, discussing what LCA is and is not is also important in the context of this report. Specifically, life cycle costing (LCC) is often confused with LCA. LCC is an economic framework that evaluates the total cost of a product system over its life. LCC can include the environmental costs, but still diverges from LCA by providing a primarily economic perspective. The Society of Environmental Toxicology and Chemistry (SETAC) published a code of practice for LCC that identifies the differences between LCC, LCA, and social LCA (SLCA) (Swarr et al., 2011). Economic and cost considerations within the scope of this report are discussed in Section 5.2.

LCA is not meant to replace detailed risk assessment of the toxicological or environmental effects of the emissions from product systems. LCA is meant to provide a high-level comparison between options, while risk assessments generally aim to quantify specific risks and to determine whether those risks fall within acceptable thresholds. While often complementary, these types of analyses do not exist within the framework of LCA. Impact assessment methods, and the impact categories within, provide a way to aggregate LCI results for interpretation in a meaningful way. The mechanisms and effects of the emissions accounted for during LCA are detailed in literature and the modeling used to develop LCIA methods. This report and the LCA section will largely avoid toxicological or environmental studies regarding fluoropolymers. These studies will be referenced if relevant inventory data and life cycle insights are provided.

5.1.1 Fluoropolymer Life Cycle Assessment Literature Review

Life cycle data are kept behind chemical industry walls due to confidentiality and proprietary concerns. The lack of data availability is compounded by missing CFs in existing LCIA methods. Thus, in cases where data exists for an LCA study, a way to turn the LCI data into impact results may not be available.

Hu et al. (2022) summarizes one of the key problems, as suggested above, when conducting an LCA of fluoropolymers: data availability. This 2022 study identifies 15 LCAs that include PVDF as an input and uses proxies to model its production and documents its own LCA of PVDF using stoichiometric methods. When specific data cannot be obtained for an LCA study, similar data can be used as a surrogate or proxy. For example, if data for a specific chemical is unavailable, data for a chemical with similar production technology and applications may be used as a proxy. This is common practice in LCA but must be done with care, as a proxy will introduce uncertainty into a life cycle model, and these proxies should be clearly documented for the audience of the LCA.

A majority of the 15 LCA studies examined lithium-ion batteries, where PVDF is a necessary component, and all 15 studies relied on proxies, such as PVF and PVC, to model PVDF. Notably, all but four of the studies obtained their proxy data fromecoinvent (Wernet et al., 2016). Depending on the selected proxy, the GWP results range from 1.6 kg CO₂e/kg of PVDF to 62 kg CO₂e/kg of PVDF.

These results highlight the uncertainty that is introduced when different proxies are used in LCA studies and the inability to identify what proxy may be representative of the input of interest. Ultimately, the Hu et al. (2022) study aims to conduct an LCA of PVDF synthesis and compare the results to those obtained using proxies. This analysis is achieved by providing the first known LCIs for PVDF production, relying on previously published literature and patents to stoichiometrically obtained input data for two synthesis routes. Note that the Hu et al. (2022) study seemingly excludes any direct emissions from and energy required for the manufacturing of PVDF. The LCI data presented in the study only focuses on the chemical inputs to PVDF production and the associated upstream emissions and energy requirements. Results from this LCA indicate that, in most cases, the use of proxies leads to significantly underestimating the environmental impacts when compared to the two PVDF cases presented in the Hu et al. (2022) study. The cumulative energy demands (CED) for both PVDF cases were significantly higher than any of the proxies under study. The same could be said for GWP except for the tetrafluoroethylene + polyethylene (TFE+PE) case, which has a higher GWP than all other proxies and the two PVDF cases. Using PVF as a proxy yielded a GWP and CED of 16.9 kg CO₂e/kg and 198.9 MJ equivalents (MJe) per kg, respectively. Conversely, the two PVDF cases based on stoichiometric methods had GWP and CED values of 54.7 and 55.8 kg CO₂e/kg and 858 and 756 MJe/kg, respectively. These results demonstrate the effect that using proxies can have on LCA results.

Holmquist et al. (2020) identifies CF availability as another key challenge to performing LCA studies of fluoropolymers and their monomers. Few CFs are available to characterize fluoropolymers and their PFAS monomers, and those that are available are not necessarily characterizing compounds of interest, such as PFOA. In addition, Holmquist et al. (2020) points out that these CFs do not consider the persistent and bioaccumulative nature of low molecular weight PFAS. To address these challenges, the study develops and proposes a framework for toxicity characterization, both ecosystem and human, which is specific to the complexity introduced with low molecular weight PFAS. The proposed framework contains two steps: (1) a translation table that converts PFAS inventory data into relevant degradation products, and (2) an impact characterization model to transform degradation product emissions into impact results. The amount of PFAS that degrades (i.e., transformation fractions) and the products it degrades into were determined using empirical studies of PFAS degradation. The impact characterization model represents a modified version of the USEtox model (Rosenbaum et al., 2008). While attempting to develop a robust framework for characterizing PFAS emissions, the authors acknowledge there are still limitations to the framework. These limitations do not lie within the proposed framework itself but are a result of limited understanding of the degradation mechanisms and ecosystem and the human toxicity effects of PFAS. Thus, the uncertainty in characterization frameworks like the one proposed can only be reduced through further empirical studies.

The study by Holmquist et al. (2020) provides a key example that, while efforts are being made to provide opportunities for better LCA studies of fluoropolymers and PFAS, there is still work that must be done. Notably, this study highlights the pervasiveness of uncertainty in LCA studies of fluoropolymers and PFAS, and this uncertainty was considered in the study conducted for this report. Another study, though not explicitly an LCA, developed CFs for textile chemicals such as fluoropolymers (Roos et al., 2018).

In a different study, Holmquist et al. (2021) leverages the characterization framework from Holmquist et al. (2020) and the CFs developed by Roos et al. (2018) to conduct an LCA of fluoropolymers used for textiles. The goal of the 2021 report is to quantify the effects of replacing fluoropolymers in the production of water-repellent shell jackets with alternative chemicals. In addition, this study aims to determine if the design and use of fluoropolymer-containing jackets affects the environmental impacts. The scope of this report (defined in Section 1.0) does not include textiles; however, this 2021 study includes LCI data for the production of fluoropolymers and thus is included in this literature review. The functional unit of the Holmquist et al. (2021) study is the life of the garment, where life span is based on studies of the use of water-repellent jackets. This consideration is notable because of the comparative nature of this LCA study. Establishing functional equivalence between fluoropolymers and their alternatives is one challenge in conducting a comparative LCA of these two products, which is discussed later in this section.

Once again, the Holmquist et al. (2021) study notes the challenge of modeling fluoropolymer production resulting from data availability and confidentiality. Like other studies reviewed here, the study uses fluoropolymer-specific LCI data where available and supplements with proxies where LCI data are unavailable. Upon investigation of the LCI data, the study appears to rely heavily on the use of proxies to fill data gaps. One notable outcome from the LCIA in the Holmquist et al. (2021) study is the identification that the impacts resulting from direct emissions from the studied system, with the exception of low molecular weight PFAS emissions, are small compared to the impacts resulting from energy use. The authors acknowledge, however, that the limitations associated with LCA studies of fluoropolymers may affect this finding. In addition, the authors note that considering how the fluoropolymer is used (i.e., the use and care of a shell jacket) is critical to evaluating its environmental performance. This is a key finding, as it indicates that fluoropolymers production requires significant energy use and that energy use contributes a large share of the environmental impacts. However, there also may be offsetting energy benefits from fluoropolymer use (e.g., reduced energy usage by aircraft because of weight reduction achieved using fluoropolymers). This result may indicate that there is no benefit, in the context of GWP, to using fluoropolymers over an alternative. However, as the authors note, the use of fluoropolymers is a critical consideration. Fluoropolymers have exceptional qualities that contribute to their longevity, and the lifetime of a product must be considered when evaluating the life cycle environmental impacts.

A D'Ambro et al. (2021) study characterizes emissions from a commercially operating fluoropolymer production facility. The study summarizes the emissions reported by a facility operated by The Chemours Company FC, LLC (Chemours) and uses that summary to model the transport of PFAS like GenX and other chemicals (D'Ambro et al., 2021). Chemours is a well-known producer of fluoropolymers like Teflon, the brand name version of PTFE, and polymerization aids like GenX, the brand name version of HFPO-DA. In 2017, the North Carolina Department of Environmental Quality (NC DEQ) found GenX in the Cape Fear River (NC DEQ, 2017). The NC DEQ identified the Chemours Fayetteville Works facility as the emission source of GenX and other PFAS to the Cape Fear River and surrounding water wells. As a result, Chemours was required to report air emissions from the Fayetteville Works facility (Chemours, 2018). Notably, Chemours reported 304.6 kg of HFPO-DA and 1,971 kg of hydrofluoric acid emissions during 2017.

These data are leveraged by D'Ambro et al. (2021) to evaluate the transport and fate of the reported air emissions using the Community Multiscale Air Quality (CMAQ) model. The new version of the CMAQ model, CMAQ-PFAS, predicted that approximately 95% of the PFAS air emissions from a fluoropolymer production facility like Fayetteville Works can be transported more than 150 km. Thus, only 5% of PFAS emissions are deposited within 150 km of a production facility. The remaining 95% of emissions can be transported across distances farther than 150 km. Although the D'Ambro et al. (2021) study does not include LCA or LCIA results, the model and results reported could be leveraged in an LCA study.

To address the emissions from the Fayetteville Works facility, the NC DEQ issued a permit on March 14, 2019 to Chemours to install a thermal oxidizer/scrubber system to reduce PFAS air emissions (NC DEQ, 2019). The permit included a 90-day testing period in which Chemours had to demonstrate a 99% reduction in air emissions. This treatment supplements carbon adsorbers that were installed in May 2018. In addition, Chemours implemented a water treatment system for the removal of PFAS, and the NC DEQ issued a discharge permit on September 15, 2022 (NC DEQ, 2022). The National Pollutant Discharge Elimination System (NPDES) permit sets emissions limits for a 180-day period of optimization, in addition to more stringent emissions limits after the 180-day period.

The LCA studies reviewed here highlight data gaps and limitations of conducting LCAs of fluoropolymer production. Note that the majority of the studies reviewed are not focused on fluoropolymers but are focused on low molecular weight PFAS, which are essential for and may be emitted during fluoropolymer production. While the review of LCA literature on fluoropolymers is the goal of this section, only one fluoropolymer LCA study was found in the literature, necessitating an equally important review of the LCA literature on PFAS due to their use in fluoropolymer production, emission during manufacturing, and the potential degradation of fluoropolymers into low molecular weight PFAS.

Product category rules (PCR) establish specific standards for LCAs of products and regulate how the results from such studies are communicated in documents like environmental product declarations. Currently, PCRs in the U.S. have largely been developed for products in the construction sector, such as concrete, flooring, and plumbing (Sustainable Minds, 2023). Due to the lack of data provided by manufacturers of fluoropolymers and fluoropolymer-containing products, the adherence to PCRs for products that may contain fluoropolymers, like coatings and electrical components, cannot be evaluated. Note that no PCRs for intermediate products, such as PTFE granules, have been identified. Based on the literature review provided in this section, developing a PCR for fluoropolymers may present significant challenges, such as data availability and missing impact assessment CFs.

As identified in this section, the area of concern regarding fluoropolymer production and use may not be the fluoropolymer itself, but the monomers, polymerization aids, and degradation products associated with fluoropolymers. The gap in LCA literature on fluoropolymer production is the result of several challenges. Due to the complexity of chemical transport in the environment, the expansive variety of chemical species, and the persistence of PFAS in the environment, the emissions from production, use, and end of life are incredibly hard to characterize. LCA studies rely on environmental and toxicological studies to provide a foundation on which LCIA methods and CFs can be developed. Although efforts are ongoing to collect these empirical data, fundamental challenges with data collection exist (Ankley et al., 2021). These challenges are compounded by the number of chemicals that fall within the PFAS spectrum and that PFAS often occur in mixtures. This lack of robust data makes it difficult to develop reliable LCIA models and CFs. These challenges and limitations are important to highlight and should be considered when reviewing the results of the LCA conducted for this report.

5.1.2 Case Study Selection

According to the market reports cited in this review, PTFE makes up over 50% of the total market volume of fluoropolymers (PLS080B). Section 4.0 highlights the nearly ubiquitous nature of PTFE. Thus, PTFE was selected as the fluoropolymer for the LCA conducted for this report. To perform a comparative analysis, stainless steel was selected as the alternative technology. Note that the appropriate alternative technology selection for comparison is highly dependent on the application; thus, a specific application of fluoropolymer and alternative technology is addressed in the following section.

5.1.3 Goal and Scope

The goal of the LCA conducted qualitatively for this report is to elucidate the environmental impacts of fluoropolymer production and use in a specified sector. More specifically, this LCA comparatively evaluates PTFE and its alternative under one of the specified sectors: industrial use in chemical processing. The specific technology application being evaluated is PTFE-coated or PTFE-lined pipe vs. stainless steel or other pipe. The results from this study are meant to contribute to the knowledge base of fluoropolymers, their alternatives, and the associated environmental impacts, not to promote the use of either technology or make policy recommendations. The functional unit for this study is 1 m of piping to be used in an unspecified chemical plant. The system boundary for this qualitative LCA, as shown in Figure 5-3, is cradle-to-gate and focuses on the production life cycle stage of PTFE. A more robust cradle-to-grave LCA will require additional LCI data and effort.

Note that when reviewing the LCIA methods, fluoropolymers and PFAS mostly were absent from established methods. As noted in Section 5.1.1 in the literature review, efforts are being made to fill these gaps (Holmquist et al., 2020; Roos et al., 2018). The frameworks and CFs reviewed above can be leveraged to perform a robust LCIA. However, the application of these methods is difficult in the context of a cradle-to-grave LCA of fluoropolymer production because of the significant gaps in available data.

Even with the progress made in characterizing fluoropolymer and PFAS emissions, considerable uncertainty is still associated with the human health and ecotoxicity impact categories. The level of uncertainty associated with these categories can produce misleading results that can lead to misinformed decision-making. This potential issue is especially true for fluoropolymers in that they do not have the empirical data to support robust impact assessment models and methods. To provide factual and reliable information, this study has omitted the human health and ecotoxicity impact categories from the LCIA, which have been deemed outside the scope of this report (defined in Section 1.0).

Based on the above findings and the scope of this report, this LCIA only includes the GWP impacts associated with the known chemical inputs into PTFE production and the associated upstream energy consumption. The CFs for the 100-year time horizon from the Intergovernmental Panel on Climate Change's Sixth Assessment Report (IPCC, 2023) were used to determine the GWP. Due to the significant data gaps identified, emissions of low molecular weight PFAS and other fluoropolymer degradation products were not considered.

5.1.4 Life Cycle Inventory

After thoroughly reviewing publicly available data and proprietary third-party databases, no complete LCI dataset was found for the production of PTFE. Notably, the results from the Vanderbilt industry survey did not yield any production or emissions data. The survey responses included only what is publicly available, such as the monomers and chemicals used in production, but did not include any quantities. This lack of transparency has been ubiquitously acknowledged in the literature and can be cited as the reason for lacking LCI data.

Third-party databases (e.g., ecoinvent) contain LCI data for chemicals used upstream of fluoropolymer production, such as TFE in the case of PTFE as the fluoropolymer. However, these databases are licensed data and therefore not available to the general public. The publicly available LCI data for PTFE production that do exist are either based off proxy data, stoichiometric calculations, or arbitrary emissions estimates; there are no ground-truth data sources. Additionally, because emissions of PFAS are not currently regulated in the U.S., no emission limits can be leveraged for LCI analysis of fluoropolymer production.

Raw Material Extraction

Figure 5-3 illustrates the PTFE production process. Rectangles and circles represent key life cycle stages and key inputs, respectively. Red arrows represent potential opportunities for PFAS emissions. PTFE is made from the polymerization of TFE, which is synthesized from chloroform and hydrogen fluoride. Hydrogen fluoride is produced via the reaction of sulfuric acid and the mineral fluorite. (Relevant raw material and market considerations are discussed in Section 5.2.)

Chloroform is produced from chlorine and methyl chloride or methane. Methane is primarily sourced from natural gas extraction, while methyl chloride is produced using methanol and hydrochloric acid. Methanol is generally produced from syngas containing carbon monoxide and hydrogen. The primary source of hydrogen is natural gas, but the syngas may be the product of other processes using other fossil-based hydrocarbons.

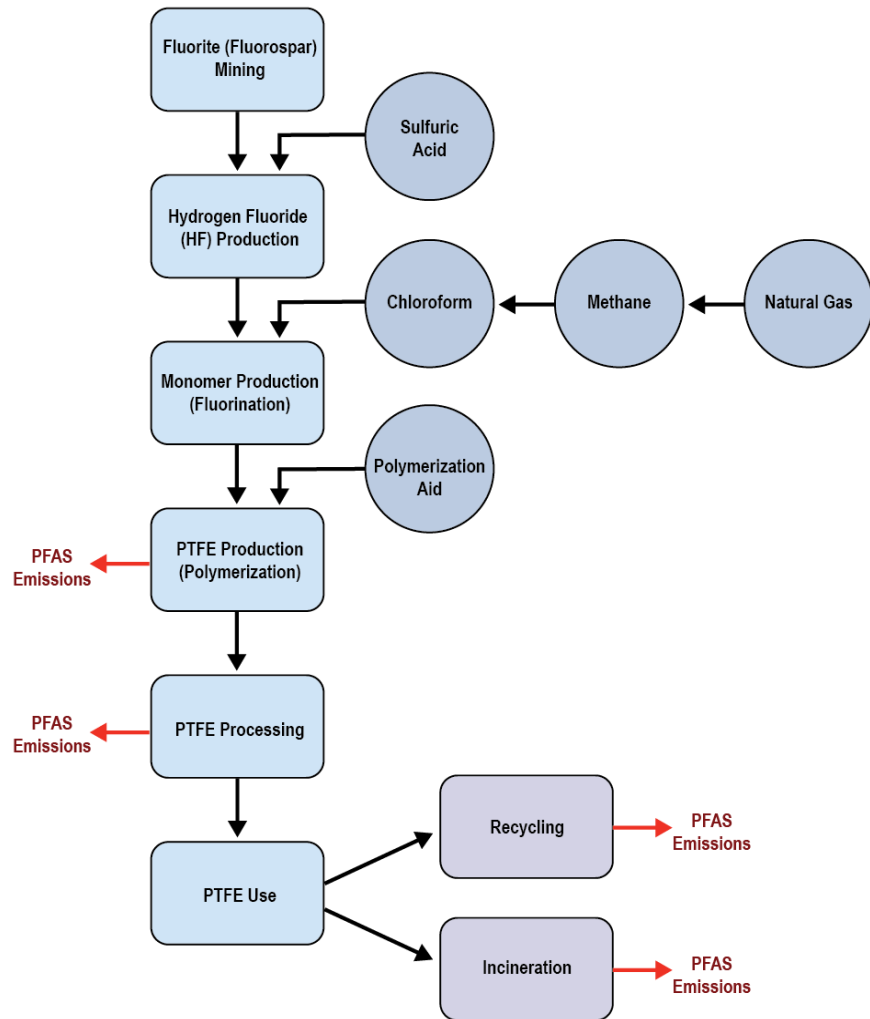


Figure 5-3. Polytetrafluoroethylene Production Process

Given the above, natural gas is assumed to be the primary resource for PTFE production and a likely source for energy requirements throughout manufacturing. More importantly, significant amounts of chlorine go into the process and represent the bulk of the mass in chloroform.

PTFE Production

The screening-level LCA is documented in Appendix B and summarized below. From a purely stoichiometric perspective, the material inputs and data sources considered for TFE production are:

- Natural gas: 0.32 kg natural gas/kg TFE (Rai et al., 2021)
- Chlorine (from a Chlor-alkali plant): 4.25 kg Cl₂/kg TFE (NREL, 2012)
- Sulfuric acid: 1.96: 1.96 kg H₂SO₄/kg TFE (NREL, 2012)
- Fluorite: 1.56 kg CaF₂/kg TFE (Lai et al., 2021).

The above inputs do not account for real-world yields or energy input for the TFE itself or chloroform. (Note that the main by-product of chloroform formation is hydrochloric acid.)

From an emissions perspective, the polymerization of TFE into PTFE may be a point of risk for low molecular weight PFAS emissions to the environment due to their use as fluorosurfactants or polymerization aids (D'Ambro et al., 2021). As noted in the literature review (Section 5.1.1), these emissions could be on the order of hundreds of kilograms per year, while production is in the thousands of tons (NC DEQ, 2019). Even with the relatively low emission rate when compared to the production volume of fluoropolymer, existing studies indicate that exposure to small amounts of low molecular weight PFAS can cause significant health effects (Fenton et al., 2021). Thus, small mass flows of low molecular weight PFAS emissions should not be considered negligible.

As previously noted, no known sources of LCI data were found for low molecular weight PFAS emissions from fluoropolymer production. In addition, impact categories like human health and ecotoxicity were excluded from the LCIA in this report due to concerns regarding the associated uncertainties. These points are important to reiterate such that the following is clear: toxicity impact categories and low molecular weight PFAS emissions were not included in this report due to uncertainty and data gaps, not because they lack importance.

PTFE-Lined Pipe Production and Specifications

Using the dimensions for a commercially available PTFE-lined pipe for 1 m of 2-in. piping with a 5 mm-thick PTFE lining, the mass of steel is 5.4 kg/m and the mass of PTFE is 1.6 kg/m for a total of approximately 7 kg/m (Mersen, 2021). Given the performance of PTFE, the steel used for the PTFE-lined pipe is assumed to be of lower grade than stainless steel. The inventory for steel production was derived from the National Renewable Energy Laboratory (NREL) U.S. Life Cycle Inventory Database (USLCI) (NREL, 2012).

Stainless-Steel Pipe Production and Specifications

Many grades of stainless and specialty steels could be used in chemical plants; determining which steels are most likely to be used requires knowledge of all of the chemicals that PTFE-lined pipe are used to process and the stainless-steel alternatives that could be used in those situations. For simplicity, 304 stainless steel is assumed to provide similar performance characteristics for this application and is therefore used as a proxy. The amount of stainless steel for 1 m of 2-in. pipe is assumed to be the same as the PTFE-lined pipe: 5.4 kg/m. The inventory for stainless-steel production was derived from the NREL USLCI database (NREL, 2012).

Use Phase

Based on the reviewed literature and responses from industry, if the PTFE material is used as specified, no emissions are specifically associated with its use in chemical processing. This assumption has been applied here and results in no fluoropolymer-related emissions during the use phase.

End of Life

Various methods are employed for the reuse, recycling, and destruction of fluoropolymers (Améduri and Hori, 2023). Once the fluoropolymer is in its final form, most evidence points to very little breakdown of the fluoropolymer, which is expected, as one of its primary attributes is its stability and resistance to corrosion. Conversely, there is a risk of low molecular weight PFAS emissions from fluoropolymers at the end of life if the fluoropolymer-containing product is incinerated at temperatures less than 850 °C (Huber et al., 2009). Due to the scope of this report and the data scarcity regarding emissions during use and end-of-life treatment of fluoropolymers, the LCIA focuses on the impacts from PTFE production using a cradle-to-gate system boundary, thus end-of-life disposal emissions cannot be determined.

5.1.5 Life Cycle Impact Assessment Results

The GWP of the material inputs into TFE production, including upstream natural gas, chlorine for chloroform, and fluorite and sulfuric acid for hydrogen fluoride production, is estimated to be 10.65 kg CO₂e/kg TFE (Table 5-1). For 1 m of 2-in. pipe with a 5 mm-thick PTFE coating, the estimated 100-year GWP for just the material inputs is roughly 29.5 kg CO₂e/m PTFE-coated, non-stainless-steel pipe. In contrast, the GWP for 1 m of stainless-steel pipe is 41.3 kg CO₂e/m stainless-steel pipe. However, if the LCI data for PTFE production were available and the energy inputs into PTFE manufacturing were taken into account, this difference would likely be much smaller.

Table 5-1. Calculation of the Global Warming Potential of the Material Inputs into Tetrafluoroethylene Production

Product	PTFE-lined pipe	Stainless-steel pipe
Pipe diameter (in.)	2	2
Steel mass (kg/m)	5.4	5.4
PTFE mass (kg/m)	1.6	0
Global warming potential ^a (kg CO ₂ e/m)	29.5	41.3

^a Global warming potential does not include LCI data for PTFE production, such as energy consumption.

LCI = life cycle inventory.

PTFE = polytetrafluoroethylene.

This result, however, is just for the material inputs to the piping. With no operations emissions in the use phase of an LCA, such as per kg of chemical produced, both of these impacts would be divided by thousands of tons of production and would be expected to be dwarfed by the energy and feedstock requirements for creating the target chemical. One of the key advantages to PTFE is its stability. Even with a perfectly selected stainless steel, the stainless steel would potentially need to be replaced over the life of the chemical processing facility, providing a slight life cycle greenhouse gas emissions edge for the PTFE-lined pipe.

From a PFAS emission standpoint, as noted above, no clear way is apparent to compare these two scenarios through a human or ecotoxicity impact assessment because few such factors are available for low molecular weight PFAS and, furthermore, such considerations are outside the scope of this report. Note that a premature assessment would likely show higher toxicity impacts for stainless steel simply from nickel production.

5.1.6 Example Life Cycle Assessment Conclusions

For this specific case study, PTFE-lined pipe and stainless-steel piping would likely emit roughly the same amount of greenhouse gases for 1 m of piping. This result is a qualitative analysis informed by estimates of greenhouse gas emissions associated with just the material inputs. Such a result is far from a fully informed, cradle-to-grave LCA that would likely require two complete plant designs for processing specific chemicals – one design with PTFE and another without (i.e., using the selected alternative). Modifying the system boundary to include the use and end-of-life phases would require modification of the functional unit, and thus, the scale at which the comparison is being made. On a full life cycle basis, the greenhouse gas emissions associated with either PTFE-lined or stainless-steel pipes implemented in a chemical processing facility are likely to result in the same order of magnitude of emissions. This result is due to the expected high mass throughput for a chemical facility, which results in low emissions from amortized inputs (i.e., one-time emissions for construction are divided by a large amount of product).

There are known issues with some stainless-steel additives, like nickel, and known issues with low molecular weight PFAS emissions from PTFE production. A quantitative comparison of toxic emissions between the two scenarios is currently not possible due to the lack of LCI data for PTFE production and CFs for these emissions. However, in the case that CFs are available, a high amount of uncertainty is likely associated with those factors, making it difficult to draw any meaningful conclusions from an LCA.

A notable takeaway from this qualitative analysis is the data challenges associated with conducting LCAs of fluoropolymers. A lack of data available from fluoropolymer producers and unregulated emissions from fluoropolymer manufacturing has created information and data gaps. Current LCA studies that have circumvented these issues by using proxies have identified the limitations and uncertainties associated with this approach. Further investigation of these issues and fluoropolymer production may lead to a more comprehensive data set and more robust analysis.

5.2 Cost-Benefit Analysis

Cost-benefit analysis (CBA) is an approach used to evaluate the economic feasibility of projects, policies, or investments. CBAs are tools that aid individuals, organizations, and governments in assessing whether a particular course of action is justified economically. The basis of a CBA is to compare the costs associated with a project or action to the benefits it generates, considering monetary values and non-monetary factors.

The focus of this report is to develop a qualitative CBA, where costs encompass financial investments, ongoing operational expenses, and potential risks and drawbacks. A qualitative CBA also includes direct and indirect costs, such as labor, materials, and any potential negative impacts. Benefits encompass the positive outcomes that may result, including increased revenue, improved customer satisfaction, improved product performance, and the potential for new technology or products.

Qualitative CBAs are well-suited for scenarios where precise data are limited or where the CBA must be conducted quickly. Qualitative CBAs are generally more flexible and adaptable to a wide range of projects and can provide narrative assessments of costs and benefits. Additionally, qualitative CBAs also emphasize the strategic and contextual aspects of a decision, which aids decision-makers in aligning projects, policies, or investments with their broader objectives.

CBA is a valuable tool but also has limitations that should be addressed to avoid unreliable and/or inaccurate results. Limitations include subjectivity in assigning values to intangible benefits, data quality reliability, discount rate sensitivity, and the exclusion of ethical and social considerations. Therefore, while CBAs are a valuable analytical tool, these limitations should be adequately addressed to make the most informed data-driven decisions.

5.2.1 Cost-Benefit Analysis Background and Literature Review

The literature review uncovered no cases of a comprehensive, quantitative CBA of a fluoropolymer compared to a well-defined alternative technology. This analysis assessed the context, requirements, and market conditions relevant to the industries and applications where fluoropolymers are currently used and reviewed literature for existing CBA studies. Some partial CBAs are summarized below. Replacing fluoropolymers would incur costs associated with research and development, innovation, testing, production process modification, retooling of manufacturing facilities, and potential supply chain disruptions.

In addition, restrictions on use of fluoropolymers may result in disruption or elimination of some products or technology. Potential adverse impacts from alternative materials or technologies replacing fluoropolymers would also need to be evaluated. Since the discovery of fluoropolymer materials and their high-performance physiochemical properties, these materials have been replacing traditional materials such as metal, glass, and high-performance coatings and composites over a wide range of applications and enabled the miniaturization and advancement of many technologies. Assessing the cost of alternative materials and production technologies depends on relative performance characteristics, material availability, and projected market demand.

This analysis approaches the CBA using a material flow analysis and LCA foundation (discussed in Section 5.1). Market research, environmental reporting and monitoring, chemical company reports, surveys, secondary literature, and prior material flow analysis and LCA research articles were consulted to obtain estimates for the amount and value of fluoropolymers flowing through the U.S. economy in their production, use, and end-of-life phases. This foundation provides the basis from which to qualitatively discuss frameworks for estimating the overall costs and benefits (both direct and indirect) of fluoropolymers for business-as-usual as opposed to phase-out and substitution as two extreme ends of potential policy scenarios for these critical industrial commodities manufactured with non-polymeric PFAS. Estimates from market research indicate that North America's share of global demand for fluoropolymers is about one-quarter that of the globe by volume and market share, where North America's share accounts for approximately 92 kt and \$1.4B in 2019, respectively.⁴⁷

5.2.2 Benefits of Fluoropolymer Use and Potential Costs of Substitution

The use of alternative technologies in favor of fluoropolymers could result in several economic implications, including production and performance efficiency losses, increased capital and maintenance costs, and regression of current technologies (Wood, 2020). Alternative technologies used in favor of fluoropolymers could also pose indirect economic implications, including potential higher safety risks, increases in emissions, and impacts to technical advancement (Wood, 2020).

The following provides a summary of critical fluoropolymer applications, and fluoropolymer substitutes of those applications that may have high replacement costs, which considers material properties, manufacturing processes, and performance characteristics.

Aerospace – PTFE and FEP are used for insulation of electrical and data transmission cables that are subject to extreme conditions. Commercial airplanes can use as much as 500 km of wire, where fluoropolymers are used as coatings to maintain reliability in variable temperature conditions and prevent potential electrical arc fires.

Few alternatives in the aerospace industry could meet the critical properties provided by fluoropolymers. For example, at extreme temperatures or conditions, cables may turn rigid causing a breakdown or a system failure, thus compromising aircraft safety.

Automotive – PTFE is used in automotive lambda sensor cables due to its resistance to high temperatures and chemicals, dielectric strength, flexibility, and electrical insulator properties. Lambda sensors adjust the fuel amount that is sent to engine cylinders by optimizing the air and fuel mixture, which reduces carbon monoxide emissions.

⁴⁷ Estimates based on PLS080B, 2021, *Fluoropolymer Materials: Technologies and Global Markets*, BCC Publishing; 2019 data and projections for 2020 and 2025.

Silicon, ethylene propylene rubber (EPR), and EPDM rubber could be considered alternatives, but these materials do not work at the required operating temperature of approximately 250 °C, which is frequently encountered in car engines where lambda sensors are installed. Additionally, alternatives do not meet the mechanical properties (e.g., elongation) required by the automotive sector for these lambda sensors.

Batteries – PTFE and PVDF are commonly used as electrode binders and separator coatings in lithium-ion batteries, wherein the materials provide interconnectivity within each electrode. This facilitates electronic and ionic conductivity, increasing the cell manufacturing productivity and overall cell safety. Due to their cohesive and adhesive properties under high voltage, fluoropolymers enable closely packed cathode active materials for high-density electrodes, which improves the energy efficiency of a single unit and helps reduce overall size.

Polyethylene or PET could be used as substitutes for PTFE and PVDF in lithium-ion batteries; however, these materials would not offer the combined set of properties that fluoropolymers provide, particularly for both fire retardancy and battery efficiency. Lead-acid batteries could also be alternatives to lithium-ion batteries; however, lead-acid batteries offer reduced energy efficiency performance because of a lower proportion of energy stored within the batteries. In addition, lead-acid batteries are heavier resulting in reduced functionality and increased energy consumption compared to lithium-ion batteries.

Building construction – Fluoropolymers are critical components in heating, ventilation, air conditioning, and refrigeration equipment because such machinery is subject to continued changes in temperature and pressure and potentially harsh chemicals (e.g., refrigerants). Materials such as PEI, PBI, polyamideimide (PAI), or phenolic resins have been proposed as potential alternatives, but these materials have not been fully tested as replacements for fluoropolymers in this application and may offer lower levels of chemical resistance.

Chemical processing – Fluoropolymers are extensively used in the chemical processing industry. In stringent conditions (e.g., applications with highly corrosive chemicals, high temperature operations, and conditions requiring inert materials to achieve high purity), PTFE, PFA, and ETFE are typically used in pipes, expansion joints, vessels, and fittings to ensure system reliability. Failure of those systems could potentially result in high-risk situations for people or the environment due to leakage, spills, or releases of corrosive and/or high-temperature substances.

When there is no need to protect equipment or chemical products from corrosion, metal or metallic alloy (e.g., black steel, stainless steel, galvanized steel, copper, brass) piping and fitting systems could be used by the chemical processing industry. However, these metals and metallic alloys would be limited to the following situations:

- Chemicals that are non-corrosive (or less corrosive) to steel.
- Processes in which short system lifetime is acceptable.
- Metallic ion impurities in the streams handled in the relevant processes do not raise concerns, from either a quality or safety perspective.

PFA and PTFE are also used for lining pumps in the chemical processing industry, with the aim to avoid corrosion under specific conditions of chemical attack. In addition, fluoropolymer-based seals (e.g., O-rings) are used in those processes to prevent leaks and releases of hazardous materials. Chrome/nickel alloys are usually considered as possible alternatives for these applications. While used for lining in pumps to operate certain chemical processes, and still in use today, these materials are not able to meet specific anti-corrosion requirements.

Infrastructure – A study was also conducted to compare economic impacts of painting a bridge with a fluoropolymer-based paint (i.e., FEVE) versus painting a bridge with polyurethane paint. The cost was determined to be approximately 26% more with the fluoropolymer-based coating compared to polyurethane; however, the polyurethane coating degrades faster and needs to be recoated frequently, and after 30 years, the total cost for such recoating would be 16% more (in total) than the fluoropolymer-based coating (Ghorbanpoor et al., 2013).

PVDF is used in pipe fittings and manifolds for plumbing systems in buildings due to its ease of installation, resistance to chemicals and corrosion, resistance to high temperature, high compatibility with many chemical substances, stability, inertness, and flame retardant and UV resistance properties. Multiple metals (e.g., brass, copper, black steel) are potential alternatives for plumbing applications but are heavier material and offers less resistance to corrosion where PVDF is used. Polyphenylsulfone (PPSU) is an alternative that can be used in plumbing applications; however, PPSU in plumbing is more fragile and less resistant to heat. In addition, PPSU is not compatible with many of the glue compositions frequently used by plumbers during installation.

Hydrogen production and use – Fluoropolymers are used in numerous renewable hydrogen applications, including electrolyzer and fuel cell manufacturing, alkaline water electrolysis, and a variety of critical hydrogen infrastructure and end-use applications (e.g., PTFE used in sealants, valves, fittings, membranes). The European renewable hydrogen industry has indicated that a ban of PFAS (polymeric and non-polymeric) would have significant detrimental effects on polymer electrolyte membrane (PEM) fuel cell and PEM electrolysis technologies. Hydrogen Europe (2023) estimated that over a 10-year timeframe, a complete PFAS ban would put at risk a total investment value in the European hydrogen energy sector of €26–36B (~\$27.6B–\$38.2B⁴⁸) and would put 147,000–203,000 direct jobs and an extra 263,000–282,000 indirect jobs at risk.

Semiconductors – Like chemical processing applications, PTFE and PFA are used in vessels, pipes, and fitting systems (e.g., diaphragms in valves) for the semiconductor industry due to their high levels of chemical resistance, temperature resistance, and flexibility. These fluoropolymers are used with the aim to protect equipment under very aggressive media while achieving a high purity of the materials involved in the process. For example, PTFE or high purity PFA-lined columns and tanks are used to produce high purity sulfuric acid for etching silicon wafers to manufacture electronic chips. This technology allows for larger wafers and a more efficient microchip production process.

To maintain the current state of the semiconductor industry, no option is currently available to replace the use in fluid systems made from fluoropolymers. A shift towards metal-based materials would potentially preclude the semiconductor manufacturing industry from reaching the standards of efficiency and sophistication that are needed by downstream user sectors (e.g., telecommunications, electronics).

Solar panels – Lorenz et al. (2014) modeled the potential earnings of different commercially available anti-soiling solar panel systems and found that an average of 3.2% yearly gain in profitability could be made by using an anti-soiling coating and an optimized cleaning strategy compared to using uncoated glass. Based on their study, the European plastics industry has estimated that European Union photovoltaics manufacturing with ETFE in favor of glass could yield savings of €43.2M (~\$46.8M) (Plastics Europe, 2017).

Fluoropolymers are widely used in the solar industry as backsheets to decrease failure rates. Prior to the integration of fluoropolymers into solar backsheets, Plastics Europe indicated that failure rates were approximately 45%, whereas with fluoropolymer film backsheets, the failure rates are as low as 0.1% (Plastics Europe, 2023b).

⁴⁸ Based on October 8, 2023 conversion rate.

5.2.3 Necessary Data for Quantitative Cost-Benefit Analysis

A range of necessary data points and/or information is needed to perform a complete CBA. This report describes several impacts that may result from the removal of fluoropolymers from the U.S. supply chain; however, most of the limited available information was qualitative and does not support an intensive CBA that addresses all required elements. To provide a comprehensive understanding of the costs and benefits of each type of the most widely used fluoropolymers would require detailed analysis of at least hundreds of specific uses across many product sectors. Thus, this CBA is necessarily limited to focused case studies. To perform a more well-rounded CBA with multiple case study analyses, the following information would need to be available.

Benefits

- **Production impacts** – Economic production benefits that may be realized through alternative fluoropolymer technologies or non-fluoropolymer alternative materials, including factors such as raw material expenses, manufacturing efficiency, energy consumption, atmospheric emissions, wastewater discharges and solid waste production, and potential scalability, to determine their potential cost-saving advantages over traditional fluoropolymers
- **Local and regional benefits** – Economic benefits for specific localities and regions that may be realized through alternative fluoropolymer technologies or non-fluoropolymer alternative materials, which consider regional supply chain dynamics, workforce availability, infrastructure readiness, and the potential for job creation and economic growth
- **End use and application benefits** – Potential benefits associated with transition away from fluoropolymers, including opportunities for enhanced performance, safety, or quality in specific industries or applications, and the assessment of any potential advancements or innovations in product development within these sectors.

Costs

- **Raw materials/precursors** – Economic costs of raw materials/precursors for fluoropolymer substitutes, which include analyzing supply chain disruptions, demand shifts, and potential regulatory changes that may affect their costs
- **Prohibitive costs** – Any potential prohibitive economic costs associated with fluoropolymer replacement technologies, which include analyzing factors such as initial investment, production expenses, market availability, regulatory compliance, and long-term economic impacts on industries relying on fluoropolymers
- **End use and application costs** – Costs of transitioning away from fluoropolymers to specific industries and applications, including potential disruptions, changes in product performance, product safety, and the development or adoption of alternative technologies or materials in these sectors.

Overall, carrying out an exhaustive CBA of removing fluoropolymers from the U.S. supply chain and replacing them with alternative materials presents several practical limitations. Fluoropolymers are used in thousands of end-use applications, and potential trade-offs would need to be considered for an enormous number of those applications. In many instances, those data are not publicly available.

Removing fluoropolymers generally or from specific uses could also lead to increased costs, not only in terms of raw material and manufacturing but also from equipment modifications and maintenance and compliance with or revision of industry standards. A transition to fluoropolymer alternatives may necessitate expensive retrofitting of existing infrastructure and machinery. The CBA should consider transition expenses and the potential economic repercussions of reduced efficiency and performance in extreme conditions without fluoropolymers.

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Appendix A. Questions Included in Industry Survey

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Industry Survey

II. Instructions

Please complete the questions in the electronic survey.

This survey is divided into the following sections:

Company Information
Fluoropolymer Manufacturing and Production
Life Cycle Assessment
Use and Competing Technologies
Cost-Benefit Assessment
Conclusion

Note that the questionnaire has branching logic and question numbering may not appear in sequential order, depending on your responses.

Additionally, some responses will be collected via the attached excel file below. Please download the file and complete your responses there.

At appropriate points in the survey, you will be asked if your response contains confidential information.

Once completed, submit the questionnaire. A completion notification will be sent to you along with a pdf of your responses.

If you need more than one session to complete the questionnaire, choose the save and return later option. An email notification will be sent to you with a link to return.

Upon final submission, you will receive an email confirmation with a pdf of all responses.

III. Company Information

Company Name	
Contact Person Name	
Title	
Telephone Number	
Email Address	
Industry Sector(s)*	
*See Industries at a Glance: NAICS Code Index : U.S. Bureau of Labor Statistics (bls.gov) for more information	

- 1. What is your company’s position in the supply chain? Check all that apply.
 - Manufacturer of fluoropolymers
 - Importer of fluoropolymers
 - Formulator of fluoropolymers
 - User of fluoropolymers in manufacturing or products
 - Other: _____

- 2. Who are the primary end users of your products? Check all that apply.
 - Component or end product manufacturer
 - Formulators
 - Consumers
 - Government agency
 - Other: _____

3. What fluoropolymers and precursors do you manufacture, import, or utilize; what is their physical form (e.g., sheeting, coatings, surfactants), and quantities in 2020 - 2022?
[Table 1]

Fluoropolymers	Abbreviation	CAS No.	Physical Forms (e.g., Solid, liquid, suspension/ solution)	Quantity (tons/ yr)		
				2020	2021	2022
copolymer of ethylene and chlorotrifluoroethylene	ECTFE	25101-45-5				
ethylene tetrafluoroethylene	ETFE	25038-71-5 / 68258-85-5				
fluorinated ethylene propylene	FEP	25067-11-2				
perfluoroalkoxy polymer	PFA	26655-00-5 / 31784-04-0				
Polytetrafluoroethylene	PTFE	9002-84-0				
polyvinylidene fluoride	PVDF	24937-79-9				
terpolymer of tetrafluoroethylene, hexafluoropropylene & vinylidene fluoride	THV	25190-89-0				
Other(s)						
Precursors						
Perfluorooctanoic acid	PFOA	335-67-1				
Perfluorooctane sulfonic acid	PFOS	1763-23-1				
Perfluorononanoic acid	PFNA	375-95-1				
Hexafluoropropylene oxide dimer acid (commonly known as GenX Chemicals)	HFPO-DA	13252-13-6				
Perfluorohexane sulfonic acid	PFH	355-46-4				
Perfluorobutane sulfonic acid	PFBS	375-73-5				
perfluoroisobutylene	PFIB	382-21-8				
ammonium perfluorooctanoate	APFO	3825-26-1				
perfluorobutyl ethylene	PFBE	19430-93-4				
Other(s)						

4. Please indicate your products' primary sector of use. Check all that apply.

- Aerospace** (Transportation Equipment Manufacturing NAICS 336, Air Transportation NAICS 481)
- Automotive** (Transportation Equipment Manufacturing NAICS 336, Truck Transportation NAICS 484, Transit and Ground Passenger Transportation NAICS 485)
- Battery** (Electrical Equipment, Appliance, and Component Manufacturing NAICS 335, Battery Manufacturing NAICS 33591)
- Building Construction** (Construction NAICS 23, Construction of Buildings NAICS 236, Heavy and Civil Engineering Construction NAICS 237)
- Chemicals and Chemical Processing** (Basic Chemical Manufacturing NAICS 3251, Resin, Synthetic Rubber, and Artificial and Synthetic Fibers and Filaments Manufacturing NAICS 3252, Pesticide, Fertilizer, and Other Agricultural Chemical Manufacturing NAICS 3253)
- Electronics** (Computer and Electronic Product Manufacturing NAICS 334)
- Infrastructure**
- Semiconductor/microprocessor** (Semiconductor and Related Device Manufacturing NAICS 334413)

- Solar Energies** (Solar Electric Power Generation NAICS 221114)
- Wind Energies** (Wind Electric Power Generation NAICS 221115)
- Other Power** (Electric Power Generation, Transmission and Distribution NAICS 221100)

The following codes and associated sectors are included because they may represent a significant fraction of a producer's, importer's or manufacturer's use of fluoropolymers. However, analysis of the use of fluoropolymers in these industries is beyond the scope of the requested reports, and therefore these codes are provided only for completeness.

- Cookware** (Metal Kitchen Cookware, Utensil, Cutlery, and Flatware (except Precious) Manufacturing NAICS 332215)
- Food** (Food Manufacturing NAICS 311)
- Pharmaceuticals** (Pharmaceutical and Medicine Manufacturing NAICS 32541)
- Medical Equipment** (Medical Equipment and Supplies Manufacturing NAICS 339100)
- Textile** (Textile Mills NAICS 313, Textile Product Mills NAICS 314)
- Other: _____

IV. Fluoropolymer Manufacturing and Production

5. Please indicate the approximate percentage of fluoropolymers and precursors sold or used in each application or sector of use by your company. Use “Other” rows and columns (add new rows and/or columns, if necessary) for sectors added in Question 4. Please complete Table 2 in Excel workbook. (M, I, F, O)

Sector of use (SU) ^a	Aerospace	Automotive	Battery	Building Construction	Chemical Processing	Electronics	Infrastructure	Semiconductor	Solar Panel	Wind energy	Other Power	Cookware	Food	Pharma	Medical applications	Textile	Other
Fluoro-polymer ↓																	
ECTFE																	
ETFE																	
FEP																	
PFA																	
PTFE																	
PVDF																	
THV																	
Other																	
Precursor ↓																	
PFOA																	
PFOS																	
PFNA																	
HFPO-DA																	
PFH																	
PFBS																	
PFIB																	
APFO																	
PFBE																	
Other																	

Fluoropolymers Manufacturing Process (M, I, F, O)

6. What type of polymerization process are you using for the manufacturing of fluoropolymers (suspension, emulsion, etc.)?

7. What fluoropolymers and precursors (fluorinated compounds) and approximate percentages of use (value or range) are your company using as polymerization aids during the manufacturing process? [Table 3]

Fluoropolymers	Abbreviation	CAS No.	Percentage of use (value or range) used as polymerization aids	Comment
copolymer of ethylene and chlorotrifluoroethylene	ECTFE	25101-45-5		
ethylene tetrafluoroethylene	ETFE	25038-71-5 /68258-85-5		
fluorinated ethylene propylene	FEP	25067-11-2		
perfluoroalkoxy polymer	PFA	26655-00-5 /31784-04-0		
Polytetrafluoroethylene	PTFE	9002-84-0		
polyvinylidene fluoride	PVDF	24937-79-9		
terpolymer of tetrafluoroethylene, hexafluoropropylene & vinylidene fluoride	THV	25190-89-0		
Other (add rows as needed)				

8. Which fluorinated polymerization aids could be removed from the manufacturing process without significant detrimental or deleterious impact on the manufacturing process?

9. List which fluorinated polymerization aids could be replaced by available alternatives (non-fluorinated substitutes) and identify the alternative?

10. For each fluoropolymer that you manufacture or process: [Table 4] **CBI**

- a. Which monomers are used in your production process?
- b. What are the molecular weight ranges of fluoropolymers produced?
- c. Which fluoropolymers are produced from recycled feedstocks?

Fluoropolymer (FP)	a) List Monomers used in Production	b) Molecular weight ranges	c) Produced from Recycled Feedstocks	Comment
copolymer of ethylene and chlorotrifluoroethylene (ECTFE)				
ethylene tetrafluoroethylene (ETFE)				
fluorinated ethylene propylene (FEP)				
perfluoroalkoxy polymer (PFA)				
Polytetrafluoroethylene (PTFE)				
polyvinylidene fluoride (PVDF)				
terpolymer of tetrafluoroethylene, hexafluoropropylene & vinylidene fluoride (THV)				
Other (add rows as needed)				

11. Formulation as copolymers:
 - a. Which polymers are formulated as copolymers?
 - b. What are the types and ratios of monomers used in the production of copolymers?
12. What physical/chemical properties are most critical for the fluoropolymers you manufacture?
13. What additives and/or polymer processing aids do you use in your fluoropolymer manufacturing process? **CBI**
 - a. Which low molecular weight additives and/or polymer processing aids are used in fluoropolymer manufacturing?
 - b. Which high molecular weight additives and/or polymer processing aids are used in fluoropolymer manufacturing?
 - c. At which points in the manufacturing aids are additives and/or polymer processing aids used?
 - d. Which polymers and polymer production methods are associated with which specific additives and/or polymer processing aids?
 - e. What processes are used to remove excess additives and/or polymer processing aids from produced fluoropolymers before products are complete?
 - f. What is the fate of excess or waste additives and/or polymer processing aids in your fluoropolymer manufacturing process?
14. What physical forms are your fluoropolymers formulated in?
 - a. What types and fractions of fluoropolymers are extrudable thermoplastics?
 - b. Which fluoropolymers are formulated as thermosets?
 - c. Which fluoropolymers do you produce through emulsion polymerization?
 - d. Physical form during storage
 - e. Stability of the physical form
15. Please list the raw materials used in the manufacturing/production of fluoropolymers and their quantities.
 - a. How is waste material disposed?
16. Please provide any publicly available information regarding the degradation mechanisms and conditions, and degradation products for each FP produced.

Use of Fluoropolymers in Manufacturing of Products **(U, O)**

17. Characteristics of fluoropolymers you need for your applications? [Table 5]
- Physical characteristics
 - Chemical characteristics
 - Stability and durability requirements

Fluoropolymer (FP)	a) Physical characteristics	b) Chemical characteristics	c) Stability and durability requirements	Comment
copolymer of ethylene and chlorotrifluoroethylene (ECTFE)				
ethylene tetrafluoroethylene (ETFE)				
fluorinated ethylene propylene (FEP)				
perfluoroalkoxy polymer (PFA)				
Polytetrafluoroethylene (PTFE)				
polyvinylidene fluoride (PVDF)				
terpolymer of tetrafluoroethylene, hexafluoropropylene & vinylidene fluoride (THV)				
Other (add rows as needed)				

18. What are alternative materials (non-fluoropolymers) with similar physical, chemical and durability characteristics that can be used as replacements for fluoropolymers in your manufacturing process?
19. Please describe the primary advantages to your industry of using specific FP
20. Recycling and Disposal of unused/excess fluoropolymers
- What fraction of unused/excess FP are recycled into your processes?
 - What fraction of unused/excess FP are recycled to the FP manufacturer?
 - What fraction of unused/excess FP are disposed?
 - What disposal methods are used for unused/excess FP disposal? Long answer

V. Life Cycle Assessment Questions (for fluoropolymer manufacturers only) (M, I, F, O)

21. Please provide the zip codes for all of the company's manufacturing locations in the United States
- Please provide the city, country for companies manufacturing locations outside the United States.
22. Is there a life cycle assessment for the fluoropolymer chemicals the company produces publicly available? (Y/N) If yes, then please provide an electronic copy.
23. Does the company produce fluoropolymers for sale or does the company produce fluoropolymers for internal utilization in downstream products? Y/N What are the specific products?

24. Are there any byproducts or coproducts generated during the production of fluoropolymers?
Y/N Can you list their names, yields (ton of byproduct/ton of fluoropolymer) and usage sector?
[Table 6]

Fluoropolymer (FP)	Sector of use	List byproducts or coproducts	Yields (ton of byproduct or coproduct/ton of FP)	Comment
copolymer of ethylene and chlorotrifluoroethylene (ECTFE)				
ethylene tetrafluoroethylene (ETFE)				
fluorinated ethylene propylene (FEP)				
perfluoroalkoxy polymer (PFA)				
Polytetrafluoroethylene (PTFE)				
polyvinylidene fluoride (PVDF)				
terpolymer of tetrafluoroethylene, hexafluoropropylene & vinylidene fluoride (THV)				
Other (add rows as needed)				

25. For each fluoropolymer raw material and precursors purchased, please specify the annual quantity used (tons), percentage imported and the country from which it was imported.
[Table 7]

Fluoropolymer (FP)	Raw materials and precursors purchased	Annual quantity used (tons)	Percentage imported	Country from which imported	Comment
copolymer of ethylene and chlorotrifluoroethylene (ECTFE)					
ethylene tetrafluoroethylene (ETFE)					
fluorinated ethylene propylene (FEP)					
perfluoroalkoxy polymer (PFA)					
Polytetrafluoroethylene (PTFE)					
polyvinylidene fluoride (PVDF)					
terpolymer of tetrafluoroethylene, hexafluoropropylene & vinylidene fluoride (THV)					
Other (add rows as needed)					

26. If the company producing fluoropolymers also produces the required precursors: what are the mass flows (annual usage) of key materials to produce the precursors? [Table 8]

Fluoropolymer (FP)	Required precursor(s)	Key materials to produce precursor(s)	Annual usage / mass flow (tons) of key materials	Comment
copolymer of ethylene and chlorotrifluoroethylene (ECTFE)				
ethylene tetrafluoroethylene (ETFE)				
fluorinated ethylene propylene (FEP)				
perfluoroalkoxy polymer (PFA)				
Polytetrafluoroethylene (PTFE)				
polyvinylidene fluoride (PVDF)				

terpolymer of tetrafluoroethylene, hexafluoropropylene & vinylidene fluoride (THV)				
Other (add rows as needed)				

27. How are raw materials/precursors transported to the production facility?
28. Please describe any supply chain issues related to fluoropolymer production and raw materials/precursors used (e.g., insufficient supply of raw materials, limitations on domestic or international transportation, import constraints).
29. What is the annual energy consumption of fluoropolymer production?
 - a. What is the energy consumption and the fraction of energy from each source onsite (e.g., natural gas, fuel oil/diesel, renewable (solar, wind), others),
 - b. What is the energy consumption and the fraction of energy from offsite electricity produced using, coal, natural gas, nuclear, solar, wind, other, etc.
 - c. What is the energy consumption and the fraction of energy from offsite thermal energy produced using coal, natural gas, nuclear, electricity, solar, wind, other?
30. What annual amounts of greenhouse gas emissions are generated during the production processes (onsite, offsite) **in metric tons of carbon dioxide equivalent per year**??
31. What additional air emissions are generated during the production processes (onsite)?
32. What solid and liquid wastes are generated during fluoropolymer production? What are the quantities (ton of wastes/ton of fluoropolymer production)? How are solid and liquid wastes managed or treated (e.g., landfill, incineration, municipal solid waste, wastewater treatment plant)? [Table 9]

Fluoropolymer (FP)	Wastes (e.g., solid, liquid, solvent)	Quantities (ton of wastes/ton of FP production)	Management/treatment method (e.g., wastewater, landfill)	Comment
copolymer of ethylene and chlorotrifluoroethylene (ECTFE)				
ethylene tetrafluoroethylene (ETFE)				
fluorinated ethylene propylene (FEP)				
perfluoroalkoxy polymer (PFA)				
Polytetrafluoroethylene (PTFE)				
polyvinylidene fluoride (PVDF)				
terpolymer of tetrafluoroethylene, hexafluoropropylene & vinylidene fluoride (THV)				
Other (add rows as needed)				

VI. Use and competing technologies

33. Does your company produce any alternative materials or products as potential replacements for FP products?
(All)
34. Please indicate how you evaluate potential alternatives to the FPs in your industry. If possible, please, add a rough estimate of the cost related to the replacement of FPs by each alternative. (U, O)
- Evaluate technical and economic feasibility, and fitness for use (e.g., same function & level of performance; if not the same, explain the difference).
 - Specify the type of use for each alternative if the FP has different uses.
 - What are the potential challenges or limitations associated with using these alternative materials?
 - Are there any specific performance parameters, specifications, or safety concerns that need to be considered when selecting and using these alternative materials?
 - If no replacements are available, what are the concerns and considerations for fluoropolymer replacement?
35. Are there specific industries or applications that have alternative materials or technologies showing promising results? (U, O)
36. What are the expected lifespan and durability requirements of the products or components using fluoropolymers versus the alternative materials? (U, O)

VII. Cost-Benefit Assessment: (U, O)

37. Please indicate the evaluation criteria for potential alternatives to the fluoropolymers for your company in the table below. If possible, please, add a rough estimate of the cost related to the replacement of fluoropolymers by each alternative.
- Evaluate technical and economic feasibility, and fitness for use (e.g., same function & level of performance; if not the same, explain the difference).
 - Specify the type of use for each alternative if the FP has different uses.
 - What is the timeline of the possible implementation of the alternative(s)? How are you considering replacing fluoropolymers in your product lines (e.g.: stop production, phase in, etc.)?

Fluoropolymer Application	Alternative technology	Cost Estimate of alternative (e.g., QC testing, waste management, recycling, disposal)	Timeline and method of substitution	Primary limitation (e.g., retooling, equipment modification, process change)	Primary Benefit (e.g., cost savings, environmental, waste reduction)	Replacement/ Longevity Concerns

38. With respect to the fluoropolymers that your company produces and/or uses, has your company prepared any benefit-cost analysis in comparison to alternatives? If so, could you share them?
39. With respect to fluoropolymers generally, rank the order of your company's priorities when considering replacing fluoropolymers in your products?
- lower costs.
 - lower carbon footprint
 - customer concerns
 - less use of natural resources
 - concerns about the persistence of fluoropolymers and degradation products in the environment.
 - concerns about consumer health and safety.
 - concerns about waste management.
 - regulatory pressures.
 - liability risks.
 - other _____
40. With respect to the fluoropolymers that you produce and/or use, what are their most important benefits (compared to the next best alternative) that should be considered in a benefit-cost analysis?
- lower cost to the producer, the intermediate processor and/or final user;
 - superior performance;
 - low toxicity;
 - small carbon footprint;
 - less use of natural resources
 - superior environmental profile;
 - safety for the consumer;
 - easy of managing as a waste;
 - comparative advantage of production in the US;
 - other.
41. Are there additional comments that you would like to provide to the study team?
42. Are there additional documents or links that you would like to provide to the study team?
43. Would you be available for a follow-on discussion with the team?
44. Would you be available to answer additional questions from the team, if needed?
45. Are there additional POC that you feel would be beneficial to the study team?

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**Appendix B. Polytetrafluoroethylene Stoichiometry and Polytetrafluoroethylene-Lined Pipe
Screening Life Cycle Assessment**

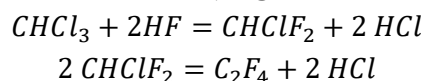
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Polytetrafluoroethylene Stoichiometry and Polytetrafluoroethylene-Lined Pipe Screening Life Cycle Assessment

This appendix provides the calculations for the screening-level comparative life cycle assessment (LCA) between polytetrafluoroethylene (PTFE)-lined pipe and stainless-steel pipe, as discussed in Section 5.1 of this report. The first part of this appendix estimates the material inputs for tetrafluoroethylene (TFE), which is polymerized to create PTFE. Then, greenhouse gas emissions are summarized as 100-year global warming potentials (GWP) are applied to each of the inputs to provide a low-end estimate for PTFE production (Table B-1). This estimate does not attempt to account for yields of some of the precursors, like chloroform, for PTFE production. The estimate also does not account for energy inputs for TFE, PTFE, or the precursors outside of what is provided in some of the cradle-to-gate inventories.

This estimate of GWP for PTFE production is then used in the second part of this appendix in a scenario comparing 1 m of PTFE-lined pipe to 1 m of stainless-steel pipe. This comparative screening-level LCA is used to provide a sense of how the GWPs would compare for these two alternatives in a notional chemical processing facility.

Tetrafluoroethylene Reactions from Chloroform (Siegmond et al., 2016)



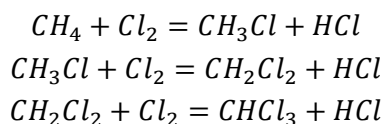
Summarily,

$$\begin{aligned} 2CHCl_3 + 4HF &= C_2F_4 + 6HCl \\ 2CHCl_3 \cdot 119.38 \frac{kg}{kmol} + 4HF \cdot 20 \frac{kg}{kmol} &= C_2F_4 \cdot 100.02 \frac{kg}{kmol} + 6HCl \cdot 36.46 \frac{kg}{kmol} \\ 238.76 kg CHCl_3 + 80 kg HF &= 100.02 kg C_2F_4 + 218.76 kg Cl \end{aligned}$$

Or for just the inputs:

$$\begin{aligned} 2.39 \frac{kg CHCl_3}{kg C_2F_4} \\ 0.79 \frac{kg HF}{kg C_2F_4} \end{aligned}$$

Chloroform (Rossberg et al., 2006)



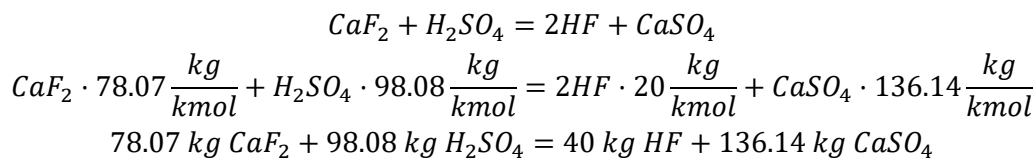
Summarily,

$$\begin{aligned} CH_4 + 3Cl_2 &= CHCl_3 + 3HCl \\ CH_4 \cdot 16 \frac{kg}{kmol} + 3Cl_2 \cdot 70.9 \frac{kg}{kmol} &= CHCl_3 \cdot 119.38 \frac{kg}{kmol} + 3HCl \cdot 36.46 \frac{kg}{kmol} \\ 16 kg CH_4 + 212.7 kg Cl_2 &= 119.38 kg CHCl_3 + 109.38 kg HCl \end{aligned}$$

Or for just the inputs and then scaled to the TFE functional unit:

$$\begin{aligned} 0.13 \frac{kg CH_4}{kg CHCl_3} \cdot 2.39 \frac{kg CHCl_3}{kg C_2F_4} &= 0.32 \frac{kg CH_4}{kg C_2F_4} \\ 1.78 \frac{kg Cl_2}{kg CHCl_3} \cdot 2.39 \frac{kg CHCl_3}{kg C_2F_4} &= 4.25 \frac{kg Cl_2}{kg C_2F_4} \end{aligned}$$

Hydrogen Fluoride (Aigueperse et al., 2000)



Or for just the inputs and then scaled to the TFE functional unit:

$$1.95 \frac{kg \text{ } CaF_2}{kg \text{ } HF} \cdot 0.79 \frac{kg \text{ } HF}{kg \text{ } C_2F_4} = 1.56 \frac{kg \text{ } CaF_2}{kg \text{ } C_2F_4}$$

$$2.45 \frac{kg \text{ } H_2SO_4}{kg \text{ } HF} \cdot 0.79 \frac{kg \text{ } HF}{kg \text{ } C_2F_4} = 1.96 \frac{kg \text{ } H_2SO_4}{kg \text{ } C_2F_4}$$

Table B-1. Screening Cradle-to-Gate Life Cycle Inputs per kilogram of Tetrafluoroethylene

Input	Amount per kg TFE	100-year GWP	GWP per kg TFE	Data Source ^a
Natural gas (as proxy for methane)	0.32 kg	0.806 kg CO ₂ e	0.258 kg CO ₂ e	Rai et al., 2021
Chlorine	4.25 kg	2.23 kg CO ₂ e	9.48 kg CO ₂ e	NREL, 2021a
Sulfuric acid	1.96 kg	0.348 kg CO ₂ e	0.682 kg CO ₂ e	NREL, 2021d
Calcium fluoride	1.56 kg	0.174 kg CO ₂ e	0.272 kg CO ₂ e	Lai et al., 2021
Total			10.7 kg CO₂e^b	

^a Full references are provided at the end of this appendix.

^b This estimate is based on mass of inputs and cradle-to-gate global warming potentials and does not consider transport of those inputs nor the energy required to actually manufacture the TFE, chloroform, or hydrogen fluoride.

GWP = global warming potential.

TFE = tetrafluoroethylene.

Pipe Calculations

PTFE stainless-steel pipe and liner dimensions are summarized in Table B-2 and Table B-3, respectively. Dimensions for 2-in. nominal pipe were derived from Mersen (2021, p 15).

Table B-2. Polytetrafluoroethylene Steel Pipe Dimensions

Outer diameter	60.3	mm
Thickness	3.9	mm
Inner diameter	52.5	mm
Steel pipe area	691.0	mm ²
Length	1,000	mm
Steel pipe volume	691,025	mm ³
	0.000691	m ³
Steel density	7750	kg/m ³
Steel mass	5.36	kg/m

Table B-3. Polytetrafluoroethylene Liner Dimensions

Outer diameter PTFE	52.5	52.5	mm
Thickness	1	5	mm
Inner PTFE	50.5	42.5	mm
PTFE area	162	746	mm ²
Length	1,000		mm
PTFE volume	161,792	746,128	mm ³
	162	746	cm ³
PTFE density	2.16		g/cm ³
PTFE mass	0.35	1.61	kg

PTFE = polytetrafluoroethylene.

The total mass of PTFE-lined pipe is summarized in Table B-4. The 1 m pipe LCA comparison is provided in Table B-5.

Table B-4. Total Mass of Polytetrafluoroethylene-Lined Pipe

Steel mass		5.36	kg/m
PTFE mass	0.35	1.61	kg/m
Total mass	5.7	6.97	kg/m

Note that Mersen (2021, p 16) shows the weight to be 7 kg/m, so the 5 mm thickness of PTFE is assumed for the final product.
PTFE = polytetrafluoroethylene.

Table B-5. One Meter Pipe Life Cycle Comparison

Component	Mass	GWP	GWP per m	Data Source ^a
Steel	5.36 kg	2.3 kg CO ₂ e/kg	12.3 kg CO ₂ e	NREL, 2021b
PTFE	1.61 kg	10.7 kg CO ₂ e/kg	17.2 kg CO ₂ e	This appendix
Total			29.5^b kg CO₂e	
304 stainless steel	5.36 kg	7.72 kg CO ₂ e/kg	41.3 kg CO ₂ e	NREL, 2021c

^a Full references are provided at the end of this appendix.

^b This estimate does not consider transportation of those inputs nor the energy required to manufacture the PTFE, chloroform, or hydrogen fluoride.

GWP = global warming potential.

PTFE = polytetrafluoroethylene.

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Appendix C. Biographical Sketches of the Fluoropolymer Review Team

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Biographical Sketches of Fluoropolymer Review Team

Project Management Team

Stephanie Jacobs, PhD, is a Biological Scientist at Savannah River National Laboratory (SRNL) and the Director of the Regulatory Center of Excellence. SRNL's Regulatory Center of Excellence provides technical, regulatory, and communications assistance to facilitate resolution of complex or difficult regulatory, policy, and stakeholder challenges. She has a BS degree in Chemistry from the University of South Carolina Aiken and a PhD in Biomedical Sciences from Augusta University. Her graduate research focused on molecular mechanisms of learning and memory. Prior to joining SRNL, she was at the South Carolina Department of Health and Environmental Control working in environmental sampling, analysis, and compliance assistance.

Dr. Jacobs has participated on teams looking at soil and groundwater remediation and regulatory considerations across the U.S. Department of Energy (DOE) complex, consent-based consolidated interim storage communications, and deactivation and decommissioning regulatory challenges. Her research has included molecular mechanisms of learning and memory, effects of substances on learning, biological breakdown of per- and polyfluoroalkyl substances (PFAS), and monitoring of microbial corrosion.

David S. Kosson, PhD, is the Gass Family Chair in Energy and the Environment, and Distinguished Professor of Civil and Environmental Engineering at Vanderbilt University, where he also has appointments as Professor of Chemical Engineering and Professor of Earth and Environmental Sciences, and is the Director of the Environmental Engineering Laboratory. Professor Kosson is the principal investigator for the multi-university Consortium for Risk Evaluation with Stakeholder Participation (CRESP) supported by DOE to improve the risk-informed basis for remediation and management of nuclear waste from former defense materials production and nuclear energy. Professor Kosson's research focuses on management of nuclear and chemical wastes, including leaching assessment, process development, and contaminant mass transfer applied to groundwater, soil, sediment, and waste systems.

Professor Kosson's research on waste management and environmental remediation allows new understanding of the fundamental behavior of chemical and radionuclide contaminants in wastes, engineered systems, and the environment to impact major decisions and policy. For example, work by his research group in collaboration with other faculty and international partners has resulted in establishment of the U.S. Environmental Protection Agency (EPA) Leaching Environmental Assessment Framework (LEAF), which is now being used for national policy decisions and regulations on waste management in the U.S. and other countries.

Professor Kosson has participated in or led many external technical reviews on nuclear waste processing and environmental remediation for DOE, including for tank wastes and a range of technology approaches at the Hanford Site, Savannah River Site (SRS), Waste Isolation Pilot Plant, and Idaho National Laboratory. For two decades, he has provided expertise and leadership for the National Academies, and as advisory to the U.S. Department of Defense (DOD), on demilitarization of chemical weapons in the U.S. and abroad. He has authored more than 200 peer-reviewed professional journal articles, books and book chapters, and other archival publications. Professor Kosson received a PhD in Chemical and Biochemical Engineering from Rutgers University, where he subsequently was Professor of Chemical and Biochemical Engineering. He also served as the Department Chairman for Civil and Environmental Engineering at Vanderbilt University from 2000–2012.

Connie Herman is the Associate Laboratory Director of the Environmental and Legacy Management Directorate at SRNL. The organization provides technical strategies and technologies for nuclear material processing, radioactive waste processing and stabilization, soil and groundwater remediation, risk assessment, and deactivation and decommissioning for the DOE Office of Environmental Management (EM) and Office of Legacy Management. The directorate shepherds competencies in materials science and engineering and biological sciences for national security programs and alternative energy applications.

Ms. Herman has been at SRS since 1990 where she has been primarily engaged in the development and deployment of technologies and processes for stabilization of nuclear waste and has managed research and development programs across the full spectrum of DOE-EM activities from inception to deployment. This program support included start-up and operations of the SRS Defense Waste Processing Facility. Ms. Herman has worked at other DOE sites where she provided technical leadership for development of the flowsheet and equipment for the plutonium disposition program at Lawrence Livermore National Laboratory and directly supported the Office of River Protection at Hanford on technical issue resolution for the Waste Treatment and Immobilization Plant. She has also participated as a subject matter expert and led independent technical assessments for several DOE-EM flowsheets and facilities, including at Hanford and Idaho.

Brady Lee, PhD is the Director of the Earth, Biological and Quantitative Systems Science Division at SRNL. He is classically trained in microbiology and has over 30 years of experience in applying biological and hybrid biological/chemical processes for environmental, bioenergy, and national security purposes. He spent the first 24 years of his career at the Idaho National Laboratory where he served as a researcher, principal investigator, and program manager. In these roles, he specialized in biogeochemistry, environmental microbiology, extremophilic microbiology, and molecular biology. Prior to joining SRNL in 2020, Dr. Lee spent 7 years at the Pacific Northwest National Laboratory (PNNL), where he led the microbiology program for the Deep Vadose Zone Program at the laboratory. He also developed a PNNL capability overview related to analysis and remediation of perfluorinated organic compounds associated with DOD activities. He currently has management oversight of a DOE-EM project looking at PFAS bioavailability. Through the years, Dr. Lee has managed projects that span from basic science at the bench-scale to full-scale remediation operations. From this research, he has written numerous technical reports, approximately 50 peer-reviewed journal articles, has received 15 patents, and has given hundreds of technical presentations at national and international meetings.

John D. Graham, PhD, is Professor of Risk and Policy Analysis at the Paul H. O'Neill School of Public and Environmental Affairs at Indiana University. He has been recognized for lifetime contributions by the Society for Risk Analysis and the Society for Benefit-Cost Analysis. From 2001 to 2006, Professor Graham served in the George W. Bush administration as Senate-confirmed Administrator, Office of Information and Regulatory Affairs, U.S. Office of Management and Budget.

Robert Seifert is the Director of the Office of Subsurface Closure and has served in this DOE-EM program for nearly 29 years. Starting in 1993 at the Paducah Gaseous Diffusion Plant, Mr. Seifert has held a number of technical and management positions as both a contractor and DOE federal employee. He joined the DOE Headquarter team in 2014. Mr. Seifert has a BS degree in Chemistry and Biology from Murray State University.

Michael (Josh) Silverman, PhD, leads the DOE Office of Environmental Protection and ES&H Reporting within the Office of Environment, Health, Safety and Security (EHSS). His innovative organization focuses on reducing DOE's environmental footprint, minimizing safety risks, and improving organizational performance, with a diverse portfolio covering environmental compliance, sustainable operations, natural and cultural resource protection, public and environmental radiation protection, organizational and safety culture, and ES&H reporting and analysis.

Dr. Silverman is designated as the Department's Federal Preservation Officer, pursuant to the National Historic Preservation Act. He is also designated as the Department's lead for PFAS, a chemical of increasing health and regulatory concern. His efforts to help DOE reduce releases of sulfur hexafluoride (SF₆), the world's most potent greenhouse gas, was recognized by the Partnership for Public Service "Service to America Medals" program.

Dr. Silverman joined DOE in 2000 after receiving his PhD in History and Policy at Carnegie Mellon University. His dissertation, “No Immediate Risk: Environmental Safety in American Nuclear Weapons Production,” examines DOE management of environment, safety, and health risks from World War II through the end of the Cold War.

Alyssa Wingard is a Chemist and an Environmental Protection Specialist with the DOE-EHSS Office of Sustainable Environmental Stewardship (EHSS-21). In her position, Ms. Wingard leads the technical management of the DOE Consolidated Audit Program – Accreditation Program (DOECAP-AP) portion of the Analytical Services Program, bringing over 30 years of analytical testing experience. She also co-chairs the PFAS working group, the DOECAP data validation working group, and the newly formed PFAS Supply Chain working group for the Department. Ms. Wingard has a BS degree in Chemistry from Virginia Tech. Prior to joining DOE, she served as a Senior Chemist for over 16 years with the DOD providing management to compliance programs, including the Overseas Drinking Water Program and the DOD Environmental Laboratory Accreditation Program.

April Kluever, PhD, is a board-certified toxicologist with a science policy background working at the US Food and Drug Administration, Executive Office of the President, and Department of Energy. She is an interagency leader in White House Per- and Poly-Fluoroalkyl Substance (PFAS) technical and policy working groups, helping to coordinate federal efforts to address PFAS. Dr. Kluever received her Ph.D. in Environmental Health Sciences from Johns Hopkins University Bloomberg School of Public Health with a specialization in Neurotoxicology and certification in Risk Sciences and Public Policy.

Julie James is the Assistant Director of CRESPIII in the Department of Civil and Environmental Engineering at Vanderbilt University. She interacts with CRESPIII university consortium members, departments, divisions, and principal investigators regarding administrative, budgetary, and compliance requirements. Ms. James reviews budget proposals annually for accuracy and completeness, ensures compliance with DOE federal policies and regulations, and organizes/triages proposals and reporting requirements in conjunction with the CRESPIII research team. She also oversees the execution and maintenance of the CRESPIII Knowledge Management system to establish a record for the DOE CRESPIII cooperative agreement to effectively communicate with DOE, primary DOE sites, key government agencies, and other designated stakeholders.

Project Support Team

Artha Petermann is a Technical Communications Specialist, with over 40 years of experience working on technical and cost proposals and licensing applications for various clients primarily for work on DOE-EM/National Nuclear Security Administration (NNSA), DOD, and U.S. Nuclear Regulatory Commission (NRC) projects. She also supports special projects in the areas of nuclear waste management/cleanup, transportation systems, medical isotopes production, and computer systems development. Areas of expertise include proposal development, document development to industry standards/requirements, technical writing and editing, graphics design and editing, promotional materials design and production, and computer systems development and implementation. Her skill set in technical communications encompasses all aspects of document creation and publication, including layout and design, templates, style guides, editing, formatting, proofreading, and production. Ms. Petermann has a BS degree in Management Science (Information Technology) and Marketing/Business Administration from Central Washington University.

Richard Stringer-Hye has served as the CRESPIII Research Librarian in the Department of Civil and Environmental Engineering at Vanderbilt University since 2020. Prior to that he was a Science and Engineering Librarian in the Science and Engineering Library at Vanderbilt since 1995. Mr. Stringer-Hye provides research support, document retrieval, and organization for the CRESPIII research team. He

graduated with a Master's in Library and Information Science (MLIS) from the University of Rhode Island and a BA degree in Geology from the University of Colorado.

Subject Matter Expert Team

Kevin G. Brown, PhD, BCEEM is a Research Associate Professor in the Civil and Environmental Engineering Department at Vanderbilt University and Management Board Member of CRESPEM. While at the Savannah River Laboratory (1986–2002), Dr. Brown was recognized as a DOE complex-wide authority in process and product control for high-level waste vitrification. Dr. Brown spent 2002–2003 at the International Institute for Applied Systems Analysis (IIASA) in Laxenburg, Austria where he estimated potential transboundary radiation doses resulting from hypothetical accidents at Russian Pacific Fleet sites – the first such studies known in the West. Dr. Brown's current research, supported by CRESPEM, focuses on life-cycle risk evaluation, model integration, and waste management issues related to proposed advanced nuclear fuel cycles and cementitious materials and barriers for nuclear applications.

In 2009, Dr. Brown participated in the External Technical Review chartered by DOE-EM to evaluate system-level modeling and simulation tools in support of SRS and DOE Office of River Protection liquid waste processing. In 2010 and 2011, Dr. Brown participated on the Tank Waste Subcommittee of the DOE Environmental Management Advisory Board (EMAB) chartered to provide independent technical reviews of liquid waste capital and operations projects related to the DOE-EM tank waste cleanup program at major DOE sites.

Dr. Brown has participated as a subject matter expert on:

- DOE construction project and peer reviews for the Hanford Tank Waste Treatment and Immobilization Plant, low-activity waste pretreatment system, and SRS Salt Waste Processing Facility (2011–2019)
- Congressionally mandated (Section 3125 of the 2021 National Defense Authorization Act) Federally Funded Research and Development Center (FFRDC) team to study supplemental treatment of Hanford low-activity waste
- DOE-directed Network of National Laboratories for Environmental Management and Stewardship (NNLEMS) evaluation of the Hanford tank waste cleanup mission and development of a research and development roadmap in support of the DOE-EM budget request to Congress.

Dr. Brown holds a BE degree in Chemical Engineering, an MS degree in Environmental and Water Resources Engineering, and a PhD in Environmental Engineering from Vanderbilt University.

Ashley Cutshaw, PhD, earned her BS degree in Biosystems and Agricultural Engineering (BAE) from the University of Kentucky and completed her PhD in BAE with a dual degree in Environmental Science and Policy at Michigan State University. Her dissertation provided a comprehensive evaluation of co-located microalgal cultivation and biorefineries using life cycle and techno-economic assessment frameworks. Dr. Cutshaw is currently a Senior Engineer at KeyLogic where she serves as a support contractor for the DOE National Energy Technology Laboratory (NETL). At NETL, she works within the life cycle analysis competency of the Strategic Systems Engineering Analysis directorate. Since joining in June 2022, she has contributed to several publicly available reports, tools, and resources.

Justin Conrad, PhD, is the Gary K. Bertsch Director of the Center for International Trade and Security (CITS) and a professor in the School of Public and International Affairs at the University of Georgia. He is also a Joint Appointee at SRNL and a member of SRNL's Regulatory Center of Excellence. Dr. Conrad's current work focuses on nuclear energy and waste policy, energy security, and regulatory policy. He has published many articles in leading academic journals and is the author of two books. He is a former U.S. Navy officer and previously worked in the public affairs industry.

Rebe Feraldi is an experienced life cycle assessment (LCA) and Biomimicry Scientist involved in setting up and managing LCAs and science-based sustainability research and projects for target setting, reporting metrics, and innovation. Ms. Feraldi, a life-long student, uses a biomimicry lens to identify opportunities for innovation at the form, process, and system levels. She is proficient in establishing and maintaining LCA projects, life cycle inventory databases, training users in data collection, modeling, quality control, analyzing, data visualization, reporting, and supporting out-of-the box thinking and pivotal process improvements to sustainability, innovation, and LCA analyses and analysis systems. She has 14 years of experience offering LCA consulting to public and private clients at local, national, and international scales. She is well-versed in environmental labeling practices and relevant government policies.

Lee Ferguson, PhD, is an Associate Professor of Environmental Science and Engineering at Duke University in Durham, North Carolina. He received BS degrees from the University of South Carolina in Chemistry and Marine Science, before earning a PhD in Coastal Oceanography at State University of New York – Stony Brook. His postdoctoral research was conducted in the area of proteomics at PNNL in Richland, Washington. Before joining Duke, Dr. Ferguson was an Assistant and Associate Professor of Chemistry at the University of South Carolina.

Jennifer Guelfo, PhD, is an Assistant Professor and an Edward and Linda Faculty Fellow in Civil, Environmental, and Construction Engineering at Texas Tech University. She joined Texas Tech University in 2018 following a postdoctoral appointment in the Brown University School of Engineering. Dr. Guelfo has a BA degree in Geology from the College of Charleston, and an MS degree in Environmental Science & Engineering and a PhD in Hydrologic Science and Engineering, both from the Colorado School of Mines. For the past 13 years, her research has focused primarily on occurrence, fate, transport, and remediation of PFAS. In addition to academia, Dr. Guelfo has a combination of consulting and industry experience, and she uses this background to engage in activities that can inform policy and bridge gaps between research and practice.

Troy Hawkins, PhD, is a Senior Scientist and leads the Fuels and Products Group of the Systems Assessment Center at Argonne National Laboratory. His research focus is on improving the environmental performance of energy and product systems, with particular focus on decarbonization, where he applies LCA and other quantitative systems analysis approaches to provide actionable insights. He has evaluated the energy and environmental impacts of conventional and alternative transportation energy systems, electricity and biopower, plastics and chemicals, and industrial processes, and has developed new methods for LCA and environmentally extended input-output analysis. He contributes to the development of Argonne's GREET (Greenhouse Gases, Regulated Emissions, and Energy Use in Technologies) model for life cycle analysis of energy systems, products, and technologies. Prior to joining Argonne, he worked as a consultant providing environmental and economic assessment for clients in the private and government sectors, led LCA research for the EPA, and worked as a researcher in the Industrial Ecology Programme at Norwegian University of Science and Technology. He holds a PhD from Carnegie Mellon University and has a BS degree in Physics from the University of Michigan.

Matt Jamieson serves as a Senior Life Cycle Analyst at NETL, as part of the life cycle analysis competency within the Strategic Systems Engineering Analysis directorate. He has been performing life cycle analyses of complex energy systems at the laboratory for 10 years and has contributed to a number of publicly available tools, reports, and peer-reviewed articles. Mr. Jamieson has a BS degree in Mechanical Engineering from the University of Minnesota – Duluth.

Alex Kugler, PhD, is an Earth Scientist on the Subsurface Signatures Discovery team at PNNL, where he develops remediation technologies and analytical methodologies to assist with regulatory compliance. He received his PhD in Geology from Miami University, where he specialized in aqueous geochemistry and geomicrobiology. He has worked on the degradation and fate and transport of PFAS, along with other environmental contaminants such as dioxin, petroleum, heavy metals, trichloroethylene (TCE), and radionuclides.

Radha Kishan Motkuri, PhD, is a Senior Principal Scientist/Chemical Engineer and Team Lead for the Applied Chemistry and Engineering team in the Earth System Science Directorate at PNNL. He serves as principal investigator, co-principal investigator, and project manager on a diverse range of materials chemistry and chemical/nuclear security projects. Dr. Motkuri has over 26 years of experience in inorganic, materials chemistry, and security (approximately 7 years). Materials chemistry emphasizes nanoporous materials, specifically focused on materials that include metal-organic frameworks, zeolites, covalent organic frameworks, hierarchical porous carbons, and mesoporous silica, for potential applications.

Joshua Torgeson is an Earth Scientist on the Signatures research team in the Earth System Science Division at PNNL. He received an MS degree in Geology from the University of Minnesota; his thesis work, "Hydrobiogeochemical interactions in the hyporheic zone of a sulfate-impacted, freshwater stream and riparian wetland ecosystem," was published in *Environmental Science: Processes & Impacts*. At PNNL, his research experience has included geochemical characterization using X-ray absorption spectroscopy (XAS), development of cost-effective sensors, radioisotope detection, and spectral-induced polarization (SIP). His XAS experience has included both extended X-ray absorption fine-structure (EXAFS) and X-ray absorption near edge structure (XANES) to investigate biogeochemical cycling in environmental systems impacted by anthropogenic activity and to assess pyrogenic organic matter dynamics. Sensor development has included ratiometric planar optodes for high-throughput monitoring of organic matter respiration and in situ monitoring of PFAS using electrical impedance spectroscopy.

Additionally, Mr. Torgeson has used his expertise in 3D modeling and additive manufacturing to optimize commercially available sensors for environmental monitoring, including drone-based nuclear decommissioning. His expertise in geochemical characterization and electrochemistry experience has proven invaluable for development of SIP as a tool for monitoring complex subsurface environments, supporting the Induced Spectral Interrogation Technology for the Environment (INSITE) project.

Scott Unger, PhD, is a Sustainability Engineer at PNNL. His research and expertise focuses on development of sustainability metrics through LCA, techno-economic analysis, and cost-benefit analysis. Previous research projects include generation of life cycle inventories for proprietary industrial chemicals, development of environmental metrics to quantify RCRA and CERCLA remediation actions, and development of environmental product declarations for multinational manufacturers of consumer and industrial products (e.g., disinfectants, vitamin supplements). He has also calculated and characterized ecotoxic impacts from national-scale increased biofuel production, developed climate action plans for municipalities in the greater Phoenix area, and calculated cradle-to-grave impacts from renewable vs. non-renewable energy systems.

Jingyi Zhang, PhD, is an Energy Systems Analyst in the System Assessment Center at Argonne National Laboratory. Her research primarily revolves around mitigating environmental impacts in diverse systems, such as algal systems, lithium-ion batteries, solar energy, wastewater treatment, and saline water desalination, by using life cycle analysis. Prior to joining Argonne, Ms. Zhang served as a postdoctoral researcher at Northwestern University. She obtained her PhD in Mechanical Engineering from Case Western Reserve University.