PFP Projects Overview

PERFORMANCE FLUOROPOLYMER PARTNERSHIP

PFAS Lists, End-of-Life, Polymers of Low Concern Assessments and Functions, Uses & Alternatives

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on behalf of PFP

Northeast Conference The Science of PFAS
Marlborough, MA

05 April 2022

Discussion Outline:

PERFORMANCE FLUOROPOLYMER PARTNERSHIP

- PFAS Chemistry – Definition & Evolution
- Identification and Classification of PFAS
- Fluoropolymers End-of-Life Project
- Polymers of Low Concern Assessments
- Fluoropolymer Uses and Alternatives
- Summary & Questions

Integrated Environmental Assessment and Management — Volume 7, Number 4—pp. 513–541

Perfluoroalkyl and Polyfluoroalkyl Substances in the Environment: Terminology, Classification, and Origins

GROUP → **Per- and Poly-fluoroalkyl substances (PFAS)**

CATEGORY → **Non-Polymers** → **Polymers**

CLASS

Non-Polymers

Perfluoroalkyl Substances

Compounds for which all hydrogens on all carbons (except for carbons associated with functional groups) have been replaced by fluorines

- (Aliphatic) perfluorocarbons (PFCs)
- **Perfluoroalkyl acids**
- Perfluoroalkane sulfonyl fluorides
- Perfluoroalkane sulfonamides
- Perfluoroalkyl iodides
- Perfluoroalkyl aldehydes

Polyfluoroalkyl Substances

Compounds for which all hydrogens on at least one (but not all) carbon have been replaced by fluorines

- Perfluoroalkane sulfonamido derivatives
- Fluorotelomer-based compounds
- Semifluorinated *n*-alkanes and alkenes

Polymers

Fluoropolymers

including fluoroelastomers

Carbon-only polymer backbone with fluorines directly attached

Perfluoropolyethers

Carbon and oxygen polymer backbone with fluorines directly attached to carbon

Side-chain Fluorinated Polymers

Variable composition non-fluorinated polymer backbone with fluorinated side chains

- Fluorinated acrylate and methacrylate polymers
- Fluorinated urethane polymers
- Fluorinated oxetane polymers

Be Clear, Specific and Descriptive

Open access:
http://dx.doi.org/10.1002/ieam.258

PFAS Definition and Evolution

Banks 1994
- Perfluoro, Perfluorinated

Kyoto Protocol, 1997
- PFC's, Perfluorocarbons

Hekster, 2002, 2003
- PFAS, Perfluorinated Substances

OECD 2007
- Lists of PFOS, PFAS, PFOA, PFCA Related Compounds and Chemicals that Degrade to PFCAs

Buck et al, 2011
- PFAS, Per- and Poly-fluorinated Substances; Aliphatic CF_3-, Some Exclusions

OECD 2018
- PFAS: $-C_nF_{2n}-$ where n $\geq$ 3 and ($-C_nF_{2n}OC_mF_{2m}-$, n and m $\geq$ 1)

ITRC 2018-2020
- PFAS: C_nF_{2n+1}-R where n > 2

EU CfE 2020
- ALL PFAS with CF_3 or CF_2

Terminology Paper
OECD 2021
- ALL PFAS with CF_3 or CF_2

Strategic Roadmap
USEPA 2021
- R-CF_2-CF(R')(R")

PFAS Lists*, Interpretation and Application

- A harmonized identification, nomenclature and agreed to terminology of PFAS is still a work in progress – spanning nearly 2 decades of multi-stakeholder efforts
- From the nearly 1000 compounds identified in 2007 (OECD) to the 4730 in 2018 (OECD) significant confusion exists on which PFAS are in actual commerce
    - A list of CAS numbers do not imply an active item in commerce[#,##]
- The EU Call for Evidence** expanded the OECD 4730 compounds value by 2X as it includes all C-F compounds with either a CF_3 and/or CF_2
- For perspective, an important goal would be to gain a picture of the commercially relevant compounds in commerce

*OECD. Lists of PFOS, PFAS, PFOA, PFCA, Related Compounds and Chemicals That May Degrade to PFCA, 2007. http://www.oecd.org/officialdocuments/publicdisplaydocumentpdf/?doclanguage=en&cote=env/jm/mono(2006)15

*OECD, Organisation for Economic Co-operation and Development, 2018. Toward a New Comprehensive Global Database of Per- and Polyfluoroalkyl Substances (PFASs): Summary Report on Updating the OECD 2007 List of Per and Polyfluoroalkyl Substances (PFASs). Series on Risk Mgmt No. 39.

[#]EPA Comptox database lists over 8000 as of Aug 2020: https://comptox.epa.gov/dashboard/chemical_lists/PFASSTRUCT; one –CF_2- needed

[##]US EPA TSCA Inventory lists ca. 602 active compounds: https://www.epa.gov/sites/production/files/2019-02/documents/pfas_action_plan_021319_508compliant_1.pdf

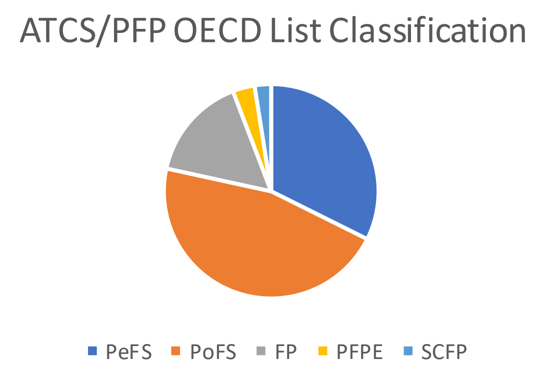
**https://echa.europa.eu/de/-/five-european-states-call-for-evidence-on-broad-pfas-restriction

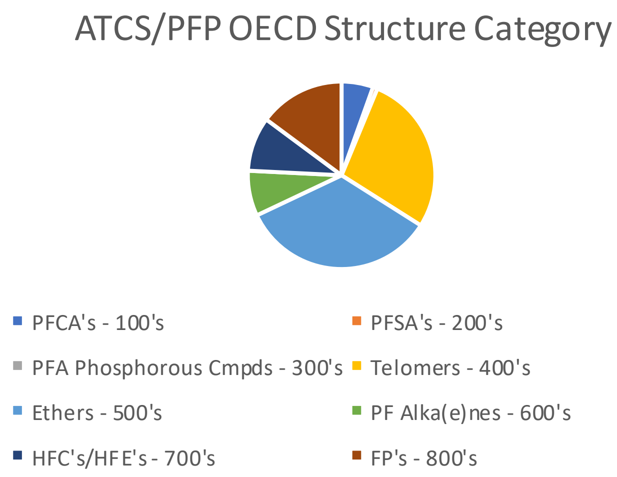
Also US EPA Definition: PFAS Strategic Roadmap: EPA's Commitments to Action 2021-2024. https://www.epa.gov/system/files/documents/2021-10/pfas-roadmap_final-508.pdf

PFAS Lists* and Interpretation

- A 2021 publication** that employed a true “bottom-up” company survey of products in commerce provided a current perspective of commercially relevant substances
- This survey included commercial products, impurities, ingredients, degradation products and metabolites

PFP/ATCS List Versus OECD Full List Splits			
Classification	ATCS/PFP Split	OECD List & Split	
PFCA's - 100's	5.5%	514	10.9%
PFSA's - 200's	0.8%	629	13.3%
PFA Phosphorous Cmpds - 300's	0.0%	23	0.5%
Telomers - 400's	27.7%	1872	39.6%
Ethers - 500's	34.0%	365	7.7%
PF Alka(e)nes - 600's	7.8%	314	6.6%
HFC's/HFE's - 700's	9.4%	746	15.8%
FP's - 800's	14.8%	267	5.6%
	Hundreds	4730	





*OECD, Organisation for Economic Co-operation and Development, 2018. Toward a New Comprehensive Global Database of Per- and Polyfluoroalkyl Substances (PFASs): Summary Report on Updating the OECD 2007 List of Per and Polyfluoroalkyl Substances (PFASs). Series on Risk Management No. 39.

**Identification and Classification of Commercially Relevant Per- and Poly-fluoroalkyl Substances (PFAS) – Buck et al, 2021, IEAM 17 (5), pp 1045-1055, https://doi.org/10.1002/ieam.4450

PFAS Lists, Interpretation and Commercial Relevance

- This 2021 publication* is the first to use a “bottom-up” approach to identify how many of the 4730 PFAS substances in the 2018 OECD/UNEP Report** are directly connected to commercial products based on input from three major global producers
- This survey included commercial products, impurities, ingredients, degradation products and metabolites
- Results showed that 256, less than 6%, of the 4730 PFAS substances presented in the 2018 OECD/UNEP Report are commercially relevant globally
- Given the number of commercially relevant substances, grouping and categorization of PFAS using classification criteria based on composition and structure can be used to identify appropriate groups for risk assessment

*Identification and Classification of Commercially Relevant Per- and Poly-fluoroalkyl Substances (PFAS) – Buck et al, 2021, IEAM 17 (5), pp 1045-1055, https://doi.org/10.1002/ieam.4450

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Fluoropolymer Combustion End-of-Life Project Objectives

1. Identify the combustion and post-combustion “conditions” (e.g., feed, T, t, [O_2], [H_2], [H_2O], air, etc.) under which commercial units typically burn products containing fluoropolymers that operate to achieve a “controlled emissions state”

   i.e., where there are no statistically significant uncontrolled emissions of measurable fluoropolymers or other C-F containing substances above background or at levels that might present a risk

2. Determine whether commercial units that are typically used in the US and Europe to combust products that contain fluoropolymers are typically operated at these conditions

FP EOL Project Objectives & Phases

Phase I – Evaluate prior studies - literature, compile commercial operating conditions, identify data gaps/needs, and recommend a study plan

Phase II – Bench-scale Tests - conduct, report, and identify effective combustion conditions

Phase III – Evaluate and report on whether commercial units used in the US and Europe to combust products containing FPs are operating at these conditions

Overall Objective of Bench Scale Study

Evaluate combustion conditions impact on formation and destruction of PIC's from the study of Fluoropolymers

(PTFE, FEP, PVDF, PCTFE)

PICS = Products of Incomplete Combustion

PERFORMANCE FLUOROPOLYMER PARTNERSHIP

FP EOL Phase I

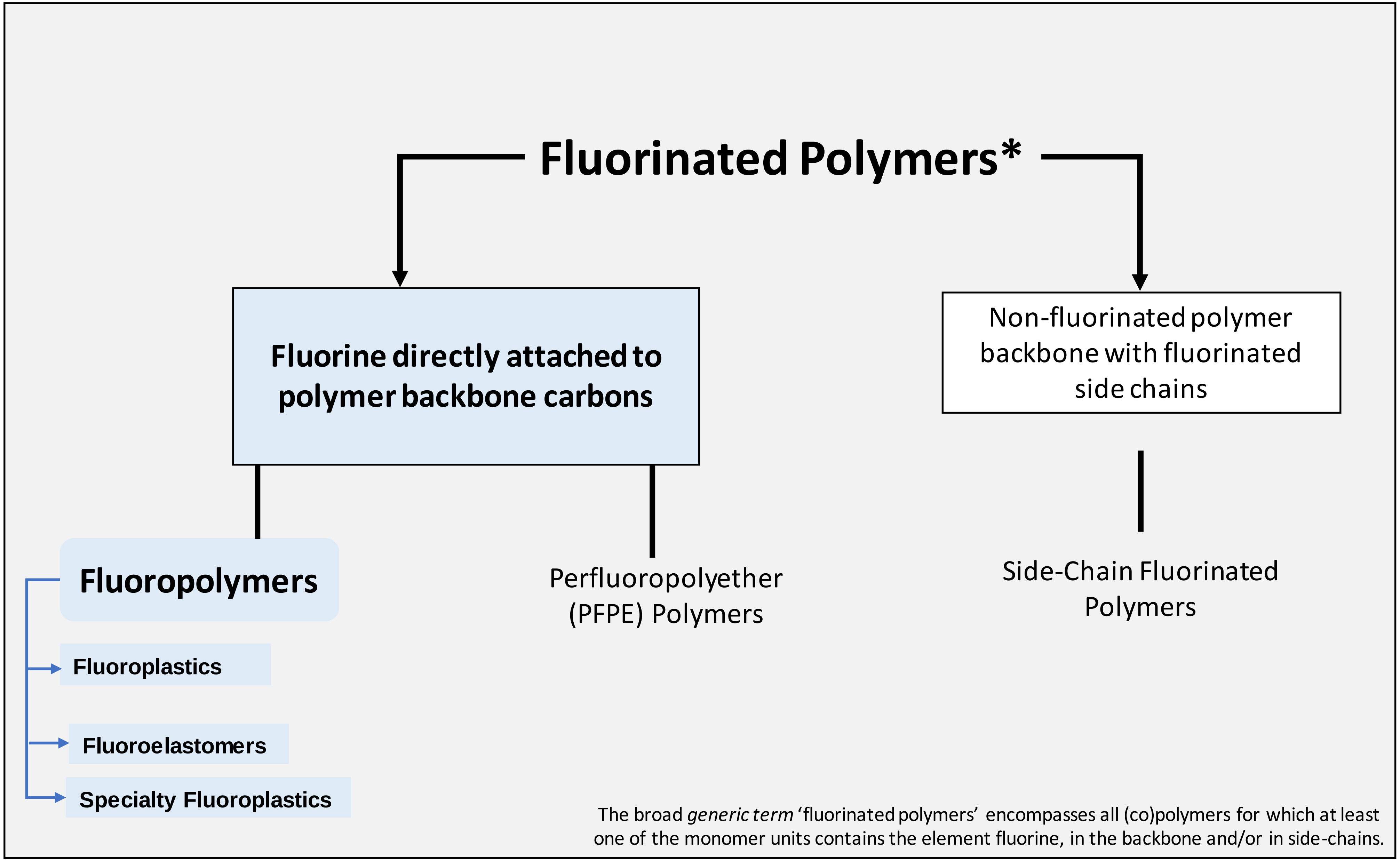
- Evaluate prior studies, identify data gaps/needs, and recommend a study plan
  - Comprehensive Literature Review
  - Commercial Operating Conditions Compilation
  - Bench-scale Study Test Plan
  - Expert Review
  - Engage with Stakeholders
  - Phase I Report – 197pp

  - **Completed August 2021**

FP EOL Phase II

- **Bench Scale Tests (BST)**
  - UDRI + subcontractors
    - ❖ Conduct Testing 3Q/4Q 2022

- **Scope Future Studies**
  - Decide on next steps as the BST is conducted

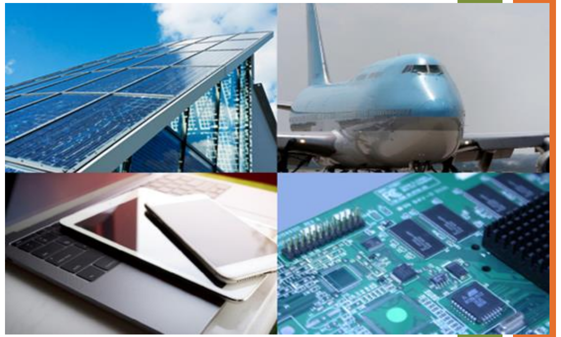


Be Clear, Specific and Descriptive

***A Critical Review of the Application of Polymer of Low Concern Regulatory Criteria to Fluoropolymers II: Fluoroplastics and Fluoroelastomers** S.H. Korzeniowski. et al, Submitted for Publication, March 2022

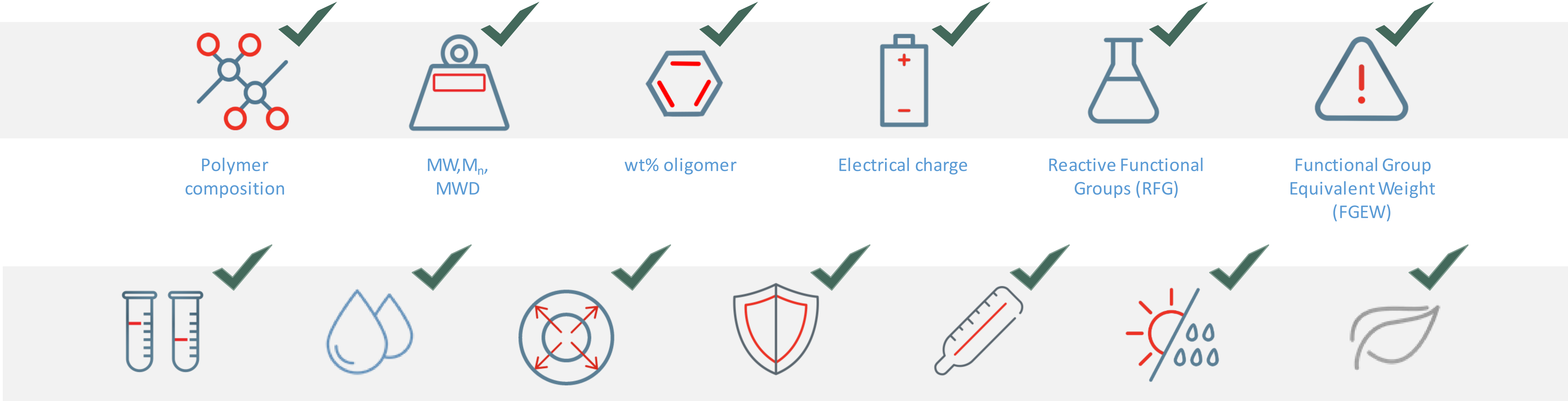
*(Fluoro)Polymers of Low Concern**

- Fluoropolymers have *material properties, have C-F in the backbone* and are large, stable, inert polymeric molecules that are too large to cross biological membranes and include Fluoroplastics and Fluoroelastomers
- Fluoropolymers have little potential for human or environmental exposure
  - They are not water soluble, not found in sources of drinking water, are non-bioaccumulative and non-bioavailable; they are not considered to be mobile in the environment and do not have any known systemic toxicity
- Research, emissions reduction, as well as industry efforts and projects continue on <u>both</u> the beginning-of-life and end-of-life part of the overall fluoropolymer life cycle#



*__A Critical Review of the Application of Polymer of Low Concern and Regulatory Criteria to Fluoropolymers__
Barbara J Henry, Joseph P Carlin, Jon A Hammerschmidt, Robert C Buck, L William Buxton, Heidelore Fiedler, Jennifer Seed, and Oscar Hernandez
Integrated Environmental Assessment and Management , **2018**, Volume 14, Number 3—pp. 316–334
#**Are Fluoropolymers Really of Low Concern for Human and Environmental Health and Separate from Other PFAS?**
Rainer Lohmann, Ian T. Cousins, Jamie C. DeWitt, Juliane Glüge, Gretta Goldenman, Dorte Herzke, Andrew B. Lindstrom, Mark F. Miller, Carla A. Ng, Sharyle Patton, Martin Scheringer, Xenia Trier and Zhanyun Wang ES&T, **2020**, https://dx.doi.org/10.1021/acs.est.0c03244

OECD Polymer of Low Concern (PLC) Criteria*



Polymer composition

MW, M_n, MWD

wt% oligomer

Electrical charge

Reactive Functional Groups (RFG)

Functional Group Equivalent Weight (FGEW)

Low MW leachables

Water/lipid solubility, octanol water partition

Particle size

Polymer stability

Thermal stability

Abiotic stability

Biotic stability

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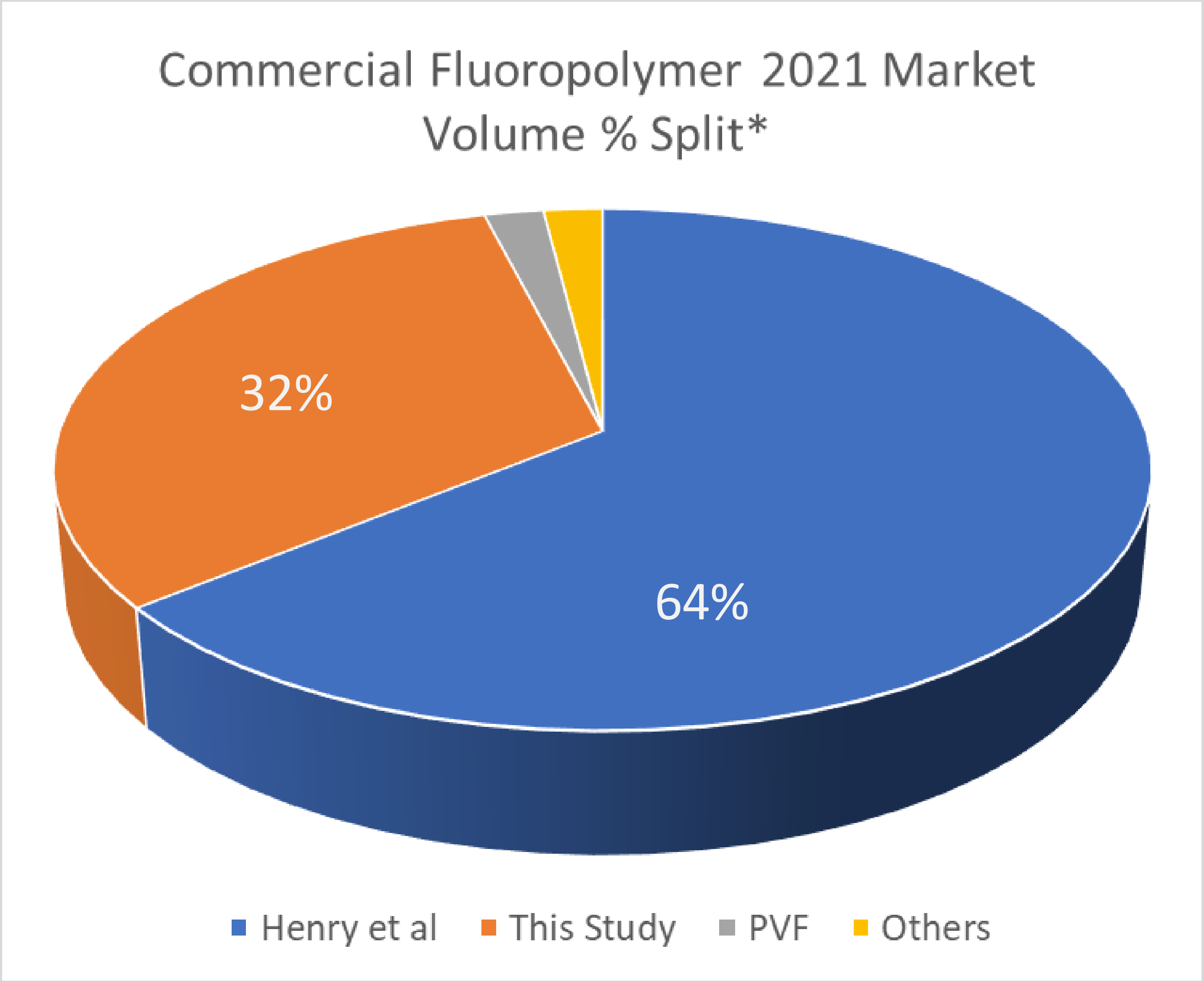
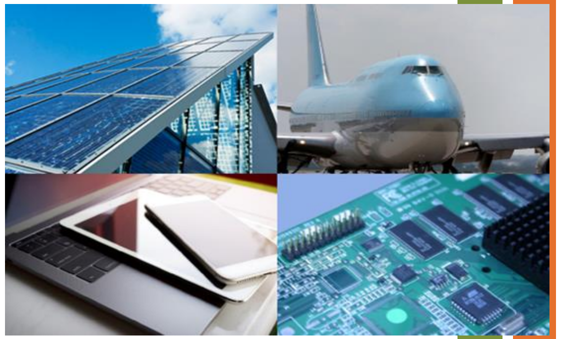


Data Supplied By Commercial Manufacturers Provide for 96% of Fluoropolymers Assessed as Meeting the PLC Criteria

***A Critical Review of the Application of Polymer of Low Concern Regulatory Criteria to Fluoropolymers II: Fluoroplastics and Fluoroelastomers** S.H. Korzeniowski. et al, Submitted for Publication, March 2022

*(Fluoro)Polymers of Low Concern**

- Key Messages from 2022 Critical Review II**:
  - Fluoropolymers have well-established safety profiles, are thermally, biologically and chemically stable, negligibly soluble in water, non-mobile, non-bioavailable, non-bioaccumulative and non-toxic
  - This study describes fourteen fluoropolymers, including fluoroplastics and fluoroelastomers, and presents data to show that they satisfy the widely accepted polymer hazard assessment criteria to be considered polymers of low concern (PLC).
  - This study combined with a prior 2018 study shows that commercial fluoropolymers are available that meet the PLC criteria representative of approximately 96% of the global commercial fluoropolymer market
  - While Critical Review II does focus on the "in-life" phase of Fluoropolymers, both the beginning-of-life and end-of-life phases of the life-cycle are directly addressed
  - The study results show that fluoropolymers are clearly a distinct and different group of PFAS and should not be grouped with other PFAS for hazard assessment or regulatory purposes



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Fluoropolymer Uses & Alternatives

Alternatives Considerations:

- **Technical feasibility**: could the alternative provide an equivalent technical function to FPs in the application concerned? Would the alternative provide the final products with the same/similar technical functionality?
- **Economic feasibility**: would adoption of the alterative incur additional costs to manufacturers, direct users or consumers? This may arise from higher unit costs, process or production changes requiring new or altered machinery or loss of functionality to the end user, which might impose additional costs. Sensitive applications might require expensive and lengthy re-approval processes.
- **Availability**: is the alternative likely to be available? Is it likely to be available in the required quantities and without undue delay?
- **Hazards and risks of the alternative**: would the overall risks to human health and the environment from the use of the alternative increase or decrease?

See ref: https://fluoropolymers.plasticseurope.org/

Fluoropolymer End Uses & Industries*

Fluoropolymer End Uses & Industries

	Industries	Transportation		Health Care		Chemical		Consumer			Telecommunications		Textiles
	End-Uses	Automotive	Aerospace	Pharma-ceuticals	Medical Devices	Oil & Gas	Chemical Process Industry (CPI)	Production of goods	Protection & Packaging	Filtration	Electronics & Semi-conductors	Internet & Wireless communications	Technical Textiles
Fluoroplastics	FP 1	●	●	●	●	●	●	●	●	●	●	●	●
	FP 2	●	●	●	●		●	●	●	●	●	●	●
	FP 3	●	●	●		●	●				●	●	
	FP 4			●		●	●						
	FP 5		●	●							●		
	FP 6	●	●								●		
	FP 7	●			●		●				●		
	FP 8	●									●		
	FP 9	●	●	●			●	●	●	●	●		
Fluoroelastomers	FE 1	●	●	●	●	●	●	●			●		
	FE 2	●	●	●	●	●	●	●	●		●		●
	FE 3		●	●	●	●	●	●			●		
Specialty	SP 1		●	●	●		●				●	●	
	SP 2	●			●		●			●	●		

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Fluoropolymer Properties & Functionalities*

Fluoropolymer Properities and Functionality

		Durable			Inert - Stable					Functional					
		Mechanical strength	Wear resistance	Low coefficient of friction	Resistance to chemicals	Weatherability	Cryogenic properties (lower than -50°C)	High operating temperature range	High limiting oxygen index	Electrical insulator - high data transmission rate	Ionic conductivity	Barrier properties	Ultra High Purity grades for clean applications	Optical clarity	Polymer processing additive (PPA)*
Fluoroplastics	**FP 1**	●	●	●	●	●		●	●			●	●		●
	FP 2	●	●	●	●	●		●	●			●			●
	FP 3	●	●	●	●	●	●	●	●	●		●			
	FP 4		●	●	●	●		●	●			●			
	FP 5	●	●	●	●	●	●	●	●			●	●	●	
	FP 6	●	●	●	●	●		●	●			●		●	
	FP 7	●	●	●	●	●	●	●	●			●		●	●
	FP 8			●	●	●	●	●	●			●	●	●	
	FP 9				●	●		●	●			●		●	●
Fluoroelastomers	**FE 1**	●	●		●	●		●	●	●		●			
	FE 2	●	●		●	●		●	●			●			●
	FE 3	●	●		●			●	●	●		●	●		
Specialty	**SP 1**			●	●			●	●	●	●	●	●	●	
	SP 2				●				●	●	●	●		●	

***A Critical Review of the Application of Polymer of Low Concern Regulatory Criteria to Fluoropolymers II: Fluoroplastics and Fluoroelastomers** S.H. Korzeniowski. et al, Submitted for Publication, March 2022

Fluoropolymer Alternatives Analysis

See ref: https://fluoropolymers.plasticseurope.org/

Key Market	Sector	Alternative/s	Example potential application	Overview of likely technical economic and environmental implications
Chemical & Power	**Chemical Industry**	Stainless Steel, Copper	Pipers, Liners, Tubing	FPs 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: Increased weight and size/design of components. Inferior resistance to corrosion and/or abrasion
		Polypropylene, PVC	Pipes, Liners	Low resistance to chemical attack and temperature hence lower corrosion prevention. Unsuitable for demanding applications, unless coated or reinforced (for instance with FPs)
Electronics	**Electronics**	Non-conductive plastics	Used in semiconductor manufacture	Unviable. The modern semiconductor industry has stringent requirements and FPs are the only material that can currently protect the processing equipment in which semiconductor 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 in order to maximise chip yields
Transport	**Automotive**	Stainless steel, aluminium, or copper	Low permeation fuel lines Protection for plastic fuel lines	Fuel lines made entirely of metal are available in the market for antique cars that do not have to meet modern standards. All metal fuel lines are prone to leakage during crash tests and leaking gasoline or diesel is an immediate fire risk at any crash site. Other polymeric alternatives have difficulties to meet fuel permeation standards and especially with the variety of alcohol containing fuels used today
		Polyetheretherketone (PEEK), polyether sulfone	Fuel hoses, lines, gaskets, seals, cables, wire insulation	They have similar temperature resistance. For example, PEEK is able to resist up to 260 °C. They are rigid, which may impact on design possibilities, and chemical resistance is lower. Also, electrical and data transmission properties are inferior

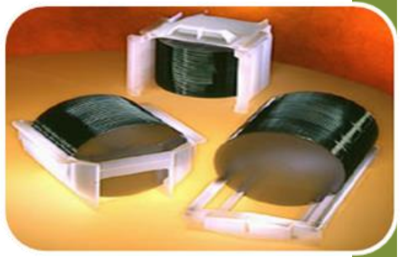
Fluoropolymer Alternatives Analysis

Key Market	Sector	Alternative/s	Example potential application	Overview of likely technical economic and environmental implications
Medical Applications		PEEK	Tubes, catheters, and other hospital material	PEEK catheters are commercially available. PEEK is a stiffer material than PTFE or Fluorothermoplastics. PEEK is an alternative for specialty catheter applications. It is biocompatible but it is generally not suitable for uses where longer term (30+ day) contact with tissue or blood is required. As a result, they are inferior to FPs for solutions such as heart patches
Textiles and Architecture	**Architecture**	Steel or Glass	Insulation materials, pipes, and tubes	They are heavier and more inflexible than FPs. Steel is not resistant to corrosion, leading to higher maintenance costs. Glass is more fragile to hail or other impact. They are not able to meet the design requirements of FPs
		Polycarbonate sheets	Membranes for architectural applications such as roofing	They are resistant to temperature and can withstand force. Polycarbonates have a tendency to yellow in external applications in contrast to Fluoropolymers. PVC/PES membranes for architectural applications are common. However, these are often coated with a protective layer (often made of PVDF, a FP) providing UV-resistance and weatherability

See ref: https://fluoropolymers.plasticseurope.org/
And https://www.oecd.org/chemicalsafety/portal-perfluorinated-chemicals/per-and-polyfluoroalkyl-substances-alternatives-in-coatings-paints-varnishes.pdf for a PFAS in PCV Report on Alternatives, March 2022

Summary & Conclusions

- The fluorinated products (PFAS) have been discussed continuously for over 20 years
  - There is still no consensus definition - it has been ever changing and
  - The number of PFAS compounds has been ever expanding with the structural definition changes
- Be clear, specific and descriptive when discussing PFAS compounds as they are not all the same.
  - Even if they all contain a C-F bond, they have dramatically different properties and characteristics
- How many PFAS are in commerce and relevant? CAS lists do not imply active compounds
  - Industry efforts indicate active compounds in commerce number in the hundreds not thousands of compounds



- Thermal treatment and destruction of PFAS compounds are a major current focus – including incineration. EOL Projects are underway in various agencies and groups (i.e. PFP)
  - PFP focus on destruction conditions, PICs and total fluorine mass balance

Summary & Conclusions (Cont.)

- Fluoropolymers have *material properties,* have C-F in the backbone and are large, stable, inert polymeric molecules that are too large to cross biological membranes and include Fluoroplastics and Fluoroelastomers
- Fluoropolymers have little potential for human or environmental exposure
  - They are not water soluble, not found in sources of drinking water, are non-bioaccumulative and non-bioavailable; they are not considered to be mobile in the environment and do not have any known systemic toxicity
- The Fluoropolymer Critical Review II when combined with a prior 2018 study shows that 18 commercial fluoropolymers are available that meet the PLC criteria representative of approximately 96% of the global commercial fluoropolymer market
- Fluoropolymers possess a unique combination of properties and unmatched functional performance critical to the products and manufacturing processes they enable and are irreplaceable in many uses

Acknowledgements

The presenter would like to thank the industry membership of PFP as well as ACC for their support and editorial comments as this presentation was developed

Disclaimer

The views and opinions expressed in this presentation are those of the presenter and are not necessarily the opinions of PFP and ACC or the companies for whom the presenter consults

Thank you!

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