# ANNEX I

# Classification of Plastics Plastics Class VI – 121 °C With Teadit 24SH



## Classification of Plastics - Plastic Class VI – 121 °C

#### (Systemic Injection Test-Intraperitoneal Administration)

(Systemic Injection Test-Intravenous Administration)

(Intracutaneous Test)

(Implantation Test)

with

**Teadit 24SH** 

## Report

#### **BSL BIOSERVICE Project No.: 041502**

Sponsor

Teadit International Produktions GmbH Rosenheimer Str. 10 A-6330 Kufstein Austria

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#### GLP-Bescheinigung/Statement of GLP Compliance (gemäß/according to § 19b Abs. 1 Chemikaliengesetz)

Eine GLP-Inspektion zur Überwachung der Einhaltung der GLP-Grundsätze gemäß Chemikaliengesetz bzw. Richtlinie 88/320/EG wurde durchgeführt in:

Assessment of conformity with GLP according to Chemikaliengesetz and Directive 88/320/EEC at:

 $\boxtimes$ Prüfeinrichtung/Test facility

Prüfstandort/Test site

#### **BSL Bioservice Scientific Laboratories GmbH** Behringstrasse 6 82152 Planegg

(Unverwechselbare Bezeichnung und Adresse/Unequivocal name and address)

Prüfungen nach Kategorien/Areas of Expertise (gemäß/according ChemVwV-GLP Nr. 5.3/OECD guidance)

2 Prüfungen auf toxikologische Eigenschaften 3 Prüfungen auf mutagene Eigenschaften (in vitro/in vivo) 9 Sonstige Prüfungen: a) Mikrobiologische Sicherheitsprüfungen b) Wirksamkeitsprüfungen an Zellkulturen

> Datum der Inspektion/Date of Inspection (Tag.Monat.Jahr/day.month.year) 11./12.02.2004

Die/Der genannte Prüfeinrichtung/Prüfstandort befindet sich im nationalen GLP-Überwachungsverfahren und wird regelmäßig auf Einhaltung der GLP-Grundsätze überwacht.

The above mentioned test facility/test site is included in the national GLP Compliance Programme and is inspected on a regular basis.

Auf der Grundlage des Inspektionsberichtes wird hiermit bestätigt, dass in dieser Prüfeinrichtung/ diesem Prüfstandort die oben genannten Prüfungen unter Einhaltung der GLP-Grundsätze durchgeführt werden können.

Based on the inspection report it can be confirmed, that this test facility/test site is able to conduct the aforementioned studies in compliance with the Principles of GLP.

München, 21.07.2004



Leitender Gewerbedirektor

I.V.



### **Results and Discussion**

In this study the test item was investigated according to USP Plastic Class VI - 121 °C. The tests performed were the Systemic Injection Test (intraperitoneal and intravenous administration, respectively depending on the extraction vehicle used), the Intracutaneous and the Implantation Test.

4 extracts of the test item (isotonic saline, 1 in 20 ethanol in isotonic saline, polyethylene glycol 400, and vegetable oil) were investigated in the Systemic Injection Test and the Intracutaneous Test. In the Implantation test at least 4 strips/animal were investigated for the potential to induce local tissue effects.

In the Systemic Injection Test no significant clinical signs and no significant changes in the weight development of the animals were obtained (Results see Annex I to this study)

The average score in the Intracutaneous Reactivity Test was 0 as compared to the injection sites of the reagent controls (Results see Annex II to this study).

In the Implantation Test no compound-related tissue reactions were found (Results see Annex III to this study).

#### Conclusions

Considering the reported data the test item Teadit 24SH meets the requirements of USP Plastic Class VI.

# ANNEX III

References

### **Critical Review**

## A Critical Review of the Application of Polymer of Low Concern and Regulatory Criteria to Fluoropolymers

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#### ABSTRACT

Per- and polyfluoroalkyl substances (PFAS) are a group of fluorinated substances that are in the focus of researchers and regulators due to widespread presence in the environment and biota, including humans, of perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA). Fluoropolymers, high molecular weight polymers, have unique properties that constitute a distinct class within the PFAS group. Fluoropolymers have thermal, chemical, photochemical, hydrolytic, oxidative, and biological stability. They have negligible residual monomer and oligomer content and low to no leachables. Fluoropolymers are practically insoluble in water and not subject to long-range transport. With a molecular weight well over 100 000 Da, fluoropolymers cannot cross the cell membrane. Fluoropolymers are not bioavailable or bioaccumulative, as evidenced by toxicology studies on polytetrafluoroethylene (PTFE): acute and subchronic systemic toxicity, irritation, sensitization, local toxicity on implantation, cytotoxicity, in vitro and in vivo genotoxicity, hemolysis, complement activation, and thrombogenicity. Clinical studies of patients receiving permanently implanted PTFE cardiovascular medical devices demonstrate no chronic toxicity or carcinogenicity and no reproductive, developmental, or endocrine toxicity. This paper brings together fluoropolymer toxicity data, human clinical data, and physical, chemical, thermal, and biological data for review and assessment to show that fluoropolymers satisfy widely accepted assessment criteria to be considered as "polymers of low concern" (PLC). This review concludes that fluoropolymers are distinctly different from other polymeric and nonpolymeric PFAS and should be separated from them for hazard assessment or regulatory purposes. Grouping fluoropolymers with all classes of PFAS for "read across" or structure-activity relationship assessment is not scientifically appropriate. Integr Environ Assess Manag 2018;14:316–334. © 2018 The Authors. Integrated Environmental Assessment and Management published by Wiley Periodicals, Inc. on behalf of Society of Environmental Toxicology & Chemistry (SETAC)

Keywords: Fluoropolymer International regulation Polytetrafluoroethylene Polymer of low concern PFAS

#### **INTRODUCTION**

The carbon-fluorine (C–F) bond is the strongest bond between C and another atom, instilling substances that contain a majority of C–F bonds with stability, inertness, and persistence (Banks et al. 1994). Per- and polyfluoroalkyl substances (PFAS) are a large group of highly fluorinated synthetic substances with diverse properties that have been used in a wide variety of industrial and consumer applications since the 1950s (Buck et al. 2011). Within the group are

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distinct substances with different properties: polymers and nonpolymers; solids, liquids, and gases; persistent and nonpersistent substances; highly reactive and inert substances; mobile and insoluble substances; and toxic and nontoxic chemicals.

The PFAS are a large, diverse group of substances that, in some respects, challenge easy distinction for assessment and management. A clearer understanding of the origin of PFAS found in the environment and assessment of their properties is needed to be able to determine which classes of PFAS require management action. Perand polyfluoroalkyl substances must be assessed taking into account their differences in chemical, physical, thermal, and biological properties. A single, globally harmonized system for PFAS classification has not yet been defined, resulting in a lack of distinction between PFAS. As regulatory frameworks continue to evolve, such as the Regulation (EC) No 1907/2006 of the European

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Parliament and of the Council on the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) (RC 2006), more work is needed to distinguish classes of PFAS to ensure that regulations are appropriate in scope and proportionality.

Two long-chain nonpolymer perfluoroalkyl acids (PFAAs), perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) (both PFAS), found widespread in the environment and living systems, led to regulatory assessment and management efforts in several countries (Buck et al. 2011; OECD 2017; USEPA 2017a). Management actions to curtail manufacture of long-chain PFAAs, including PFOS and PFOA, and substances that may degrade to form them (also known as "precursors") have been taken (EC 2006; ECHA 2015; USEPA 2017a). Both PFOS and PFOA have been determined by regulators to be persistent, bioaccumulative, and toxic (PBT) substances (EC 2006; ECHA 2015). A current concern is the potential for certain side-chain polymer PFAS to degrade in the environment to PFOS and PFOA or lower homologues (Liu and Mejia-Avendaño 2013). In addition, PFOS (a nonpolymeric perfluoroalkyl substance) and related substances have been listed as persistent organic pollutants (POPs) under Annex B of the Stockholm Convention (UNEP 2009), and PFOA and other related substances (UNEP 2011), as well as perfluorohexane sulfonic acid (PFHxS) and related substances are being evaluated for listing (UNEP 2017a). As a result, questions about the health and environmental safety of PFAS as a group have been raised (Scheringer et al. 2014; Blum et al. 2015).

These findings have prompted expanded regulatory interest and concern about PFAS as a group, spurring additional assessment and management actions. The German Environment Agency, Umweltbundesamt (UBA), published a proposal to implement new assessment criteria and procedures for identifying persistent (P), mobile (M), and toxic (T) substances under the European Union REACH chemical registration process (UBA 2017). The UBA has concluded that PM and/or PMT substances constitute "an irreversible threat to sources of drinking water and the quality of drinking water" in Germany. This has prompted the designation of PFAS substances as posing an "equivalent level of concern" under Article 57(f) of REACH and thereby has prompted the need for a new paradigm for chemical assessment and authorization. The Swedish Chemicals Agency, Kemikalieinspektionen (KEMI), announced agreement among 37 government agencies and research institutions in the European Union (EU) to expand cooperation to reduce the risks and increase the knowledge of PFAS, thereby endorsing the UBA view on the hazards posed by all PFAS substances (KEMI Swedish Chemicals Agency 2016). The KEMI announcement indicated that all perfluoralkyl substances should be considered as extremely persistent in the environment, and many are water soluble, mobile in soil, and likely to contaminate waterways and drinking water supplies. A risk assessment report prepared by KEMI is forthcoming (ChemNews 2016).

The PFAS are divided into 2 primary categories: nonpolymers and polymers (Figure 1). Figure 1 shows that these 2 categories are divided into 5 classes of PFAS. The fluoropolymer class of PFAS is the focus of the present paper. The nonpolymer category includes perfluoroalkyl substances and polyfluoroalkyl substances. The polymer category includes fluoropolymers, perfluoropolyethers, and side-chain fluorinated polymers. Polymers generally have very different physical, chemical, and biological properties than do nonpolymer chemical substances of low molecular weight. Precise criteria that distinguish polymers from nonpolymers have been established (OECD 1993).

There are distinct differences between the 5 classes of PFAS. For example, PFOA, in the class nonpolymer perfluoroalkyl substances, is small, mobile, and persistent; has been assessed and determined to be a PBT chemical (ECHA 2015); and is in the final stage for recommendation of listing as a POP under the Stockholm Convention (UNEP 2017b). Regulatory and industry management actions on PFOA include precursor substances that may degrade to form PFOA (USEPA 2017a). An example in the class of nonpolymer polyfluorinated substances, 8:2 fluorotelomer alcohol, is known to degrade under environmentally relevant conditions to form PFOA (Liu and Mejia-Avendaño 2013). It is therefore a precursor substance to PFOA and subject to regulatory management (Liu and Mejia-Avendaño 2013). Polymers derived from 8:2 fluorotelomer alcohol are examples of the side-chain fluorinated polymers class. These polymers may degrade to form PFOA and therefore are subject to regulatory management. Lastly, perfluoropolyethers class is a complex class of PFAS, which contains O linkages in the polymer backbone.

In the present paper, we address fluoropolymers, a class of PFAS polymers (Figure 1). Fluoropolymers are high molecular weight solid plastics that have been studied extensively.

The present paper brings together fluoropolymer toxicity data, human clinical data, and physical, chemical, thermal, and biological data for review and assessment to show that fluoropolymers satisfy widely accepted assessment criteria to be considered as "polymers of low concern" (PLC) and to show that fluoropolymers are distinctly different enough from other classes of PFAS to not be grouped with them for hazard assessment or regulatory purposes.

# PERFORMANCE CHARACTERISTICS AND USES OF FLUOROPOLYMERS

Since the discovery of polytetrafluoroethylene (PTFE) in 1938 (Plunkett 1987), the use of fluoropolymers has grown considerably to take advantage of their unique physicalchemical, thermal, and biological properties. The 4 fluoropolymers addressed in the present paper, polytetrafluoroethylene (PTFE), fluorinated ethylene propylene (FEP), ethylene tetrafluoroethylene (ETFE), and tetrafluoroethylene copolymers with perfluoroalkyl vinyl ethers (e.g., perfluoroalkoxy polymer, PFA), accounted for approximately 70% to 75% of the world fluoropolymer consumption in 2015 (IHS 2016). The representative fluoropolymer discussed in the present paper, PTFE, made up 58% (by weight) of 2015 worldwide fluoropolymer consumption (IHS 2016). Fluoropolymers are high molecular weight plastics with unique properties attributable to the strong C-F bonds, the strongest bond between C and another atom, making



Figure 1. Per- and polyfluoroalkyl substances (PFAS).

them highly stable (Olabisi and Adewale 2015). Carbon atoms alone form the fluoropolymer backbone, each surrounded by an envelope of F atoms. Fluoropolymers are generally very high molecular weight (>100 000 Da); have high thermal, chemical, photochemical, oxidative, hydrolytic, and biological stability; have low flammability, neutral electrical charge, and resistance to degradation; have negligible residual monomers and low molecular weight oligomer content; have limited low molecular weight leachables; and have no reactive functional groups of concern (Gangal and Brothers 2015).

The unique properties of fluoropolymers include durability, mechanical strength, inertness, thermal stability in foreseeable use conditions, and resistance to chemical, biological, and physical degradation (Hougham et al. 1999). Table 1 shows performance characteristics required in various commercial fluoropolymer applications (Gangal and Brothers 2015; Dams and Hintzer 2016). For example, medical devices are successful when they are made from "biocompatible" biomaterials, that is, the material has the ability to perform with an appropriate host response in a specific situation (Williams 1987). The inertness of PTFE allows for its acceptance into the body. Moreover, PTFE flexibility and

durability deliver mechanical integrity for the device's lifetime. The microstructure of PTFE can be modified to meet specific physiological needs (e.g., porous and open structure to facilitate tissue ingrowth), enhancing its utility in medical devices. In terms of end-use function, PTFE's inertness, physical properties (Ebnesajjad 2011), and the low level of residual monomer, oligomers, and low molecular weight leachables (Supplemental Data p 32-55) meet the requirements for low levels of contaminants and particulates in manufacturing environments essential for the food and beverage, pharmaceutical, medical, and semiconductor industries (Olabisi and Adewale 2015). Manufacturing applications requiring ultrapure high efficiency particulate air (HEPA) filtration use the finely controlled microporous PTFE membranes. Other components requiring a high degree of contamination control associated with patient care (e.g., dialysis tubing) also find the properties of PTFE essential. Durability in harsh conditions makes PTFE a superior material of choice in aerospace, environmental controls, energy production and storage, and electronics, as well as in technical apparel. The thermal stability of PTFE and FEP fluoropolymers provides improved fire safety risk over other polymers when used in plenums and structural

				Fluoropo	olymer chara	Icteristics				
	Dur	able		lnert		Functional			Stable	
Commercial application	Mechanical strength	Low particulation	Resistance to chemicals	Nontoxic, biocompatible, biological degradation resistant	Flexibility	Friction resistance	Low dielectric constant	Low leachables	Resistance to photolysis, oxidation, hydrolysis	Stability
Aerospace	×	Ι	×	Ι	×	×	×	Ι	×	×
Automotive industry	×	Ι	×	Ι	×	×	×	I	×	×
Medical devices	×	×		×	×	×	Ι	×	×	×
Pharmaceutical manufacture	×	×	×	×	×	I	I	×	Ι	×
Consumer outdoor apparel	×	I		×	×	I	I	×	Ι	I
Technical clothing (military, firefighters, first responders, medical personnel)	×	1	×	×	×	×	I	×	×	×
Consumer electronics	×	I	×	Ι	×	×	×	I	×	×
Wireless communications	×	I	×	Ι	×	×	×	I	×	×
Satellite navigation systems	×	I	×	Ι	×	×	×	I	×	×
Semiconductor industry	Ι	×	×	I	I	Ι	×	×	I	I
Building construction	×	Ι	Ι	×	×	Ι	×	Ι	×	×
Energy production and storage	×	×	I	Ι	Ι	Ι	×	×	×	×
Food and beverage production	×	×	×	×	×	×	Ι	×	×	I
Food protection and packaging	×	×	×	×	×	Ι	Ι	×		I
Drinking water filtration	I	×	×	×	I	I	I	×	×	I
Environmental protection	Ι	×	×	×	I	I	I	×	×	×

Table 1. Fluoropolymer functionality and commercial applications

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geometries in aviation and standard building construction (Olabisi and Adewale 2015). In addition, chemical resistance to acids, bases, solvents, and chemical attack, combined with its unique conformable strength, makes PTFE an ideal coating for chemical process equipment, lining for process piping, sealants for gaskets and hoses, and fabricated parts for pumps, gears, and other mechanical parts that need this extreme resistance for functionality (Olabisi and Adewale 2015). The low dielectric constant of PTFE ensures the integrity of high speed-low signal loss systems as employed in the aerospace industry for flight controls, communication, and protection from extreme cold, moisture, and altitude changes (Dams and Hintzer 2016). These are lifesaving applications that are used in satellite systems for navigation, wireless communications, in-flight navigation, and shielding from electronic interference. Civil and military aviation depends on reliable performance of these systems for long service hours with minimal maintenance down times. In addition, PTFE provides reduced friction of moving parts (e.g., cable chains), preventing particulation during automated manufacturing in cleanroom environments (Dams and Hintzer 2016). This friction reduction is also uniquely beneficial in light load bearings, gears, cams, and other mechanical machine parts as well as in weaving fibers, yarns, and greases (Dams and Hintzer 2016).

#### ASSESSMENT OF POLYMERS

#### History

Prior to the mid-20th century, regulation of new chemical substances, mixtures, and polymers in general was very limited. National chemical inventories were created with notification requirements for new chemical substances, mixtures, and polymers. In the United States, new chemicals submitted to the US Environmental Protection Agency (USEPA) under the Toxic Substances Control Act (TSCA) (USC 1976) for addition to the US chemical inventory are reviewed for potential physical, chemical, and biological effects (environmental and mammalian), as well as for potential exposure to the environment and human populations. Over time, the USEPA regulatory scientists gained enough knowledge through the review of the thousands of data packages to develop tools to assist in the identification of physical-chemical properties, potential hazard, and potential exposure to assist in and expedite the chemical review and assessment process (Auer et al. 1990; Wagner et al. 1995; USEPA 2012; USEPA 2017b).

The predictive power and reliability of these approaches were tested and refined (Wagner et al. 1995). Over time, it was recognized that many of the physical-chemical properties, such as molecular weight, limit the ability of the chemical to cross the cell membrane and therefore limit its bioavailability. Further examination of general physicalchemical properties and their relationship to hazard potential of a given chemical led to the development of general principles or criteria for the identification of chemicals, including polymers, with low hazard potential. These criteria were developed for use by USEPA for its hazard evaluation of new polymers. The USEPA made this methodology available to the public to assist submitters interested in developing low hazard polymers (USEPA 1997a). In 1984, the USEPA published the polymer exemption rule to exempt low hazard polymers from certain notification requirements under the new chemicals program (USFR 1984). The polymer exemption rule incorporated the hazard criteria as part of the criteria to determine eligibility for exemption (USEPA 1997a, 2010).

The hazard criteria that support the PLC concept represent an extension of these principles and practices developed for (nonpolymeric) chemicals and rely heavily on physicalchemical properties that determine a chemical's bioavailability. In 1993, the Organisation for Economic Co-operation and Development (OECD) Expert Group on Polymers found that sufficient data existed to create a consensus document identifying the essential data elements to qualify a polymer as a PLC to human health and the environment (OECD 1993). By 2007, the OECD Expert Group on Polymers agreed that, "Polymers of low concern are those deemed to have insignificant environmental and human health impacts" (OECD 2009). Thus, there was agreement within the OECD that polymeric chemicals meeting these criteria have a low hazard potential. However, the integration of the criteria into a risk management framework may differ from country to country according to their individual regulatory mandate.

In a recent report commissioned by the European Commission (EC) (BIO by Deloitte 2015), the following countries agreed on the polymer properties predictive of adverse human health and environmental hazard: Australia, Canada, China, Japan, South Korea, Philippines, New Zealand, Taiwan, and the United States. Further, the report identified the eligibility criteria to be considered a PLC with respect to potential for adverse impact on health and the environment. The report also compiled existing polymer regulations outside the EU and proposed alternative options for EU polymer registration, including defining a category of a PLC and grouping polymers into families.

The PLC criteria are described in the following section. Note that there are some policy components, such as elemental composition, as well as the physical-chemical attributes, in the PLC criteria.

#### POLYMER OF LOW CONCERN CRITERIA

Here we describe each of the eligibility criteria for PLC and provide an assessment for the representative fluoropolymer PTFE. We will show that fluoropolymers, including PTFE, satisfy the widely accepted assessment criteria to be considered PLCs (Table 2) and therefore are considered to be of low hazard to human health and the environment.

#### Polymer composition

The polymer composition criterion requires structure and elemental composition of the polymer be described and identified (e.g., by Chemical Abstracts Service [CAS] number).

		Flu	oropolymers	
	PTFE	ETFE	FEP	PFA
Assessment criteria <sup>a</sup>	CAS 9002-84-0	CAS 25038-71-5, 68258-85-5	CAS 25067-11-2	CAS 26655-00-5, 31784-04-0
Structure	$\{CF_2 - CF_2\}_n$	$\begin{array}{c} \hline \mathbf{CH}_2 \text{-} \mathbf{CH}_{2,n} & \hline \mathbf{CF}_2 \text{-} \mathbf{CF}_{2,m} \end{array}$	$ \begin{array}{c} (CF_2 - CF_2)_{n} & (CF_2 - CF_2)_{m} \\ & (CF_3)_{m} \end{array} \end{array} $	$\begin{array}{c} (CF_2-CF_{2^n} & CF_2-CF \\ O \\ R_t \\ m \end{array}$
Polymer composition (must have C, H, Si, S, F, Cl, Br, or I covalently bound to C)	Yes	Yes	Yes	Yes
Molecular weight	389 000– 8 900 000 <sup>bc</sup>	_	—	_
(M <sub>n</sub> > 1000 Da and oligomer content < 1%)	520 000– 45 000 000 <sup>bd</sup>	530 000–1 200 000 <sup>ef</sup>	241 000– 575 000 <sup>eg</sup>	200 000– 450 000 <sup>eh</sup>
$\begin{array}{l} Molecular weight distribution \\ MW \div number average M_n (M_n \\ and heterogeneity of MW \\ distribution indicate if majority \\ are >1000 \ or <1000 \ Da, which \\ could penetrate the cell) \end{array}$	2.3 <sup>i</sup>	1.4–2.7 <sup>f</sup>	1.55–2.09 <sup>9</sup>	1.7 <sup>j</sup>
Wt % oligomer (see Figure 2) (<5% for <1000 Da oligomers, <2% for <500 Da oligomers)	Negligible	Negligible	Negligible	Negligible
lonic character (cationic polymers associated with aquatic toxicity; polycationic with adverse human health effect)	Neutral	Neutral	Neutral	Neutral
RFGs <sup>k</sup> (some highly reactive functional groups associated with adverse human health and ecotoxicology effects, e.g., acrylates, isocyanates, anhydrides, aziridines)	<1 (see section Reactive functional groups and RFG ratio to MW)	<1 (see section Reactive functional groups and RFG ratio to MW)	<1 (see section Reactive functional groups and RFG ratio to MW)	<1 (see section Reactive functional groups and RFG ratio to MW)
FGEW <sup>k</sup> (typical value) (the lower the FGEW, the more reactive the polymer and the higher the potential for health and environmental impact)	>10 <sup>5</sup> -10 <sup>7</sup>	>10 <sup>5</sup> -10 <sup>6</sup>	>105	>10 <sup>5</sup>
Low molecular weight leachables (MW < 1000 Da able to enter cell)	<1 ppm	No active leachables by USP class VI <sup>I</sup> (121 °C)	No active leachables by USP class VI <sup>I</sup> (121 °C)	No active leachables by USP class VI <sup>I</sup> (121 °C)
Residual monomers (monomers have lower MW than polymers; typically more hazardous than polymers)	<1 ppm	<50 ppb	<50 ppb	<50 ppb
Ratio of residual monomers to molecular weight (typical value) (more low MW monomer content per mole increases bioavailability and hazard potential)	$\sim 10^{-13}$ to $10^{-15}$	$\sim 10^{-13}$ to $10^{-14}$	~10 <sup>-13</sup>	~ 10 <sup>-13</sup>
Structural similarities to RFG of concern (increases potential risk of adverse effects)	None	None	None	None
Reference standard see also ISO 1133 (ISO 2011), ISO 12086 (ISO 2006)	ASTM D 4894 (ASTM 2015a), D 4895 (ASTM 2015b)	ASTM D 2116 (ASTM 2016a)	ASTM D 3159 (ASTM 2015c)	ASTM D 3307 (ASTM 2016b)
				(Continued)

 Table 2.
 Fluoropolymers and PLC criteria

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		Table 2. (Continued)		
		Fluo	propolymers	
	PTFE	ETFE	FEP	PFA
Assessment criteria <sup>a</sup>	CAS 9002-84-0	CAS 25038-71-5, 68258-85-5	CAS 25067-11-2	CAS 26655-00-5, 31784-04-0
Physical-chemical properties				
Water solubility (per USP 2011) (water solubility <10 mg/L showed generally low health concerns; 10 mL/L to 10000 mg/ L had potential health concern)	Practically insoluble or insoluble (1 × 10 <sup>-5</sup> mg/L)	Practically insoluble or insoluble	Practically insoluble or insoluble	Practically insoluble or insoluble
Octanol-water partition coefficient, $K_{OW}$ (higher $K_{OW}$ associated with lipophilicity and a high potential to bioaccumulate or bioconcentrate)	NA	NA	NA	NA
Particle size (median mass aerodynamic diameter,	100–500 µm (powders)	50–250 µm (powders)	50–250 µm (powders)	50–250 μm (powders)
MMAD, should be $>5\mu\text{m}$ )	—	2–4 mm (pellets)	2–4 mm (pellets)	2–4 mm (pellets)
Stability				
Hydrolysis (breaking into M <sub>n</sub> < 1000 Da increases hazard potential)	Stable	Stable	Stable	Stable
Light (hv) (breaking into M <sub>n</sub> < 1 000 Da increases hazard potential)	Stable	Stable	Stable	Stable
Oxidation (breaking into M <sub>n</sub> < 1000 Da increases hazard potential)	Stable	Stable	Stable	Stable
Biodegradation (aerobic and anaerobic) (breaking into M <sub>n</sub> < 1000 Da increases hazard potential)	Stable	Stable	Stable	Stable
Thermal stability at normal foreseeable use maximum continuous temp (°C) (breaking into $M_n < 1000$ Da increases hazard potential)	260	150	200	260
Meets PLC criteria <sup>a</sup> (Y/N)	Yes	Yes	Yes	Yes

ASTM = American Society for Testing and Materials; CAS = Chemical Abstracts Service; Da = dalton; ETFE = ethylene tetrafluoroethylene; FEP = fluorinated ethylene propylene; FGEW = functional group equivalent weight; ISO = International Organization for Standardization; MMAD = median mass aerodynamic diameter; Mn = number average molecular weight; MW = molecular weight; MWD = molecular weight distribution; OECD = Organisation for Economic Cooperation and Development; PFA = perfluoroalkoxy polymer; PFPE = perfluoropolyether; PLC = polymer of low concern; PTFE = polytetrafluoroethylene; PVDF=polyvinylidene fluoride; PVF=polyvinyl fluoride; RFG=reactive functional groups; USEPA=US Environmental Protection Agency; USP=US Pharmacopeia.

<sup>a</sup>See OECD 2009 and BIO by Deloitte 2015 for details on characteristics of a "polymer of low concern."

<sup>b</sup>Molecular weight is number average molecular weight.

<sup>c</sup>Berry and Peterson 1951; Doban et al. 1956.

<sup>d</sup>Suwa et al. 1973.

<sup>e</sup>Molecular weight is weight average molecular weight.

<sup>f</sup>Tuminello et al. 1993.

<sup>g</sup>Tuminello 1989.

<sup>h</sup>Putnam 1986. <sup>i</sup>Chu et al. 1989.

<sup>j</sup>Frick et al. 2012.

<sup>k</sup>For definition of reactive functional group; lists of low-, moderate-, and high-concern functional groups; and FGEW limits, see USEPA Polymer Exemption Guidance Manual (USEPA 1997b), BIO by Deloitte 2015 (p 191–192), and USEPA 2010. See Supplemental Data.

In the USP<88> testing for "class VI," 2 g of the plastic (e.g., FEP, ETFE, or PFA) were extracted at 121 °C in: 1) 0.9% sodium chloride solution, 2) sesame oil, NF, 3) alcohol saline, and d) polyethylene glycol. The acute systemic toxicity and intracutaneous reactivity tests were conducted with those extracts. The intramuscular implantation was conducted with the plastic. Passing these 3 tests indicates that any leachables were not released in concentrations capable of causing these adverse effects, but does not result in a quantitative concentration of leachables. (See USP 2018.)

Note: The following are not addressed in this paper: PFPEs, side-chain fluorinated polymers, fluoroelastomers, PVF, and PVDF.

Molecular weight, number average molecular weight, MW distribution, and % oligomer < 1000 Da

The number average molecular weight (M<sub>n</sub>) and oligomer content are the most commonly used criteria for PLC assessment. The EU assessment report (BIO by Deloitte 2015) states that the "most potential health concern polymers have a number average molecular weight, Mn, < 1000 Da and oligomer content >1%." The higher the oligomeric content, the more likely a polymer is to be a health or ecotoxicological (OECD 2009, p 9). In fact, when comparing the potential health concern of polymers with varying percent oligomer content, "...the distribution of potential health concern polymers showed an increased incidence of higher oligomer content that began at 5% for <1000 Da and 2% for <500 Da oligomeric content" (OECD 2009, p 24).

Molecular weight (MW) is an important predictor of biological effect because very large molecules (>1000–10000 Da) are too large to penetrate cell membranes (Supplemental Data in Beyer 1993, p 14). Because large molecular weight polymers cannot enter the cell, they cannot react with "target organs," such as the reproductive system, and are not bioavailable. "Therefore, as the  $M_n$  of a polymer increases, a reduced incidence of potential health concern effects might be expected" (OECD 2009, p 20).

An additional PLC consideration is the weight percent oligomers <1000 Da. Oligomers may be composed of, for example, dimers, trimmers, and tetramers, meaning they have 2-, 3-, and 4-monomer units, respectively. The EU report (BIO by Deloitte 2015) concluded that most potential health concern polymers have  $M_n$  of <1000 Da and oligomer content of >1%: "...the distribution of potential health concern polymers showed an increased incidence of higher oligomer content that began at 5% for <1000 Da and 2% for <500 Da oligomeric content" (OECD 2009, p 24).

Molecular weight distribution (MWD), also known as "polydispersity index," measures the heterogeneity of size of polymer molecules in a polymer. The MWD is an important parameter for predicting potential biological effects of polymers because although  $M_n$  may be a large value, low MW oligomers <1000 Da may be present, which could penetrate the cell.

#### Electrical charge (ionic character)

Electrical charge or ionic character can be anionic, cationic, amphoteric, or nonionic. Specifically, cationic polymers have been associated with aquatic toxicity (Auer et al. 1990; USEPA 1997a). Polycationic polymers that are water soluble or dispersible are of concern due to adverse human health (inhalation) effects (NICNAS 2016).

#### Reactive functional groups and RFG ratio to MW

A "reactive functional group" (RFG) is defined as an atom or associated group of atoms in a chemical substance that is intended or can be reasonably anticipated to undergo facile chemical reaction (USFR 2012). Some highly reactive functional groups (or a high ratio of RFGs per mole) have been associated with adverse human health and ecotoxicology (e.g., acrylates, methacrylates, isocyanates, anhydrides, aziridines) (USEPA 2010). Methods have been demonstrated to identify the functional end groups on fluoropolymers (Pianca et al. 1999).

The functional group equivalent weight (FGEW) is used to determine if the RFGs in a polymer are substantially diluted by polymeric material to allow the polymer to be a PLC (USEPA 1997b). The FGEW of a polymer is defined as the ratio of the  $M_n$  to the number of functional groups in the polymer. It is the weight of a polymer that contains 1 formula weight of the functional group. The FGEW is used as an indication of the degree of reactivity of the polymer; the lower the FGEW, the more reactive the polymer and the higher the potential for health and environmental impact (OECD 2009, p 10).

#### Low MW leachables

Low MW leachables are chemical molecules, either inorganic or organic, that migrate (i.e., leach) out of the polymer. These could be residual monomers or oligomers resulting from incomplete polymerization processes, surface residues, or other chemicals used in the manufacturing processes (e.g., initiators, catalysts, chain transfer agents, surfactants). Chemical analysis, by techniques such as thermal gravimetric analysis (TGA), gas chromatography mass spectrometry (GC-MS), or liquid chromatography mass spectrometry (LC-MS) are used to identify low MW leachables.

Low MW leachables are critically important to the potential for a polymer to affect health and the environment, given that they may be able to migrate out of the polymer and cross cell membranes to potentially react with biomolecules. In a report to the EU (BIO by Deloitte 2015) the polymer policies for 10 countries around the world, including the EU REACH handling of polymers, were reviewed. The report concluded that "Polymers with <1% MW <1000 Da and low water extractivity are not able to cause systemic effects which are toxicologically or ecotoxicologically relevant."

Monomers, by nature, are reactive. Unreacted monomer left in a polymer may migrate out of the polymer to react with biomolecules to cause potential adverse effects. Regulatory authorities (BIO by Deloitte 2015) and the OECD Expert Group on Polymers (OECD 2009) agree that the residual monomer content of a polymer is critical to determining if it qualifies to be a PLC.

#### Particle size

Particle size is also a PLC criterion. Particles that are small enough to reach the deep lung upon inhalation are often associated with adverse health effects. Therefore, to qualify as a PLC, median mass aerodynamic diameter (MMAD) of the polymer particle size should be greater than  $5 \,\mu$ m.

#### Structural and elemental composition

In the United States, Chemical Categories of Concern are the result of the review of new chemicals by the USEPA under the TSCA (see https://www.epa.gov/reviewing-new-chemicalsunder-toxic-substances-control-act-tsca/chemical-categoriesused-review-new). New chemicals submitted to the USEPA under the TSCA for addition to the US chemical inventory are reviewed for potential chemical, physical, and biological effects (environmental and mammalian). The USEPA groups Premanufacture Notice (PMN) chemicals with shared chemical and toxicological properties into categories, enabling both PMN submitters and USEPA reviewers to benefit from the accumulated data and past decisional precedents, allowing reviews to be facilitated. The categories describe the molecular structure, boundary conditions such as MW, equivalent weight, the log of the octanol-water partition coefficient, log P, or water solubility, and standard hazard (mammalian and ecological) and (environmental) fate tests to address concerns. The categories include chemicals for which sufficient history has been accumulated so that hazard concerns and testing recommendations vary little from chemical to chemical within the category. (See Supplemental Data, p 30, for details on USEPA's chemical categories.)

#### Elemental composition

The elemental composition is a factor in the assessment of the eligibility of polymers for reduced notification requirements. The exclusion of polymers under this step is not a conclusion of hazard but a determination that the elemental composition does not fall within the parameters of the polymer set under which this rule was formulated, and consequently, these polymers would have to follow the standard notification and review process. These elemental requirements differ across jurisdictions as covered in the report to the EU on global regulatory approaches to polymer assessment (BIO by Deloitte 2015). For example, in the EU under REACH it is proposed that polymers composed from among these elements, covalently bound to C, have reduced hazard: H, N, O, Si, S, F, Cl, Br, or I (BIO by Deloitte 2015). In contrast, the USEPA Polymer Exemption Rule states that a polymer is eligible for reduced agency review when it has at least 2 of the following elements: C, H, O, N, S, or Si (USFR 1995).

# Water and lipid solubility and the octanol-water partition coefficient

Water solubility is the extent to which a compound will dissolve in water. According to the OECD 2009 meeting of the Expert Group on Polymers, polymers with "negligible" water solubility, or those described as "hydrophobic" have been represented with a water solubility of 0.000001 mg/L  $(1 \times 10^{-6} \text{ mg/L}; \text{ assigned arbitrarily})$  (OECD 2009). That is equivalent to 1 ppt, a very conservative definition.

Based on the data set studied, the OECD Expert Group on Polymers concluded "A higher proportion of polymers with intermediate water solubility values (10 mL/L-10000 mg/L) displayed potential health concern. Polymers with water solubility <10 mg/L showed generally low health concerns" (OECD 2009, p 10). Although not a solubility metric, a polymer capable of absorbing its weight in water was associated with increased inhalation cancer risk in rats (OECD 2009).

The octanol-water partition coefficient ( $K_{OW}$ ) is another criterion to assess chemicals and their environmental and health impact. The  $K_{OW}$  is a physical-chemical property at equilibrium to represent the lipophilic or hydrophilic nature

of a chemical, the distribution of a compound in octanol, representing the lipophilic nature, to its solubility in water, representing the aqueous nature. The higher the  $K_{\rm OW}$ , the more lipophilic the compound. Typically, a  $K_{\rm OW}$  >5000 or a log  $K_{\rm OW}$  >5 means high lipophilicity and, thus, a high potential to bioaccumulate or bioconcentrate. Numerous studies showed that  $K_{\rm OW}$  was useful for correlating structural changes of drug chemicals with the change observed in some biological, biochemical, or toxic effect (LaGrega et al. 2010). It has been found to be related to water solubility, soil or sediment adsorption coefficients, and bioconcentration factors for aquatic life. According to the Stockholm Convention, a bioconcentration factor of >5000 and a log  $K_{\rm OW}$  >5 is used as a criterion for bioaccumulation.

#### Stability

Stability is resistance to physical, chemical, or biological transformation. Loss of stability in the polymer breaks it down into smaller pieces, producing low MW species. As was previously described in the Polymer of Low Concern section under the *Molecular weight*, *number average molecular weight*, *MW distribution*, *and* % *oligomer* < 1000 Da heading, molecules with  $M_n$  <1000 Da are capable of crossing cell membranes, making unstable polymers potentially hazardous to health and the environment.

#### Abiotic stability

Polymers are stable; monomers are not. Abiotic degradation may involve sunlight, water, or oxygen. Photochemical transformation is a reaction involving the radiation energy of sunlight (ultraviolet radiation) that may break a bond in a molecule to change it to another chemical entity. Hydrolytic degradation of polymers is another potential way to break the polymer bonds, creating smaller oligomers that may be bioavailable. Chemical oxidation is a reaction involving the loss of electrons from 1 atom to another.

#### Biotic stability: aerobic, anaerobic, and in vivo

Biotic stability is assessed by whether or not the polymer is degraded by microorganisms under oxygenated (aerobic) or anoxic (anaerobic) conditions; in vitro and in vivo stability studies demonstrate this. In vivo biodegradation involves the breaking of the polymer bonds by the action of bacteria, enzymes, and oxidants within the organism.

#### Thermal stability

Thermal stability of a polymer can be assessed when used as intended under normal, foreseeable use conditions or in extreme temperatures during disposal, such as by incineration. Thermal stability testing may involve Thermal Gravimetric Analysis (TGA), which determines mass loss over time and temperature of a test substance.

#### ASSESSMENT OF FLUOROPOLYMERS ACCORDING TO PLC CRITERIA

Characteristics of a PLC have been described in the preceding section. These criteria represent the combined

experience and knowledge of global regulatory authorities on factors demonstrated to be predictive of health and environmental hazards of polymers (OECD 2009; BIO by Deloitte 2015). Four fluoropolymers were assessed according to the PLC criteria. The results are summarized in Table 2, and an expanded discussion on specific criteria is provided in the remainder of this section.

#### Polymer composition

Fluoropolymers satisfy the PLC criterion of polymer composition. Polytetrafluoroethylene is a homopolymer of tetrafluoroethylene (TFE). Polytetrafluoroethylene can be a homopolymer (1 monomer) or it can be a modified homopolymer containing TFE widely and not more than 1% of another fluoromonomer (see ASTM 2015). Polytetrafluoroethylene contains only C and F having a  $-CF_{2}$ backbone terminated on both ends of each polymer chain with -CF<sub>3</sub>. In unique cases, based on production method and ingredients used, commercial PTFE may have end groups that contain O, H, N, or S, depending on the initiator or chain transfer agent used in polymerization (Pianca et al. 1999). Polytetrafluoroethylene meets the compositional criterion to be a PLC.

#### Molecular weight, Mn, MWD, and % oligomer < 1000

Fluoropolymers satisfy the PLC criterion of MW, M<sub>n</sub>, MWD, and % oligomer <1000. Fluoropolymers are practically insoluble in water and all organic solvents. Therefore, standard MW methods are not applicable for fluoropolymers like PTFE and have been replaced by standardized indirect methods that use specific gravity and melt flow index to determine MW of PTFE and fluoropolymers (see Supplemental Data, p 27-28). Standard Specific Gravity (SSG) and Melt Flow Rate (MFR) are more conveniently and frequently used with fluoropolymers rather than rheological and dynamic light scattering methods (Chu et al. 1989; Starkweather and Wu 1989; Tuminello 1989; Tuminello et al. 1993). Polytetrafluoroethylene has an  $M_n$  of 500000 to 9000000 Da (Berry and Peterson 1951; Doban et al. 1956; Suwa et al. 1973; Putnam 1986; Chu et al. 1989; Tuminello 1989; Tuminello et al. 1993; Frick et al. 2012). Therefore, PTFE, as a very high molecular weight polymer, cannot cross cell membranes, is not bioavailable, and cannot bioaccumulate or be toxic (see Supplemental Data, p 14). High molecular weight fluoropolymers, such as PTFE, therefore meet the PLC criterion for having MW that prevents them from entering the cells. Polytetrafluoroethylene has negligible (<<1%) oligomeric content (Starkweather and Wu 1989), as does FEP (Figure 2.) In summary, fluoropolymers are high molecular weight polymers with narrow MWD and negligible oligomer content.

#### Reactive functional groups and RFG ratio to MW

Fluoropolymers satisfy the PLC criterion of RFGs and RFG ratio to MW. Polytetrafluoroethylene most typically has a terminal –CF<sub>3</sub> group that is not an RFG. When this is not the case, the most common terminal group is -COOH, which is

categorized by the USEPA as a low-concern functional group. In unique cases, based on production method and ingredients used, PTFE may have end groups that may contain O, and H, N, or S, depending on the initiator or chain transfer agent used in polymerization. Fluoropolymers have a very high MW, which yields an FGEW on the order of 10<sup>5</sup> or more, well beyond the FGEW threshold of concern.

#### Low MW leachables

0.5

0.4

0.3

0.2

0.1

0.0

10<sup>2</sup>

~(m)\*Mw (

1000 Da

10<sup>3</sup>

Negligible

oligomer content

< 1000 Da

10<sup>4</sup>

Fluoropolymers satisfy the PLC criterion of low MW leachables. Concentration of leachables from fluoropolymers, particularly PTFE "fine powder" (ASTM [2015] 4895-16 Type I fine powder definition), are typically very low (<1 ppm) (see Supplemental Data). This finding can be explained by the sensitivity of the PTFE polymerization reaction to contamination and is due to the postpolymerization processing steps aggressively exercised to wash out residuals and drive off volatiles. In order to achieve high MW polymerization of TFE, all traces of telogenic H- or Cl-bearing impurities must be removed (Ebnesajjad 2011; Supplemental Data).

In the analysis done on PTFE (see Supplemental Data, p 32), residual TFE monomer was not detected in PTFE resin by headspace GC-MS with a limit of detection of 1 ppm. In addition, publicly available analytical data from independent industry authorities demonstrate that TFE is not detected in finished articles made from fluoropolymers at detection limits down to about 0.01 ppm wt/wt (SPI 2005). Table 3 compares the molecular weight and the 8-h time weighted average (TWA) (American Conference of Governmental Industrial Hygienists [ACGIH], threshold limit value [TLV]), for monomers used to make fluoropolymers (ACGIH 2010). The TWAs are the exposure levels to which a worker could be exposed in an 8-h shift without adverse effects. The monomers have significantly lower MW, have lower TWAs, and are reactive. Note that the fluoropolymers are high MW, have no TWAs, and are inert. Table 3 illustrates that polymers do not have the same health hazards or MWs as their monomers.



Substance	CAS Nr	Molecular weight	ACGIH TLV 8-h TWA
Monomer: TFE	116-14-3	100	2 ppm
Monomer: Ethylene	74-85-1	28	200 ppm
Monomer: HFP	116-15-4	150	0.1 ppm
Monomer: PPVE	1623-05-8	266	200 ppm (vendor limit)
Polymer: PTFE	9002-84-0	389 000-45 000 000	None
Polymer: ETFE	25038-71-5, 68258-85-5	530 000-1 200 000	None
Polymer: FEP	25067-11-2	241 000-575 000	None
Polymer: PFA	26655-00-5, 31784-04-0	200 000-450 000	None

Table 3. Fluoropolymer and monomer molecular weight and TLV data

 $\label{eq:account} ACGIH = American Conference of Governmental Industrial Hygienists (ACGIH 2010); CAS = Chemical Abstracts Service; ETFE = ethylene tetrafluoroethylene; FEP = fluorinated ethylene propylene; HFP = hexafluoropropene; PFA = perfluoroalkoxy polymer; PVE = perfluoropropylvinyl ether; PTFE = polytetrafluoroethylene; TFE = tetrafluoroethylene; TLV = threshold limit value; TWA = time weighted average.$ 

#### Elemental composition

Fluoropolymers meet the widely accepted elemental composition criterion (BIO by Deloitte 2015). The USEPA, in updating its Polymer Exemption Rule, which applies to new polymers only, changed some review procedures to address certain side-chain fluorinated polymers that may degrade into small, mobile, and persistent substances (USFR 2010). This has contributed to confusion regarding the assessment of fluoropolymers. The exclusion of polymers under this step is not a conclusion of hazard, but a determination that the elemental composition does not fall within the parameters of the polymer set under which this rule was formulated, and consequently, these polymers would have to follow the standard notification and review process.

When USEPA updated the polymer exemption rule in 2010, the agency excluded polymers containing  $-CF_3$  or larger chains that are covalently bound to C. The agency's rationale for the change was "...because the Agency has receiving information which suggests that polymers containing PFAS (perfluoroalkyl sulfonates) or PFAC (perfluoroalkyl carboxylates) may degrade and release fluorochemical residual compounds in the environment. Once released, PFAS or PFAC are expected to persist in the environment, may bioaccumulate, and may be highly toxic..." (USFR 2006).

Although USEPA recognized that PFAS and PFAC chemicals with longer C chain lengths (C7 and longer) may be of greater concern, it stated that there is insufficient evidence at this time, however, to definitively establish a lower C chain length limit to meet the "will not present an unreasonable risk" finding, which is the determination necessary to support an exemption under section 5(h)(4) of TSCA. The USEPA believes that it is possible for polymers containing these other types of perfluoroalkyl moieties to also degrade over time in the environment, thereby releasing the perfluoroalkyl moiety (USFR 2006).

The updated USEPA polymer exemption definition in 2010, summarized in the Objective and Rationale section for the Final Rule, may imply that new fluoropolymers with pendant or terminal –CF3 groups, such as FEP, do not meet

the polymer exemption eligibility for reduced PMN reporting (USFR 2010). However, the summary definition in USFR (2010) lacks critical context found in the preamble to the Final Rule, which elaborates the conditions that would be necessary to exclude a perfluoro chemical from the polymer exemption:

- The first condition is cited above, "...polymers containing PFAS (perfluoroalkyl sulfonates) or PFAC (perfluoroalkyl carboxylates)..." where the C or S atom is an integral part of the polymer molecule; <u>and</u>
- the second condition notes that, polymers containing fluorotelomers or "...perfluoroalkyl moieties that are covalently bound to either a carbon or sulfur atom where the carbon or sulfur atom is an integral part of the polymer molecule can be attached to the polymers using conventional chemical reactions."

For the PFAS and PFAC as described by USEPA, the agency offers a clarification about the nature of the linkage, stating "How these materials are incorporated into the polymer is immaterial (they may be counter ions, terminal/ end capping agents, or part of the polymer backbone)" (USFR 2010). The key characteristic is the presence of a -CF3 group that is attached to, or forms part of, the polymer backbone and "this link (between the polymer backbone and the -CF3 group) is susceptible to degradation and cleavage." (USFR 2010). Thus, in USEPA's review, the presence of-CF3 group is important because it is a structural alert to consider potential degradation products. The USEPA will make a determination whether the potential degradation of the polymer in question presents an unreasonable risk to health and the environment under TSCA. As shown in Table 2, these fluoropolymers are not subject to degradation.

# Water and lipid solubility and the octanol-water partition coefficient

Fluoropolymers, such as PTFE, are not soluble in octanol or water. Therefore, it is not possible to measure or calculate a

 $K_{OW}$ . Because solubility in octanol is predictive of lipid solubility, PTFE cannot dissolve in cell membrane lipids to gain access to cellular contents, nor is it small enough to enter the cell due to its very high MW. Because PTFE cannot enter the cells, it is not capable of bioaccumulation or bioconcentration in aquatic life.

#### Stability

Under normal, foreseeable uses, fluoropolymers are stable. Stability is resistance to physical, chemical, or biological transformation. Loss of stability in the polymer breaks it down into smaller pieces, producing low MW species. Molecules with  $M_n < 1000$  Da are capable of crossing cell membranes, making unstable polymers potentially hazardous to health and the environment. Fluoropolymers, in general, have exceptional chemical and thermal stability; that is why they are so unique and useful. This is due to very strong C-F bonds that are stable under even extreme conditions (Gangal and Brothers 2015). Polytetrafluoroethylene is inert and chemically resistant to all solvents except molten alkali metals, chlorine trifluoride, and oxygen difluoride. Polytetrafluoroethylene, as a representative fluoropolymer, has the best chemical resistance of all currently known polymers and is insoluble in all known solvents, including water (Drobny 2006).

#### Abiotic stability

Polymers are stable; monomers are not. Photochemical transformation is a reaction involving the radiation energy of sunlight (ultraviolet radiation) that may break a bond in a molecule to change it to another chemical entity. Although PTFE will rapidly degrade in ionizing radiation (e.g., gamma radiation or high energy electron-beam radiation), it is resistant to photolysis (Drobny 2006). Photoinduced reactions with fluoropolymers do not occur. In addition, hydrolysis is a reaction involving the breaking of a bond in a molecule using water. The fluorine envelope surrounding the C backbone of PTFE is very hydrophobic. Fluoropolymers, such as PTFE, are hydrolytically stable, water resistant, and are not subject to hydrolysis catalyzed degradation (Arkles 1973). Finally, chemical oxidation is a reaction involving the loss of electrons from one atom to another. Because the C-F bond is one of the strongest known, and F is the most electronegative element, the C-F bond is thermodynamically stable, unfavorable to lose electrons (i.e., to oxidize) (Arkles 1973).

#### Biotic stability: aerobic, anaerobic and in vivo

Fluoropolymers like PTFE are biologically inert and not degraded by microorganisms under oxygenated (aerobic) or anoxic (anaerobic conditions); in vitro and in vivo studies demonstrate this. In vivo degradation involves the breaking of the polymer bonds due to bacteria and other enzymes and oxidants. For example, PTFE hernia patches explanted from patients and examined by scanning electron microscopy, attenuated total reflectance Fourier transform infrared spectroscopy, modulated differential scanning calorimetry, and optical microscope showed no degradation in vivo (King et al. 2013).

#### Thermal stability

Fluoropolymers, when used as intended under normal, foreseeable use conditions as specified in Table 2 (or "continuous processing temperature") are thermally stable (Puts et al. 2014). The fluoropolymer industry has provided significant information on appropriate use of fluoropolymers (SPI 2005). Thermal gravimetric analysis determines mass loss over time and temperature of a test substance. Polytetra-fluoroethylene is one of the most thermally stable polymers. Polytetrafluoroethylene's continuous processing temperature is 260°C (SPI 2005). This means that PTFE could remain for decades at 260°C and not decompose (SPI 2005 see percent mass lost per hour at maximum continuous processing temperature).

Outside of normal, foreseeable use conditions (also known as "misuse"), when fluoropolymers are held at temperatures above their recommended processing temperatures, they degrade. Upon decomposition, fluoropolymers generate volatile degradation products (SPI 2005). At 450 °C, the decomposition of PTFE "only proceeds at a rate on the order of one percent per hour. It is not until considerably above the polymer first-order transition temperature (329°C) that substantial decomposition is observed" (Arkles and Bonnett 1974). As the temperatures increase above recommended processing temperatures, the rate of generation rises and may sufficiently degrade the polymer to produce hazardous gaseous byproducts and polymer (particulate) fume fever (SPI 2005). Temperature, availability of O, the physical form of the polymer article, and the residence time at elevated temperature factor into the ultimate nature of the decomposition products (SPI 2005), mainly fluoroalkenes, hydrogen fluoride, oxides of C, and lower molecular weight fluoropolymer particulates. For PTFE, TFE is the principle gaseous product observed at temperatures near 330 °C. See Supplemental Data for additional information regarding overheating PTFE.

#### PRODUCT-SPECIFIC REGULATORY REQUIREMENTS

Certain product-specific regulations, such as those for medical devices and food contact for the United States and the EU, require the development of additional data beyond what is required to conduct a PLC evaluation. The following text will discuss food contact requirements for the United States and the EU, and medical device requirements.

## Data requirements for food, pharmaceutical, and medical device applications

There are country-specific data requirements for fluoropolymer use in food, pharmaceutical, and medical device applications because the intended use of these products has the potential to directly or indirectly introduce the product into the human body. An extensive fluoropolymer data set has been developed by W.L. Gore for these uses. The clinical history of the safe implantation of more than 40 million PTFE medical devices over 40 y, extensive toxicity data, preclinical data, and chemical extractables and migration testing confirmed that fluoropolymers are not bioavailable. Although the data requirements have evolved over time for contacting food, pharmaceuticals, or use in medical devices, the data (some of which are provided in the present article, the Supplemental Data for the present paper, regulatory submissions, and product literature) confirm the conclusion that fluoropolymers are safe for these intended uses and support the conclusion that fluoropolymers should be considered PLCs.

# Polymer of low concern data and US and European Union food contact requirements

In general, the data required to support a PLC determination are helpful, but insufficient to qualify a material for food contact use. Submissions to the US Food and Drug Administration (USFDA) to support new food contact substances require extensive data submissions, including, for example, the nature and amount of nonvolatile extractives (USFDA 2017). Fluoropolymers, however, are not new substances in applications where they come in contact with food and have longstanding acceptance by regulators. In the United States, the USFDA is responsible for regulation of materials that come in contact with food and are considered "indirect food additives," specifically polymers (USFR 2016a). Food storage or food packaging materials, such as the fluoropolymers PTFE, FEP, and PFA, are "perfluorocarbon resins" acceptable for use by application and material type, provided they meet the extractable limits specified in the regulation (USFR 2016b).

Similarly, the European Food Safety Agency (EFSA) provides recommendations to the European Commission (EC) within the EU for the regulation of food contact materials, requirements for their evaluation, and authorization of acceptable uses (EC 2004). Polymer clearance is based in part upon the fact that polymers will not migrate into food due to their high molecular weight. The EU focuses on potential low molecular weight moieties, such as residual monomers and leachables, rather than on the polymer itself. The EU food contact regulation requires that monomers, other starting substances, and additives used to produce food contact polymers should be risk assessed and authorized (EU 2011). The regulation lists authorized substances that are permitted to have food contact (EU 2011). This regulation also sets the specific migration limit (SML), which is the maximum permitted amount of substance in food that has been determined not to pose a risk to human health, specifically for individual chemicals (e.g., monomer) (EU 2011). Note that these limits exist whether or not the substance is present in the food contact material (FCM). The monomers, other starting substances, and additives used to produce fluoropolymers for food contact (e.g., PTFE, FEP, and PFA) have been authorized for food contact uses. Representative SMLs for these monomers, additives, and starting substances relevant for fluoropolymers are given in the Supplemental Data (p 14).

Polymer of low concern data and medical device regulatory requirements

Satisfaction of the PLC criteria is insufficient to satisfy medical device requirements. Formal biocompatibility evaluations are required by the USFDA and other global regulatory authorities to support submissions for approval of medical devices and pharmaceuticals (e.g., combination products, such as drug-eluting stents or prefilled single-dose syringes). The International Organization for Standardization (ISO) 10993 Biocompatibility of Medical Devices standards describe a broad array of biocompatibility tests that require consideration for each new device or significant changes to existing devices (ISO 2009). Over the years, medical devices containing PTFE (or expanded PTFE) have been evaluated using ISO 10993 and US Pharmacopeia (USP) Class VI standards (USP 2011) and have been determined to be biocompatible in their intended uses.

The ISO 10993 standards provide guidance for evaluation of the biological response to a medical device. The USFDA, as well as most international regulatory agencies, recognizes and uses ISO 10993 standards to guide safety evaluations of medical devices submitted for their approval. Requirements to demonstrate the biocompatibility of medical devices are set forth in ISO 10993-1, and regulatory authority-specific requirements (e.g., PMDA 2003; USFDA 2016). In addition, country pharmacopeial organizations also specify testing required for biological reactivity of drugs (e.g., US Pharmacopiea, EU Pharmacopiea, Japan Pharmacopiea). The ISO requirements are categorized by the nature of body contact (e.g., mucosal membrane, circulating blood, tissue, bone, dentin) and duration of contact (<24 h,  $\geq$ 1 d  $\leq$ 30 d, >30 d). Depending on the nature and duration of contact, requirements include cytotoxicity, irritation, sensitization, implantation, acutesubchronic-chronic systemic toxicity, material-mediated pyrogenicity, hemocompatibility (e.g., hemolysis, thrombogenicity, and complement activation), genotoxicity (in vitro and in vivo), carcinogenicity, and developmental toxicity. (See Supplemental Data p 15 for a list of ISO 10993 biocompatibility tests.)

# MEETING PLC CRITERIA PRECLUDES A FINDING THAT A CHEMICAL IS OF HIGH CONCERN

Just as regulatory frameworks have mechanisms to identify materials of low concern such as PLCs, they also have mechanisms to identify chemicals of high concern. For example, under REACH, a mechanism exists to identify substances of very high concern (SVHCs). Having demonstrated that fluoropolymers like PTFE should be considered PLCs, we will also demonstrate that these fluoropolymers cannot be SVHCs under REACH, do not meet the PM and PMT criteria proposed by UBA, and do not meet the criteria for listing as a POP under the Stockholm Convention. Fluoropolymers and EU REACH SVHC, CMR, PBT, vPvB, and endocrine disrupting chemical (EDC) criteria

According to the European Chemicals Agency (ECHA), SVHCs are defined in Article 57 of Regulation (EC) Nr 1907/ 2006 ("the REACH Regulation") (EC 2006) and include substances that are

- "Carcinogenic, mutagenic or toxic to reproduction (CMR), meeting the criteria for classification in category 1 or 2 in accordance with Directive 67/548/EEC. This directive was replaced in beginning of 2009 by the new EU regulation (EC) No 1272/2008 on classification, labeling and packaging of chemical substances and mixtures, the so-called CLP Regulation. According to the new CLP Regulation these substances shall be classified as 1a or 1b."
- "Persistent, Bioaccumulative and Toxic (PBT) or very Persistent and very Bioaccumulative (vPvB) according to the criteria in Annex XIII of the REACH Regulation."
- "Identified, on a case-by-case basis, from scientific evidence as causing probable serious effects to human health or the environment of an equivalent level of concern as those above (e.g., EDCs)."

Under REACH, polymer substances are not registered, but the monomers they are composed of are registered, and the registration must be supported by data submissions that are tiered on the basis of tonnage (see EC 2006, Annex VII). The REACH definition of polymer includes materials with as few as 3 repeating units. But such a small molecule would not meet common industry standard definitions for fluoropolymers (ASTM 2015). It is highly unlikely that fluoropolymers meeting the PLC criteria would exhibit the criteria of an SVHC under REACH. Fluoropolymer data developed for other regulatory needs support the predictive value of the PLC assessment criteria and demonstrate the low hazard potential of this class of PFAS. Due to their physical-chemical properties, PLCs are not bioavailable to cause toxicity or to bioaccumulate. Toxicity study data on PTFE in the Supplemental Data (p 15–27), for example, demonstrate a lack of toxicity, including genotoxicity. Although fluoropolymers are persistent, they are not bioaccumulative or toxic and therefore do not meet the PBT criteria.

#### Fluoropolymers and German UBA-proposed PMT criteria

As regulatory frameworks continue to evolve, more work is needed in the area of PFAS classification to ensure that regulations are appropriate in scope and proportionality. Although some well-known PFAS would qualify as PM or PMT substances as proposed by the UBA (2017), fluoropolymers do not possess these characteristics. Although fluoropolymers are highly stable (persistent), they do not meet the criteria to be mobile or toxic. To demonstrate this point, PTFE, a high molecular weight fluoropolymer and a member of the PFAS group, is assessed (in the last 4 paragraphs of this section) according to the proposed UBA criteria (UBA 2017). Briefly, the changes to PM and/or PMT assessment proposed by UBA address applicability, persistence, mobility, and toxicity. The UBA proposes an initial step involving assessment of the chemical composition of a substance to determine if the substance is within the applicability domain of the proposed new assessment criteria. The UBA notes that currently only identifiable organic and organometallic chemicals are considered, and purely inorganic substances or substances of unknown or variable compositions, complex reaction products, or biological material are excluded (UBA 2017).

With respect to persistence, UBA proposes that the criterion for persistence be the same as in Annex XIII of REACH, which considers degradation half-lives in marine water, fresh- or estuarine water, marine sediment, and soil as part of the PBT/very persistent, very bioaccumulative (vPvB) assessment criteria; these degradation half-life criteria range from 40 to 180 d. The UBA proposes that a substance meets the persistent criterion if the degradation half-life in marine water at pH 6 to 8 and 12 °C is higher than 60 d, the half-life in fresh- or estuarine water at pH 6 to 8 and 12 °C is higher than 40 d, the half-life in marine sediment at pH 6 to 8 and 12 °C is higher than 180 d, the half-life in fresh- or estuarine water sediment at pH 6 to 8 and 12 °C is higher than 120 d, or the half-life in soil at pH 6 to 8 and 12 °C is higher than 120 d.

The UBA proposes that the mobility criterion for a persistent chemical should be determined on the basis of 2 considerations. First, the water solubility of a substance at pH 6 to 8 and 12 °C must be greater than or equal to 150  $\mu$ g/L, and the log  $K_{\rm OC}$  at pH 6 to 8 and 12 °C must be less than or equal to 4.5. The UBA notes that the mobility criterion should be applied only to substances that have fulfilled the criterion for persistence.

Lastly, with respect to toxicity, UBA proposes a 5-part test for involving data to understand if the substance is carcinogenic, germ cell mutagenic, or toxic for reproduction; if there is other evidence of chronic toxicity; and if there is evidence for effects on or via lactation. The derived no adverse effect level (DNEL) must be less than or equal to  $9 \,\mu g \cdot k g^{-1} d^{-1}$ . The UBA notes that the first 2 considerations are the same criteria defined in Annex XIII of REACH as part of the PBT/vPvB assessment criteria regarding human health. The next 2 criteria specifically address concerns for drinking water exposure and are based on Regulation EC No 1272/2008 (EC 2008) and Cramer class II (Cramer et al. 1978) for substances exhibiting moderate or low biological activity, respectively. The DNEL criterion is based on Kalberlah et al. (2014).

Regardless of the arguments concerning the scientific foundation and credibility of the changes proposed by UBA to REACH PM and PMT assessment criteria, the central question with respect to PTFE is whether chemical-specific assessment would lead to an outcome different from that assuming PTFE behaved similarly to other PFAS substances. Polymers, including fluoropolymers, are different from nonpolymeric chemicals and may be regulated differently. Because of these differences, it is recognized that some data requirements may not be applicable to polymers (EU 2011) For example, as we have shown, the physical-chemical criteria of PLC are predictive of lack of hazard. With respect to applicability, PTFE is not a substance currently registered under REACH because it meets the REACH definition of a polymer substance: "a molecule that contains a sequence of at least 3 monomer units, which are covalently bound to at least one other monomer unit or other reactant" (EC 2006). However, because PTFE is an identifiable organic substance, the proposed UBA framework for assessment using the proposed PMT criteria would be applicable. Further, PTFE is highly stable and persistent in the environment. It is resistant to thermal degradation, being stable for decades at temperatures up to 260°C (SPI 2005); is stable in terms of hydrolysis, oxidation, and light (Brydson 1999); and is stable in terms of anaerobic and aerobic degradation (King et al. 2013). Therefore, PTFE would fulfill the UBA's proposed persistence criterion.

In contrast, PTFE is practically insoluble in water and, therefore, is not mobile in the environment. Using the descriptive solubility table for the USP (2011), the water solubility of PTFE would be classified as practically insoluble ( $1 \times 10^{-5}$  mg/L or 0.01 µg/L) to very slightly soluble ( $1 \times 10^{-4}$  mg/L or 0.1 µg/L) (USP 2011). The mobility of PFTE is 1000 to 10000× lower than UBA's proposed mobility criterion. Therefore, PTFE does not fulfill UBA's proposed mobility criterion and would not be classified as a PM or PMT substance.

A similar negative finding for PTFE pertains to toxicity. The average molecular weight of PTFE is too large for the polymer to cross a cell membrane, which means it is not bioavailable or toxic. Polytetrafluoroethylene has been tested extensively in the United States and European Union to assess commercial applications for food contact and global medical device regulations (see Supplemental Data for additional details). Results demonstrate the absence of toxicity. Therefore, PTFE does not fulfill UBA's proposed toxicity criterion and would not be classified as a PM or PMT substance (Table 4).

#### Fluoropolymers and the Stockholm Convention POP criteria

In addition to country and regional regulations, there are global legally binding instruments, such as the United Nations Environment Programme–administered conventions on chemicals and waste (UNEP 2001), such as the Stockholm Convention on Persistent Organic Pollutants. The Convention aims to eliminate POPs by eliminating their production, reducing their use, or limiting their use through a cradle-tograve approach. For the listing of new chemicals into the Convention, numeric or other criteria have been set for the screening of proposed compounds. Stockholm Convention Criteria (annex D) are compared to those of the USEPA, EU REACH, and the UBA-proposed PMT (Table 4). Fluoropolymers meet the persistence criterion only, not the bioaccumulative, toxic, or mobile criteria.

Fluoropolymers satisfy widely accepted criteria to be considered PLCs. Their physical-chemical properties prevent bioavailability, bioaccumulation, toxicity, and degradation. They have negligible monomer, oligomer, and leachable content and no reactive functional groups with high toxicity. These comparisons of PLC and various regulatory assessment criteria demonstrate that, in the realm of PFAS, high molecular weight fluoropolymers like PTFE have vastly different properties than do other PFAS, and therefore, they are truly a separate class of materials that must be assessed on their own merits as has been done here. They also underscore the value of a global regulatory definition of a polymer.

#### **FUTURE WORK**

It is important to acknowledge that the manufacture and end-of-life phases of the fluoropolymer life cycle are not the subject of the present paper. The following reflections are provided on how these may be explored in future work. Fluoropolymer manufacture includes fluoromonomers and a wide array of initiators, catalysts, et cetera, including polymer production aids, some of which are fluorosurfactants (nonpolymer PFAS) (see Supplemental Data, p 8, for more information about them). Historically, perfluorocarboxylic acids such as PFOA and perfluorononanoic acid (PFNA) were used as polymer production aids in the manufacture of fluoropolymers. They are no longer used by leading global fluoropolymer manufacturers (USEPA 2017a), who are now using alternative substances such as fluorinated polyether carboxylates (see Supplemental Data Table S2). The toxicological and environmental properties (e.g., persistence, bioavailability, and mobility) of these alternatives are very important. Future work should delve into fluoropolymer manufacture and describe the safety, health, and environmental management practices and controls employed; should describe the applicable regulations; and should assess substances used in fluoropolymer manufacture, their human health and environmental attributes, and their mass balance.

At end-of-life when a fluoropolymer has fulfilled its intended use and will be disposed of, the fate of fluoropolymers should be investigated further. Although there are sufficient data to demonstrate that fluoropolymers such as PTFE do not degrade in the environment or release substances of toxicological or environmental concern (Hintzer and Schwertfeger 2014), the downstream, end-of-life process of incineration merits future work. For instance, at temperatures above 450°C, PTFE begins to degrade, releasing hazardous substances such as hydrofluoric acid. There are published studies on the incineration of fluoropolymers under normal, foreseeable municipal waste incinerator conditions targeting specific analytes (Taylor 2009). Presently, most legislation addresses the release of hydrogen fluoride (HF) as the only critical parameter; limit values are for stack emissions (e.g., EU 2000). Future work should investigate incineration under a range of relevant foreseeable use conditions to determine more comprehensively the substances formed and their amounts. Such an incineration study is underway with results to be published upon completion (W.L. Gore 2017). In addition, the practice of the open burning of fluoropolymers, or for that matter of any polymer, is unacceptable and unsafe. Responsible incineration of fluoropolymers, adhering to regulatory guidelines, at the end of their life cycle is appropriate.

Criterion	United States <sup>a</sup>	Stockholm Convention <sup>b</sup>	REACH <sup>c,d</sup>	Germany <sup>d,e</sup>
Persistence (	half-life)			
Р	Water, soil,	Water >60 d	Marine water > 60 d	Same as REACH
	sediment > 60 d	Soil, sediment >180 d	Estuarine water > 40 d	
			Fresh or estuarine sediment or soil $> 120 \text{ d}$	
vP	Water, soil, sediment > 180 d		Marine, fresh, estuarine $H_2O > 60 \ d$	
			Marine, fresh, or estuarine sediment > 180 d	
			Soil > 180 d	
Bioaccumula	tion			
В	Aquatic BCF $>$	Aquatic BCF or $BAF > 5000$	BCF > 2000	
	1000	$Log K_{OW} > 5$		
vB	BCF > 5000		BCF > 5000	
Toxicity				
	Fish	Toxic or ecotoxic	Long-term aquatic NOEC or $EC10 < 0.01$	1) Carcinogenic, germ cell mutagenic, or toxic for reproduction <sup>d</sup> ;
	Low > 10 mg/L	(No numeric criteria)	Classified as carcinogen category 1A or 1B; mutagen 1A or 1B; reproductive toxin 1A, 1B, or 2 <sup>d</sup>	2) other evidence of chronic toxicity <sup>d</sup> ; and
	Moderate 0.1 mg/L– 10 mg/L			3) evidence for effects on or via lactation <sup>d</sup> .
	High < 0.1 mg/L			4) $DNEL^{f} \leq 9\mu\mathrm{g}\cdot\mathrm{kg}^{-1}\mathrm{d}^{-1}$
			Specific target organ toxicity (STOT RE 1 or 2) upon repeated (chronic) exposure) <sup>d</sup>	
Long-range transport (potential	for)	Long-range transport (potential for): Presence through monitoring or modeled data; t <sub>1/2</sub> (air): 2 d		
Mobility				Mobility: water solubility at pH 6–8, 12 °C, must be $\geq$ 150 µg/L, and the log $K_{OC}$ at pH 6–8, 12 °C must be $\leq$ 4.5.

Table 4	Comparison	of	United	States	Stockholm	Convention	FU	RFACH	and	German	Criteria
	Companson	UI.	United	Junes	JUCKHOIIII	Convention	- 20	NLACH	, and	German	Cintenia

BAF = bioaccumulation factor; BCF = bioconcentration factor; DNEL = derived no adverse effect level; EU = European Union; M = mobile; P = persistent; REACH = Registration, Evaluation, Authorisation and Restriction of Chemicals; STOT RE = specific target organ of toxicity repeat exposure; T = toxic; v = very. <sup>a</sup>USEPA 1999. <sup>b</sup>UNEP 2001

<sup>c</sup>ECHA 2014 <sup>d</sup>EC 2008

<sup>e</sup>UBA 2017 <sup>f</sup>Barlow 2005; Kalberlah et al. 2014.

Recycling, reuse, and closed loop systems are alternative options at the end of life. Recent work has shown, on a small scale, the ability to convert fluoropolymers back to their monomers for capture (Schlipf 2014; Invertec 2017). This approach to a closed loop economy for fluoropolymers merits additional work and discussion, as does the recycling and reuse of melt-processable fluoropolymers, such as FEP.

#### CONCLUSIONS

The present review has brought together fluoropolymer toxicity data, human clinical data, and physical-chemical characteristics, using PTFE as an example to show that fluoropolymers satisfy the widely accepted regulatory assessment criteria to be considered as PLCs. Fluoropolymers are high molecular weight, have narrow molecular weight distribution, and have negligible oligomer content and organic and inorganic leachables. Data show that fluoropolymers have thermal, chemical, photochemical, hydrolytic, and biological stability. Polytetrafluoroethylene has been extensively tested to comply with US and EU food contact and global medical device regulations (e.g., USFDA, CFDA, Korea MFDS, Japan PMDA), including ISO 10993 biocompatibility testing and preclinical animal testing. Toxicology studies on PTFE demonstrate the absence of acute or subchronic systemic toxicity, irritation, sensitization, local toxicity on implantation, in vitro and in vivo genotoxicity, hemolysis, complement activation, or thrombogenicity. The data presented demonstrate that the fluoropolymer class of PFAS is well defined, meets PLC criteria, and should be considered as distinctly different from other classes of PFAS. The grouping of all PFAS together is not supported by the scientific data.

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Data Accessibility—All data and information used in this manuscript have been made available in tabulated form (Tables 1–4) by the authors and are included in the paper and the Supplemental Data.

#### SUPPLEMENTAL DATA

The Supplemental Data contains descriptive and more detailed information as highlighted in the paper.

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**Figure S1**. Where does polytetrafluoroethylene (PTFE) come from?

**Figure S2.** Fluoropolymer primer: polytetrafluoroethylene (PTFE) polymerization scheme.

**Figure S3.** Fluoropolymer primer: polytetrafluoroethylene (PTFE) finishing scheme.

**Figure S2.** A fluorinated ethylene propylene (FEP) fluoropolymer molecular weight distribution from a rheological study.

Table S1. Polytetrafluoroethylene (PTFE) polymerization andpost polymerization aids

 Table S2. Alterative fluoropolymer processing aids: Sources of data

Table S3. Solubility table from USP 34 NF 29 General Notices, Section 5.3.0, p 6

Table S4. European Union (EU) specific migration limits (SMLs) for monomers in representative fluoropolymers Table S5. Biocompatibility tests, conditions, and acceptance criteria results for expanded polytetrafluoroethylene patch Table S6. US Environmental Protection Agency's (USEPA's) chemical categories of concern, 2010

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#### **Critical Review**

## A critical review of the application of polymer of low concern regulatory criteria to fluoropolymers II: Fluoroplastics and fluoroelastomers

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#### Abstract

Fluoropolymers are a distinct class of per- and polyfluoroalkyl substances (PFAS), high molecular weight (MW) polymers with fluorine attached to their carbon-only backbone. 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. Fluoropolymers have documented safety profiles; are thermally, biologically, and chemically stable, negligibly soluble in water, nonmobile, nonbioavailable, nonbioaccumulative, and nontoxic. Although fluoropolymers fit the PFAS structural definition, they have very different physical, chemical, environmental, and toxicological properties when compared with other PFAS. This study describes the composition, uses, performance properties, and functionalities of 14 fluoropolymers, including fluoroplastics and fluoroelastomers, and presents data to demonstrate that they satisfy the widely accepted polymer hazard assessment criteria to be considered polymers of low concern (PLC). The PLC criteria include physicochemical properties, such as molecular weight, which determine bioavailability and warn of potential hazard. Fluoropolymers are insoluble (e.g., water, octanol) solids too large to migrate into the cell membrane making them nonbioavailable, and therefore, of low concern from a human and environmental health standpoint. Further, the study results demonstrate that fluoropolymers are a distinct and different group of PFAS and should not be grouped with other PFAS for hazard assessment or regulatory purposes. When combined with an earlier publication by Henry et al., this study demonstrates that commercial fluoropolymers are available from the seven participating companies that meet the criteria to be considered PLC, which represent approximately 96% of the global commercial fluoropolymer market. Integr Environ Assess Manag 2023;19:326–354. © 2022 The Authors. Integrated Environmental Assessment and Management published by Wiley Periodicals LLC on behalf of Society of Environmental Toxicology & Chemistry (SETAC).

KEYWORDS: Applications, Fluoropolymers, Low concern, PFAS, Property Combinations

This article contains online-only Supporting Information.

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#### INTRODUCTION

"Fluoropolymers are high MW polymers with fluorine atoms directly attached to their carbon-only backbone" (Ebnesajjad, 2017). The carbon–fluorine (C–F) bond is the strongest bond between carbon and another atom and imparts unique, outstanding, and beneficial properties and extraordinary functional performance to fluoropolymers (Ameduri, 2020; Ameduri & Sawada, 2017a, 2017b; Banks et al., 1994; Fluoropolymer Products Group of Plastics Europe [FPG], 2021a; Scheirs, 2007). These properties include chemical, biological, and thermal stability, heat and chemical resistance, unique dielectric properties, and durability. Additional fluoropolymer properties include fire resistance, weather resistance, nonwetting, and nonstick. Fluoropolymers are regarded as irreplaceable in many applications because their unique combination of specific properties, which are critical to ensure optimal performance in many applications, cannot be achieved or guaranteed by alternative materials (FPG, 2021a, 2017; Henry et al., 2018; Performance Fluoropolymer Partnership of the American Chemistry Council [PFP], 2020).

Per- and polyfluoroalkyl substances (PFAS), a universe of substances with widely diverse properties that have been used in industrial and consumer applications since the 1950s, include fluoropolymers as a distinct class (Buck et al., 2011; Henry et al., 2018). A single, globally harmonized definition for PFAS has not yet been agreed upon. PFAS have been defined differently based on their structure and atomic composition (Buck et al., 2021; Wallington et al., 2021). For example, the USEPA's working PFAS structure definition is "a structure that contains the unit R-CF<sub>2</sub>-CF(R')(R"), where R, R', and R" do not equal "H" and the carbon-carbon bond is saturated (note: branching, heteroatoms, and cyclic structures are included" (USEPA, 2021a). The European Chemicals Agency (ECHA) employed a much broader PFAS structural definition (ECHA, 2020). A recent Organisation for Economic Cooperation and Development (OECD) report, which defined PFAS as fluorinated substances that contain in their structure at least one fully fluorinated methyl or methylene carbon atom (without any H/Cl/Br/l atom attached to it), that is, with a few noted exceptions, any chemical with at least a perfluorinated methyl group (-CF<sub>3</sub>) or a perfluorinated methylene group (-CF<sub>2</sub>-; OECD, 2021). This report acknowledges that the term "PFAS" is broad, general, and nonspecific, which does not inform whether a compound presents risk or not, but only communicates that the compounds under this term share the same structural trait of having a fully fluorinated methyl or methylene carbon moiety. Further, the report highlights that, among the substances defined as PFAS, there are distinct substances with very different properties: polymers and nonpolymers; solids, liquids and gases; persistent and nonpersistent substances; highly reactive and inert substances; mobile and insoluble (immobile) substances; and (eco) toxic and nontoxic chemicals. In addition, the report recognizes that PFAS have diverse molecular structures (e.g., neutral, anionic, cationic, or zwitterionic; with or without aromatic rings; nonpolymers or polymers; low or high molecular weight (MW), and thus diverse physical, chemical, and biological properties (e.g., involatile or volatile; water soluble or water insoluble; reactive vs. inert; bioaccumulative or nonbioaccumulative) and as such highly recommends that such diversity be properly recognized and communicated in a clear, specific, and descriptive manner when communicating about PFAS.

There is considerable media and public confusion and misunderstanding regarding PFAS, as the many different chemicals and groups are often not clearly differentiated under the broad term PFAS. Per- and polyfluoroalkyl substances, a large, diverse group of substances with vastly different properties, is too broad to allow effective, sciencebased assessment and regulation of chemical compounds as an entire group. This point has been raised in recent publications that suggest approaches to effectively group PFAS for regulatory assessment (American Chamber of Commerce in Europe [Amcham], 2020a; Buck et al., 2021; Bundesverband der Deutschen Industrie e.V. [BDI], 2021; Fiedler et al., 2020; Miller et al., 2020; Orgalim, 2021; Royal Society of Chemistry [RSC], 2021; Sha et al., 2019; Wallington et al., 2021). A clear understanding of the origin of PFAS found in the environment, the PFAS that are commercially relevant (Buck et al., 2021), and assessment of their properties are needed to be able to determine which classes of PFAS require management action. PFAS must be assessed based on their chemical, physical, thermal, and biological property differences and uses (Amcham, 2020a; BDI, 2021; Buck et al., 2021; RSC, 2021; Wallington et al., 2021). As regulatory frameworks, such as the EU REACH regulation, continue to evolve, more work is needed to distinguish clearly among PFAS based on their properties to assure that regulations are appropriate in scope, proportionate, and are science-based.

Per- and polyfluoroalkyl substances are divided into two primary categories: nonpolymers and polymers (Buck et al., 2011). Polymeric PFAS, generally known as "fluorinated polymers," include fluoropolymers (discussed here), perfluoropolyethers (PFPE), and side-chain fluorinated polymers (SCFP; Buck et al., 2011; Henry et al., 2018 and Supporting Information: Figure 6.1). This article deals strictly with fluoropolymers. Neither PFPE nor SCFP are discussed here.

The nonpolymer category includes perfluoroalkyl substances and polyfluoroalkyl substances. Certain nonpolymer PFAS substances, for example, short- and long-chain perand polyfluoroalkyl carboxylic acids and sulfonic acids, received regulatory scrutiny recently due to their toxicity, as well as their persistence, potential to bioaccumulate, and/or mobility in the environment. Regulatory processes have been launched worldwide to address these concerns related to specific nonpolymer PFAS. These targeted regulatory measures have evolved increasingly into restrictions on the entire family of PFAS. For example, five Member States of the European Economic Area have initiated a procedure to prepare a joint restriction proposal under the EU REACH Regulation to limit the risks to human health and the environment from the manufacture and use of all substances in the PFAS family based on structure alone (ECHA, 2020). Although fluoropolymers fit the PFAS structural definition, they have vastly different physicochemical, environmental, and toxicological properties than other PFAS in addition to substantial societal benefits and importance (Fluoropolymer Products Group of Plastics Europe [FPG], 2017, 2021a). For

these reasons, fluoropolymers should be considered separately and not aggregated with all other PFAS for regulatory action. Concurrently, the USEPA prepared a PFAS Strategic Roadmap laying out how it plans to evaluate and potentially regulate PFAS (USEPA, 2021a). Recognizing that there are many PFAS very diverse in their physical form, chemical structure and composition, functional characteristics, and toxicity profiles, USEPA "is conducting new research to better understand the similar and different characteristics of specific PFAS and whether and how to address groups and categories of PFAS."

Fluoropolymers have documented safety profiles, are thermally, biologically, and chemically stable, negligibly soluble in water, nonmobile, nonbioavailable, nonbioaccumulative, and nontoxic (Henry et al., 2018). Some fluoropolymers have been demonstrated to meet the "polymers of low concern" (PLC) criteria, and as such do not present notable concern for human health or the environment (Henry et al., 2018). PLC criteria were developed over time within regulatory frameworks around the world as an outcome of chemical hazard assessment processes, which identified physical-chemical properties of polymers that determine polymer bioavailability and thereby report a polymer's potential hazard. For example, many of the physicochemical properties, such as MW, limit the ability of a polymer to cross the cell membrane and therefore limit its bioavailability (Kostal, 2016; Lipinski et al., 2001; USEPA, 2012). The USEPA built on this knowledge to adopt a polymer exemption rule to exempt low-hazard polymers from certain regulatory notification requirements under the Toxic Substances Control Act's (TSCA) new chemicals program (United States Federal Register [USFR], 1984). An OECD expert group on polymers reached consensus on these criteria and their respective metrics, documenting the data required for a polymer to qualify as a PLC to human health and the environment (OECD, 1993). Subsequently, an additional OECD work group concurred that PLC have "insignificant environmental health and human health impacts" (OECD, 2009). In addition, the European Commission commissioned a report (BIO by Deloitte, 2015) wherein several member countries agreed on the polymer properties predictive of adverse human health and environmental hazard. The report outlined eligibility criteria for a polymer to be considered a PLC. In 2019, the industry-led European Centre for Ecotoxicology and Toxicology of Chemicals (ECETOC) developed a "Conceptual Framework for Polymer Risk Assessment" ("CF4Polymers"; ECETOC, 2019). CF4Polymers provides guiding elements to be considered in assessing potential ecological and human health hazards and risks posed by polymer substances. CF4Polymers also considers specific life-cycle stages of polymer products and their associated routes of exposure. The authors of the CF4Polymers framework support the PLC approach as a means to accomplish polymer risk assessments. They specifically support the findings of Henry et al. (2018) and state that they are "...unaware of scientific evidence to justify generally assigning fluoropolymers the same level of regulatory concern as other PFAS" (ECETOC, 2019). In 2020, the European Commission contracted a study to propose criteria for the identification of polymers requiring registration (PRR) under REACH (Wood, 2020a). The Wood report states that the authors consider that fluoropolymers meet the criteria to be considered PLC, "following the recommendations of Henry et al." Considerable debate and comment on proposals have been put forward as the process and discussion advances (American Chamber of Commerce in Europe [Amcham], 2020b; FPG, 2021a; Hafer, 2021).

Four major fluoropolymers have previously been demonstrated to meet the criteria as PLC (Henry et al., 2018). This 2018 study raised interest in gathering similar data for additional commercial fluoropolymer products, both in scope and polymer type. In this study, seven global fluoropolymer manufacturers from the USA, Europe, and Asia collaborated to gather and present data for 14 additional fluoropolymers. In addition to information describing chemical composition, uses, performance properties, and functionalities of the 14 fluoropolymers, author company data for each of the PLC criteria are presented and discussed. The results demonstrate that each of the 14 commercially manufactured fluoropolymers in this study satisfy the widely accepted assessment criteria to be considered PLC and merit such designation. The study results add further evidence to demonstrate that fluoropolymers are demonstrably different and should not be grouped with other PFAS for hazard assessment or regulatory purposes.

#### USES, PERFORMANCE PROPERTIES, AND FUNCTIONALITY OF FLUOROPLASTICS AND FLUOROELASTOMERS IN THIS STUDY

The fluoropolymers described and evaluated in this study are high-performance materials used in commercial and industrial applications. Described herein are the industries and sectors (Table 1) and the performance properties and functionalities (Table 2) of the study fluoropolymers. The unparalleled combination of properties makes fluoropolymers critical materials for a broad range of applications and industrial sectors including automotive, aerospace, energy production and storage, and electronics (Table 1). Fluoropolymers are an important driver of the European Green Deal (FPG, 2021a) and UN Sustainability Development Goals (United Nations [UN], 2021), supporting smart mobility, clean energy, and sustainable industry. They are used in various components of renewable energy installations, such as hydrogen and photovoltaic panels and facilitate advanced energy storage and conversion technologies such as lithium-ion batteries (FPG, 2021a). Fluoropolymers are (i) durable, stable, and mechanically strong in harsh conditions; (ii) chemically inert, meeting the requirements for low levels of contaminants and particulates in manufacturing environments that are critical to the food and beverage, pharmaceutical, medical, and semiconductor industries; and (iii) biocompatible, nonwetting, nonstick, and highly resistant to

	Transpo	rtation	Health	care	Č	emical		Consumer		Telecomm	unications		Infra- structure	Rer	newable energ	λŧ
										Electronics	Internet and		Construc-			
						Chemical		Protection		and	wireless	Textiles	tion and			
End uses	Automotive	Aerospace	Pharma- ceuticals	Medical devices	Oil and gas	process industry (CPI)	Production of goods	and packaging	Filtration	semicon- ductors	communica- tions	Technical textiles	archi- tecture	Energy production	Hydrogen production	Energy storage
Fluoroplastics																
PVDF	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•
in the property lines																
PVDF copolymer	•	•	•	•		•	•	•	•	•	•	•	•		•	•
ECTFE copolymer	•	•	•		•	•				•	•		•			
ECTFE terpolymer			•		•	•										
PCTFE		•	•							•						
FEVE	•	•								•			•			
EFEP	•			•		•				•						
CPT	•									•						
THV	•	•	•			•	•	•	•	•			•	•		•
Fluoroelastomers																
FEPM	•	•	•	•	•	•	•			•			•	٠		
FKM	•	٠	•	•	•	•	•	٠		•		•	•	٠	•	•
FFKM		•	•	•	•	•	•			•						
Specialty																
Amorphous		•	•	•		•				•	•				•	•
lonomer	•			•		•			•	•				•	•	•
<i>lote</i> : See also Chapte bbreviations: CPT, EVE, fluoroethylene-v	er 5 in the Supp chlorotrifluoroe inyl ether; FKN	oorting Inforr ethylene-tetra 1, HFP-VF2 p	nation. ifluoroethyle olymer and	ane; ECTFE HFP-VF2-TI	E, ethylen FE polyme	e-chlorotrifluc rs; FFKM, TFI	roethylene; E-PMVE perf	EFEP, ethy luoroelastom	lene-tetraflu er; PCTFE, <sub> </sub>	oroethylene <sup>.</sup> oolychlorotri	hexafluoropr	opylene; FE e; PVDF, pol	EPM, trifluc lyvinylidene	oroethylene- e fluoride; Th	propylene 4V, TFE-HFP	opolymer VF2.

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functionality
and
properties
polymer
Fluoro
2
<b>FABLE</b>

		Durabl	Ð				Inert-	-Stable		
See Supporting Information: Chapter 2 for property descriptions	Mechanical strength	Wear resistance	-lexibility	Low coefficient of friction	Resistance to chemicals	Weatherability	Cryoger properties ( y than -50	nic (lower 1 °C)	High operating temperature range	High limiting oxygen index
Fluoroplastics										
PVDF Homopolymer	•	•		•	•	•			•	•
PVDF Copolymer	•	•		•	•	•			•	•
ECTFE Copolymer	•	•		•	•	•	•		•	•
ECTFE Terpolymer		•		•	•	•			•	•
PCTFE	•	•		•	•	•	•		•	•
FEVE	•	•	•	•	•	•			•	•
EFEP	•	•		•	•	•	•		•	•
СРТ				•	•	•	•		•	•
THV			•		•	•			•	•
Fluoroelastomers										
FEPM	•	•	•		•	•			•	•
FKM	•	•	•		•	•			•	•
FFKM	•	•	•		•				•	•
Specialty										
Amorphous			•	•	•				•	•
lonomer			•		•					•
					Funct	tional				
See Supporting Information: Chapter 2 for property descriptions	Electrical insulator— high data transmission rate	- Ionic conductivii	Piezo-6 ty prop	electrical Bar erties prop	rrier Nons erties prope	Ultra hì stick grades srties appli	igh purity for clean O cations c	)ptical :larity	Low refractive index—used for optical effects	Polymer processing additive (PPA) <sup>a</sup>
Fluoroplastics										
PVDF Homopolymer				•	•		•		•	•
PVDF Copolymer				•	•				•	•
										(Continued)

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			TAE	3LE 2 (Continue	ed)				
					Functional				
See Supporting Information: Chapter 2 for property descriptions	Electrical insulator— high data transmission rate	lonic conductivity	Piezo-electrical properties	Barrier properties	Nonstick properties	Ultra high purity grades for clean applications	Optical clarity	Low refractive index—used for optical effects	Polymer processing additive (PPA) <sup>a</sup>
ECTFE Copolymer	•			•					
ECTFE Terpolymer				•					
PCTFE				•	•	•	•	•	
FEVE				•			•		
EFEP				•	•		•	•	•
CPT				•	•	•	•	•	
THV				•			•	•	•
Fluoroelastomers									
FEPM	•			•					
FKM				•	•				•
FFKM	•			•		•			
Specialty									
Amorphous	•	•		•	•	•	•	•	
lonomer	•	•		•			•		
ote: See Chapter 5 in the Supp obreviations: CPT, chlorotriflu	orting Information. sroethylene-tetrafluoroethy	ylene; ECTFE, eth	ylene-chlorotrifluoroe	ithylene; EFEP, €	ethylene-tetrafluc	oroethylene-hexafluoropr	opylene; FEF	PM, trifluoroethylene-	propylene copolymer;

FEVE, fluoroettylene-vinyl ether; FKM, HFP-VF2 polymer and HFP-VF2-TFE polymers; FFKM, TFE-PMYE perfluoroettylene; PVDF, polyvinylidene fluoride; THV, TFE-HFP-VF2, PVDF, polyvinylidene fluoride; PVDF, polyvi  $\triangleleft$ 

temperature, fire, and weather (Table 2). Fluoropolymers are the preferred choice of material because of their unique combination of properties that are not achievable from other materials or via other functions. As a result, fluoropolymers have become a critical mainstay for our society providing vital, reliable functionality to a broad range of industrial and consumer products.

Three fluoropolymer types are included in this study: fluoroplastics, fluoroelastomers, and specialty fluoroplastics. Here, we describe briefly each included in this study. Additional details about each polymer are provided in the Supporting Information: Chapter 5.

#### Fluoroplastics

The fluoroplastics included in this study are: polyvinylidene fluoride (PVDF) homopolymer, PVDF copolymer, ethylene-chlorotrifluoroethylene (ECTFE) copolymer, ECTFE terpolymer, polychlorotrifluoroethylene (PCTFE), fluoroethylene-vinyl ether (FEVE), ethylenetetrafluoroethylene-hexafluoropropylene (EFEP) terpolymer, chlorotrifluoroethylene-tetrafluoroethylene (CPT) terpolymer, and tetrafluoroethylene, hexafluoropropylene, vinylidene fluoride (TFE-HFP-VF2 [THV]) terpolymer as well as the specialty fluoroplastics, amorphous fluoropolymers, and fluorinated ionomers. Typical monomers used in the manufacture of fluoroplastics include tetrafluoroethylene (TFE), hexafluoropropylene (HFP), vinylidene fluoride (VDF or VF2), chlorotrifluoroethylene (CTFE), vinyl fluoride (VF), trifluoroethylene (TrFE), and perfluoroalkyl vinyl ethers (PAVEs), which include trifluoromethyl trifluorovinyl ether (PMVE), pentafluoroethyl trifluorovinyl ether (PEVE), and heptafluoropropyl trifluorovinyl ether (PPVE). In some copolymers, monomers that do not contain fluorine attached to the olefinic carbons may be used. These include ethvlene, propylene, perfluoroalkyl-substituted ethylenes, and others (Ebnesajjad, 2000, 2003; Grot, 2011).

#### Fluoroelastomers

The fluoroelastomers included in this study are: trifluoroethylene-propylene copolymer (FEPM), HFP-VF2 polymer and HFP-VF2-TFE polymers (FKM), and TFE-PMVE perfluoroelastomer (FFKM). Typical monomers used in the manufacture of fluoroelastomers include VDF, HFP, TFE, CTFE, PAVEs, as well as propylene, 1-hydropentafluoropropene (HPFP), and 2,3,3,3tetrafluoropropene (HFO-1234yf; FPG, 2021a). Although fluoroelastomers are based on many of the monomers that are also used for the synthesis of fluoroplastics, they are different because of the specific composition, flexibility with subambient glass transition temperatures, as well as their elastomeric properties, resulting from the crosslinking process. Cross-linking, known as curing or vulcanizing, is a hardening process to form chemical bonds between polymer chains that gives polymers their elasticity (Améduri et al., 2001; Drobny, 2016).

#### PVDF homo- and copolymers

Polyvinylidene fluoride fluoropolymers are specified by end users across the world for their outstanding combination of properties. Because they have high temperature resistance, low permeability, and high mechanical strength, and provide chemical resistance to a wide range of aggressive chemicals, PVDF fluoropolymers are used as a contact surface for the production, storage, and transfer of corrosive fluids (chemically resistant to halogens and acids) in the chemical processing industry, oil and gas transportation, and cables industry (Arkema, 2021a; Gujarat Fluorochemicals Limited, 2018, 2022; Solvay, 2021a). The outstanding resistance to sunlight/UV exposure make PVDF suitable for architectural coatings. The outdoor aging and weathering properties of PVDF resin led to its use in longlasting paints for coating metal sheet for the past 50 years. PVDF resins can also be used to protect thermoplastics through coextrusion or film lamination techniques to obtain antigrime and antigraffiti surfaces with exceptional weathering properties. PVDF fluoropolymers also exhibit radiation resistance, desirable burn characteristics, flame, and smoke properties, easy processing on industry-standard equipment, and easy postprocessing steps, such as welding and fabrication. PVDF is used as a binder in lithium-ion batteries as well as PVDF film for solar power panels because of its high thermal and electrochemical stability, its stability under harsh environmental conditions, and its strong adhesion properties are critical to achieving environmental goals.

#### ECTFE (co- and terpolymers)

Ethylene chlorotrifluoroethylene (ECTFE) is a semicrystalline and melt-processable fluoropolymer obtained by the copolymerization of the two monomers, ethylene and chlorotrifluoroethylene, with an essentially 1:1 alternating structure (Ebnesajjad, 2017). Due to its chemical structure, ECTFE offers a unique combination of properties including chemical resistance, high thermal rating, and very good mechanical properties (Solvay, 2021b). ECTFE terpolymer with added hexafluoroisobutylene monomer displays enhanced stress-cracking performances resulting from chainstructure modifications of the polymer. ECTFE is used widely in anticorrosion applications such as coatings or in self-supporting construction (pipes) and architectural films (Solvay, 2021c). One of the principal advantages of ECTFE fluoropolymer is the ease with which it can be processed. It is a true thermoplastic that can be handled by conventional techniques of extrusion as well as by blow, compression, injection, rotational, and transfer molding. Powder coating methods are also applicable. ECTFE embodies an exemplary trade-off among general properties, offering high chemical and mechanical resistance combined with easy processing of the resin.

#### PCTFE

Polychlorotrifluoroethylene is a homopolymer of chlorotrifluoroethylene. PCTFE is melt processable and can be extruded or molded (Satokawa, 1990). PCTFE has outstanding mechanical properties, especially hardness, and chemical resistance compared with PTFE and PFA, although it is slightly inferior to PFA and FEP in heat resistance and chemical resistance (Daikin, 2021a; Satokawa, 1990). PCTFE has been applied widely in the semiconductor industries and aerospace industries (Curbell, 2021; Daikin, 2021a). In addition to distinguished thermal and chemical stability, it has very low moisture absorption and permeation; therefore, PCTFE is used in pharmaceutical packaging (Honeywell, 2021).

#### FEVE

Fluoroethylene-vinyl ether fluoropolymer resins are manufactured by copolymerization of fluoroethylene monomer and a vinyl ether monomer and consist of alternating fluoroethylene and alkyl vinyl ether segments (AGC Chemicals Company, 2021a; Parker & Blankenship, 2015). They were developed in 1982 as the first solvent-soluble fluoropolymers in the world (Darden & Parker, 2021; Kojima & Yamabe, 1984; Munekata, 1988; Yamabe et al., 1984). The alternating fluorinated segments provide outstanding UV stability, weather resistance, and chemical resistance, while the vinyl ether segments provide solvent compatibility and cross-linking sites (Parker & Blankenship, 2015; Scheirs, 2007). FEVE resins are used to make ultraweatherable coatings for architectural, aerospace, automotive, bridge, and industrial maintenance markets (Hoshino & Morizawa, 2017).

#### EFEP

Ethylene-tetrafluoroethylene-hexafluoropropylene is a terpolymer of ethylene, tetrafluoroethylene, and hexafluoropropylene. It was designed to have many of the properties of ETFE. It has a lower processing temperature, which allows it to be coextruded with conventional thermoplastic polymers such as polyamide, ethylene vinyl alcohol (EVOH), and modified polyethylene. EFEP can be extruded, injection molded, and blow molded, and it is used in many applications such as those identified in Supporting Information: Chapter 4.7 (Daikin, 2011a). EFEP is a meltprocessable resin with good processability because of its low melting point. It also has excellent mechanical properties, provides chemical resistance, low permeability, exceptional weatherability, and good heat resistance. Other prominent features include inherent flame retardancy as well as good optical properties given that EFEP is highly transparent and has both a low dielectric constant and loss tangent.

#### СРТ

Chlorotrifluoroethylene-tetrafluoroethylene is a terpolymer of chlorotrifluoroethylene, tetrafluoroethylene, and perfluoroalkyl-vinyl-ether. It is a melt-processable polymer and resin, which is readily processed because of its lower melting point. It can be melt-molded as a thermoplastic resin by extrusion, injection, and compression molding. CPT is a modified perfluoroalkoxy fluoropolymer (PFA), which utilizes chlorotrifluoroethylene to provide low permeability to PFA, and it has many outstanding properties as a hybrid polymer of PFA and PCTFE as shown below. It has demonstrated permeation resistance to organic solvent, chemicals, water vapor, and gasoline (Daikin, 2011b). CPT offers superior permeation resistance against gasoline and flexible fuel and can be part of construction meeting the LEV III requirements (US environmental protection regulations in this automotive application). CPT also has notable barrier properties against many kinds of organic solvents and strong acids, especially HF, HCl, and HNO<sub>3</sub>. This is very useful for semiconductor applications (Daikin, 2021b). In addition to the features noted above, CPT also provides heat resistance, excellent weatherability, flame retardancy, and good optical properties owing to its high transparency.

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THV fluoropolymers are a group of fluorinated thermoplastic polymers composed mainly of tetrafluoroethylene (TFE), hexafluoropropylene (HFP), and vinylidene fluoride (VDF; Domininghaus, 1998; Hintzer & Schwertfeger, 2014; Hull et al., 1997). The melting point of the different grades ranges from approximately 100 °C to nearly 250 °C. THV fluoropolymers are easy to process due to their broad processing windows. Different THV grades exhibit high flexibility, high transparency, bondability to fluorinated and nonfluorinated materials, and very good permeation resistance against fuels and other chemicals. The polymers are used as a barrier layer in fuel hoses, for transparent films and tubing, as matrix materials in composites, and the bonding layer in multilayer construction (Dams & Hintzer, 2017; Hull et al., 1997). The high transparency of the special film makes it an ideal adhesive film for laminated glass and the optimal protective film for surfaces. THV grades compete against other fluorothermoplastic materials for applications that require transparency and low refractive index as well as with fuel barrier materials. Commercial nonfluorinated materials cannot be used as substitutes for THV because of the unique combination of properties. Polymethylmethacrylate (PMMA) is used in conjunction with THV to provide differences in refractive index to create the total reflection needed for polymer optical fibers (Park et al., 2008). Transparent polymers, such as PMMA or polycarbonate, do not have the same chemical resistance or UV resistance to compete directly with THV.

#### FEPM

Trifluoroethylene-propylene copolymer elastomers, ASTM D1418, are high MW fluoropolymers with alternating tetrafluoroethylene and propylene segments (Kojima et al., 1977). They are also known as TFE-P copolymers. Various articles can be produced by means of compression molding, extrusion, injection molding, and calendering. FEPM elastomers are compounded and cured (cross-linked) to deliver unique and valuable properties by providing exceptional heat resistance with a continuous service temperature higher than 200 °C, outstanding chemical resistance with little or no deterioration even in contact with strong acids, bases, and oxidants at high temperatures, steam resistance, and high electrical resistivity on the order of  $10^{15}$ – $10^{16} \Omega$ /cm (bulk resistivity). Formulated FEPM components are now used worldwide in many critical industrial applications where they must function safely in harsh environments, thereby extending the life of critical components and reducing downtime and costly repairs. FEPM elastomers are used in a range of applications including thermal power plants, oil and gas industry, ocean development, chemical and nuclear plants, automotive, aerospace, heavy-duty diesel, electronics, machinery, renewable energy, food processing, and medical. Their noted heat and chemical resistance make them especially valuable in oil and gas extraction (downhole) applications, where reliability is essential to cost effective and environmentally responsible production (Hull, 1983). FEPM elastomers are also used in high-performance wire and cable applications as insulating materials with the highest heat resistance, for example, lightweight, high-voltage automotive cables and motor cables for Japanese high-speed bullet trains (AGC Chemicals Company, 2021b).

#### Fluoroelastomers (FKM)

FKM are a family of fluoroelastomer materials defined by ASTM international standard D1418 (ASTM, 2021). FKM fluoroelastomers contain vinylidene fluoride (VDF) as a monomer combined with a variety of other fluoromonomers to create a palette of polymers with properties tailored for specific uses (Dams & Hintzer, 2017; Drobny, 2016; Van Cleeff, 1997; Worm & Grootaert, 2001). Cross-linked FKM fluoroelastomers are amorphous polymers designed for demanding service applications in hostile environments characterized by broad operating temperature ranges in contact with industrial chemicals, oils, or fuels (Worm & Grootaert, 2001). FKM fluoroelastomers are used mainly in fabricated parts (e.g., o-rings, gaskets, seals) to provide barriers against a wide range of fluids under severe service conditions (Drobny, 2016). Their design allows stable extrusion and molding processes and fitting in a wide range of processing constraints, reducing the risk of failure and increasing productivity. FKM fluoroelastomers provide high temperature and aggressive fluids resistance and retention of properties over a wide and demanding range of operating use conditions (high and low temperatures) for sealing and fluid transport applications, offering far superior performance than hydrocarbon elastomers. Applications include aerospace, automotive, oil and gas, chemical processing, electrical, office equipment, food, pharmaceuticals, and consumer wearables. Additionally, uncured FKM fluoroelastomers are used as a polymer processing additive (PPA) or polymer extrusion aids in small amounts (50-2000 ppm) dispersed in polyolefins such as high-density polyethylene (HDPE) and linear low-density polyethylene (LLDPE), significantly improving their film extrusion characteristics, reducing melt fracture and die build-up, as well as increasing productivity, minimizing energy and

water footprint, and enabling the extrusion of thin films (Lavallée, 2020; Shell, 2020).

#### FFKM

Perfluoroelastomers, designated by ASTM D1418 as FFKM, are a fully fluorinated class of elastomers that are typically made up of tetrafluoroethylene (TFE), a perfluoro (alkyl vinyl ether; PAVE), and a cure site monomer(s) (Ohkura & Morizawa, 2017). FFKM elastomers offer superior chemical and temperature resistance, excellent resistance to gas and liquid permeation, and resistance to weather and ozone with operating temperatures ranging from -40 °C to 325 °C (Drobny, 2016; Greene-Tweed, 2021a, 2021b). These polymers can also be compounded to meet the special requirements of upstream, midstream, and downstream oil and gas exploration due to their superior properties (Barnwell, 2021; Daemar, 2021). Because of these properties, FFKM elastomers are used in a wide variety of applications such as critical sealing solutions for the aerospace, pharmaceutical, medical, chemical processing, semiconductor, and oilfield industries (Atkinson, 2018; Marshall, 2017).

#### Amorphous fluoropolymers

Amorphous fluoropolymers are copolymers of TFE and specialty monomers that yield linear, high molar mass noncrystalline polymers (AGC Chemicals Company, 2021c; Gangal & Brothers, 2010; Hintzer et al., 2013; Korinek, 1994; Resnick & Buck, 1997, 1999). Amorphous fluoropolymers have the outstanding chemical and thermal stability and surface properties of semicrystalline perfluoropolymers as well as the unique properties associated with amorphous materials such as optical clarity and high gas permeability. The optical properties are outstanding, with more than 90% transmission, and thereby low dissipation, over a wide range of wavelengths (e.g., 200-2000 nm). TFE/PDD (2,2-bistrifluoromethyl-4,5-difluoro-1,3-dioxole) copolymers have the lowest refractive index known for a solid organic polymer (Groh & Zimmermann, 1991). This unique combination of properties makes amorphous fluoropolymers unmatched for uses in degassing, fiber optics, photolithography, antireflective coatings, passivation and protective coatings for medical, military, and aerospace devices, as well as electronic applications (Gangal & Brothers, 2010; Hintzer et al., 2013).

#### Fluorinated ionomers

Fluorinated ionomers are copolymers of TFE and a perfluorovinylether monomer containing an ionic group, typically a sulfonic acid or carboxylic acid (Grot, 2011, 2013). Fluorinated ionomers can be extruded or cast into film and converted into ion exchange materials (IXMs). IXMs come in a variety of useful forms offering a broad range of solutions for different applications (AGC Chemicals Company, 2021d; Asahi-Kasei, 2021; Chemours, 2021a). These forms include ion exchange membranes (IEMs), dispersions, and resins. IEMs must possess the required ion transport properties for the electrochemical cell in which they reside to perform well and work effectively. Some of these properties include high ionic conductivity, chemical resistance, high operating temperature range, low permeability, and balanced durability and performance (Chemours, 2021b).

Ion exchange membranes (IEMs) stand to play a noteworthy role in today's modern world (Chemours, 2021b) and as such, are utilized in a wide range of applications and enduse industries including electrochemical processing, energy production, and hydrogen production. IEMs revolutionized the chlor-alkali industry (Grot, 2013), the manufacture of primarily caustic soda and chlorine, by eliminating the use of hazardous materials such as mercury and asbestos (Asahi-Kasei, 2021) and, in doing so, reducing energy consumption. Water electrolysis, the process of converting water into hydrogen and oxygen, relies on IEM technology. Although this process requires electricity, renewable energy sources such as solar or wind power can be utilized, allowing the potential for hydrogen to be a "clean" energy source (Science Center, 2021). Hydrogen fuel cells, some of which use a type of IEM known as a proton exchange membrane, can then convert hydrogen to electricity, a crucial technology to reach the stated target of the EU New Green Deal (EC, 2021).

#### STUDY METHODOLOGY AND DATA

Seven global fluoropolymer manufacturers (AGC Chemicals Americas, Arkema, The Chemours Company, Daikin Industries, Gujarat Fluorochemicals Limited, Solvay Specialty Polymers, and 3M Company) participated in this study and contributed data, writing, critique, and analysis. The companies noted above are members of the US-based Performance Fluoropolymer Partnership (PFP) and/or EU-based Fluoropolymer Product Group (FPG).

This study provides data on 14 fluoropolymers, building on a prior study (Henry et al., 2018). The study was chartered within two global industry groups. Participants put forward candidate fluoropolymers of notable commercial importance for the study and provided company and published data that address the PLC criteria. Thirteen PLC criteria that relate to the polymer structure and properties, including three to physicochemical properties and five to stability, set forth in BIO by Deloitte (2015) and presented in prior work on four fluoropolymers (Henry et al., 2018), are addressed in this study (Figure 1). These criteria are briefly described in Table 3 with further description provided in Supporting Information: Chapter 3 and in the prior work (Henry et al., 2018). Participants provided company and published data and a description of methods and/or public references to demonstrate the origin of the data provided. These methods and references are provided in detail in Supporting Information: Chapter 4. The PLC criteria data were compiled and are presented in Tables 4 and 5.

The data assessment was done in two ways: Companies could self-assess the PLC data if they had the technical resources to do so or they could submit their PLC data to a third-party contractor for an independent technical review. The third-party consultant hired by PFP was GSI Environmental Inc. The objective was to be able to publish the references and methods behind the PLC data provided for each fluoropolymer in the study. In cases where the data and/or methods contained confidential business information, the third-party consultant independently evaluated the information supplied before it was shared in a blinded, aggregate form with the participating project companies. In several cases—FKM, PVDF, and ionomers several companies submitted data for the same fluoropolymer. The data were combined and are presented in Tables 4 and 5. There is no intentional company attribution for the data presented.

The following describes further how the study data were generated and compiled.

- A third-party consulting company (GSI) was engaged to comment independently on data, methods, and references initially supplied by study participants for their respective fluoropolymers. Several study participants used this third-party consultant.
- Following the initial third-party assessment and assembly of the master data Tables 4 and 5 as well as the FKM data in Supporting Information: Table 4.11, a series of subsequent assessments were conducted (within PFP)



FIGURE 1 OECD polymer of low concern (PLC) criteria add (C) 2021 W.L.Gore & Associates

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#### TABLE 3 Polymer of low concern (PLC) criteria descriptions

(See Supporting Information: Chapter 3 for additional details) Criterion	Description
Polymer composition	The polymer composition criterion requires structure and elemental composition of the polymer be described and identified (e.g., by Chemical Abstracts Service [CAS] number).
Molecular weight, number average molecular weight, MW distribution, and % oligomer <1000 Da	The number average molecular weight (Mn) and oligomer content are the most commonly used criteria for PLC assessment. The EU assessment report (BIO by Deloitte, 2015) states that the "most potential health concern polymers have a number average molecular weight, Mn, <1000 Da and oligomer content >1%." The higher the oligomeric content, the more likely a polymer is to be a health or ecotoxicological (OECD, 2009, p. 9).
	Molecular weight (MW) is an important predictor of biological effect because large molecules (>1000–10 000 Da) are too large to penetrate cell membranes (Supporting Information: in Beyer, 1993, p. 14). Because large molecular weight polymers cannot enter the cell, they cannot react with "target organs," such as the reproductive system, and are not bioavailable. "Therefore, as the Mn of a polymer increases, a reduced incidence of potential health concern effects might be expected" (OECD, 2009, p. 20).
	An additional PLC consideration is the weight percentage of oligomers that are <1000 Da. Oligomers may be composed of, for example, dimers, trimers, and tetramers, meaning they have 2- monomer, 3- monomer, and 4-monomer units, respectively. The EU report (BIO by Deloitte, 2015) concluded that most potential health concern polymers have Mn of <1000 Da and oligomer content of >1%: "the distribution of potential health concern polymers exhibited an increased incidence of higher oligomer content that began at 5% for <1000 Da and 2% for <500 Da oligomeric content" (OECD, 2009, p. 24).
	Molecular weight distribution (MWD), also known as "polydispersity index," measures the heterogeneity of size of polymer molecules in a polymer. The MWD is an important parameter for predicting potential biological effects of polymers because, although Mn may be a large value, low MW oligomers <1000 Da may be present, which could penetrate the cell.
Ionic character	Electrical charge or ionic character can be anionic, cationic, amphoteric, or nonionic. Specifically, cationic polymers have been associated with aquatic toxicity (Auer et al., 1990; USEPA, 1997a).
Reactive functional groups and RFG ratio to MW	A "reactive functional group" (RFG) is defined as an atom or associated group of atoms in a chemical substance that is intended or can be reasonably expected to undergo facile chemical reaction (USFR, 2012). Some highly reactive functional groups (or a high ratio of RFGs per mole) have been associated with adverse human health and ecotoxicology (e.g., acrylates, methacrylates, isocyanates, anhydrides, aziridines; USEPA, 2010).
	The functional group equivalent weight (FGEW) is used to determine if the RFGs in a polymer are substantially diluted by polymeric material to allow the polymer to be a PLC (USEPA, 1997). The FGEW of a polymer is defined as the ratio of the Mn to the number of functional groups in the polymer. The FGEW is used as an indication of the degree of reactivity of the polymer; the lower the FGEW, the more reactive the polymer and the greater the potential for health and environmental impact (OECD, 2009, p. 10).
Low MW leachables	Low MW leachables are chemical molecules, either inorganic or organic, that migrate (i.e., leach) out of the polymer. These could be residual monomers or oligomers resulting from incomplete polymerization processes, surface residues, or other chemicals used in the manufacturing processes (e.g., initiators, catalysts, chain transfer agents, surfactants).
	Low MW leachables are critically important to the potential for a polymer to affect health and the environment, given that they may be able to migrate out of the polymer and cross cell membranes to potentially react with biomolecules. A report to the EU (BIO by Deloitte, 2015) concluded that "Polymers with <1% MW < 1000 Da and low water extractability are not able to cause systemic effects which are toxicologically or ecotoxicologically relevant."
	Monomers, by nature, are reactive. Unreacted monomers left in a polymer may migrate out of the polymer to react with biomolecules to cause potential adverse effects. Regulatory authorities (BIO by Deloitte, 2015) and the OECD Expert Group on Polymers (OECD, 2009) agree that the residual monomer content of a polymer is critical to determining if it qualifies as a PLC.

(See Supporting Information: Chapter 3 for additional details) Criterion	Description
Particle size	Particle size is also a PLC criterion. Particles that are small enough to reach the deep lung upon inhalation are often associated with adverse health effects. Therefore, to qualify as a PLC, median mass aerodynamic diameter (MMAD) of the polymer particle size should be >5 µm.
Structural and elemental composition	In the US, Chemical Categories of Concern are the result of the review of new chemicals by the USEPA under the TSCA (see https://www.epa.gov/reviewing-new-chemicals-under-toxic-substances-control-act-tsca/chemical-categories-used-review-new). The categories describe the molecular structure, boundary conditions such as MW, equivalent weight, the log of the octanol–water partition coefficient, log <i>P</i> , or water solubility, and standard hazard (mammalian and ecological) and (environmental) fate tests to address concerns.
Elemental composition	The elemental composition is a factor in the assessment of the eligibility of polymers for reduced notification requirements. The exclusion of polymers under this step is not a conclusion of hazard but a determination that the elemental composition does not fall within the parameters of the polymer set under which this rule was formulated, and consequently, these polymers would have to follow the standard notification and review process. These elemental requirements differ across jurisdictions as covered in the report to the EU on global regulatory approaches to polymer assessment (BIO by Deloitte, 2015). For example, in the EU under REACH it is proposed that polymers composed from among these elements, covalently bound to C, have reduced hazard: H, N, O, Si, S, F, Cl, Br, or I (BIO by Deloitte, 2015). In contrast, the USEPA Polymer Exemption Rule states that a polymer is eligible for reduced agency review when it has at least two of the following elements: C, H, O, N, S, or Si (USFR, 1995).
Water and lipid solubility and the octanol-water partition coefficient	Water solubility is the extent to which a compound will dissolve in water. According to the OECD (2009) meeting of the Expert Group on Polymers, polymers with "negligible" water solubility, or those described as "hydrophobic" have been represented with a water solubility of 0.000001 mg/L ( $1 \times 10^{-6}$ mg/L; assigned arbitrarily; OECD, 2009). That is equivalent to 1 ppt, a very conservative definition.
	Polymers with water solubility <10 mg/L showed generally low health concerns.
	The octanol–water partition coefficient ( $K_{ow}$ ) is another criterion to assess chemicals and their environmental and health impact. The $K_{ow}$ is a physical–chemical property at equilibrium to represent the lipophilic or hydrophilic nature of a chemical, the distribution of a compound in octanol, representing the lipophilic nature, to its solubility in water, representing the aqueous nature. The higher the $K_{ow}$ , the more lipophilic the compound. Typically, a $K_{ow}$ >5000 or a log $K_{ow}$ >5 means high lipophilicity and, thus, a high potential to bioaccumulate or bioconcentrate. According to the Stockholm Convention, a bioconcentration factor of >5000 and a log $K_{ow}$ >5 is used as a criterion for bioaccumulation.
Stability	Stability is resistance to physical, chemical, or biological transformation. Loss of stability in the polymer breaks it down into smaller pieces, producing low MW species. As was previously described in the Polymer of Low Concern section under the molecular weight, number average molecular weight, MW distribution, and % oligomer <1000 Da heading, molecules with Mn <1000 Da are capable of crossing cell membranes, making unstable polymers potentially hazardous to health and the environment.
Abiotic stability	Polymers are stable; monomers are not. Abiotic degradation may involve sunlight, water, or oxygen. Photochemical transformation is a reaction involving the radiation energy of sunlight (ultraviolet radiation) that may break a bond in a molecule to change it to another chemical entity. Hydrolytic degradation of polymers is another potential way to break the polymer bonds, creating smaller oligomers that may be bioavailable. Chemical oxidation is a reaction involving the loss of electrons from one atom to another.
Biotic stability: aerobic, anaerobic, and in vivo	Biotic stability is assessed by whether the polymer is degraded by microorganisms under oxygenated (aerobic) or anoxic (anaerobic) conditions; in vitro and in vivo stability studies demonstrate this. In vivo biodegradation involves the breaking of the polymer bonds by the action of bacteria, enzymes, and oxidants within the organism.
Thermal stability	Thermal stability of a polymer can be assessed when used as intended under normal, foreseeable use conditions or in extreme temperatures during disposal, such as by incineration. Thermal stability testing may involve Thermogravimetric Analysis (TGA), which determines mass loss over time and temperature of a test substance.

TABLE 3 (Continued)

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	Fluoroplastics				
Supporting Information Data: Chapter	4.1 PVDF	4.2 PVDF-HFP copolymer	4.3 ECTFE	4.4 ECTFE	4.5 PCTFE
	Polyvinylidene fluoride	Vinylidene fluoride, hexafluoropropene copolymer	Ethylene, chlorotrifluoroethylene copolymer	Ethylene, chlorotrifluorethylene, hexafluoroisobutylene terpolymer	Polychlorotrifluoroethylene
PLC assessment criterion <sup>a</sup>	CAS 24937-79-9	CAS 9011-17-0	CAS 25101-45-5	CAS 54302-04-04	CAS 9002-83-9
Structure	-(CF <sub>2</sub> CH <sub>2</sub> ) <sub>n</sub>	-(CF <sub>2</sub> -CH <sub>2</sub> ) <sub>n</sub> -[CF(CF <sub>3</sub> ) -CF <sub>2</sub> ] <sub>m</sub> -	-(CF <sub>2</sub> -CFCI-CH <sub>2</sub> -CH <sub>2</sub> )n-	$-(C_4H_2F_6)_n-(C_2H_4)_m-(C_2CIF_3)_n-$	-(CF <sub>2</sub> -CFCI) <sub>n</sub> -
Polymer composition (must have C, H, Si, S, F, Cl, Br, or I covalently bound to carbon)	Yes	Yes	Yes	Yes	Yes
Molecular weight (Mn) <sup>b</sup> (Mn >1000 Da and oligomer content <1%)	70 000-300 000	80 000-300 000	Mn >50 000	Mn >50 000	70 000–400 000 average based on grade type
Molecular weight distribution Mw <sup>c</sup> ÷ number average M <sub>n</sub>	2–3	2–3	1.1	1.7	m
Wt% oligomer (<5% for <1000 Da oligomers, <2% for <500 Da oligomers)	Negligible	Negligible	Negligible	Negligible	Negligible
lonic character	Neutral	Neutral	Neutral	Neutral	Neutral
Reactive functional groups (RFGs) <sup>d</sup> and functional group equivalent weight (FGEW)	None and N/A	None and N/A	None and N/A	None and N/A	None and N/A
Low molecular weight leachables	No active leachables by USP class VI (121 °C)	No active leachables by USP class VI (121 °C)	No active leachables by USP class VI (121 °C)	No active leachables by USP class VI (121 °C)	Negligible
Residual monomers	<50 ppb	<50 ppb	<50 ppb	<50 ppb	<0.1 wt%
Ratio of residual monomers to molecular weight (typical value)	~10 <sup>-12</sup> _~10 <sup>-13</sup>	~10 <sup>-12</sup> _~10 <sup>-14</sup>	~10 <sup>-13</sup>	~10 <sup>-13</sup>	<10 <sup>-5</sup>
Structural similarities to RFG of concern	None	None	None	None	None
Reference standard	ASTM D3222-18a	ASTM D5575-18	ASTM D3275-81	ASTM D3275-81	
					(Continued)

TABLE 4 Fluoroplastics and PLC criteria

(Continued)	
TABLE 4	

	Fluoroplastics				
Supporting Information Data: Chapter	4.1 PVDF	4.2 PVDF-HFP copolymer	4.3 ECTFE	4.4 ECTFE	4.5 PCTFE
Physical-chemical properties					
Water solubility and octanol/ water partition coefficient, K <sub>ow</sub>	Insoluble/practically insoluble and N/A	Insoluble/practically insoluble and N/A	Insoluble/practically insoluble and N/A	Insoluble/practically insoluble and N/A	Insoluble/practically insoluble and N/A
Particle size (median mass aerodynamic diameter, MMAD, should be >5 µm)	Powders: 5–300 µm pellets: 2–4 mm	Powders: 5–300 µm pellets: 2–4 mm	D50%: 50–70 µm (typical)	D50%: 50–70 µm (typical)	Pellet: 2-4 µm, flake: 0.54 mm powder: 5–300 micron
Stability					
Hydrolysis, light (hv), Oxidation, biodegradation (aerobic and anaerobic)	Stable	Stable	Stable	Stable	Stable
Thermal stability at normal foreseeable use maximum continuous temp. (°C)	150°C	150 °C	150 °C	150 °C	120 °C
Meets <sup>a</sup> PLC criteria (Yes or No)	Yes	Yes	Yes	Yes	Yes
Fluorinated polymerization aid (PA) used? (Yes or No)	No	S	No	So	No
Recommended processing/ application (use) temperature (T°C)	Processing: 200 °C– 250 °C Use max temp: 150 °C	Processing: 180 °C– 250 °C Use max temp: 100 °C–140 °C depending on HFP content	Processing: 250 °C-280 °C Use max. Temp: 150 °C	Processing: 250 °C–280 °C Use max. Temp: 150 °C	Molding: 230 °C –330 °C and Use Max same as above at 120 °C
	Fluoroplastics				
Supporting Information Data: Chapter	4.6 FEVE	4.7 EFEP	4.8 CPT		4.9 THV
	Fluoroethylene-vinyl ether copolymer	1-Propene, 1,1,2,3 hexafluoro-, pc ethylene and 1 tetrafluoroethy	,3,3- 1,1,1,2,2 lymer with [(trifl ,1,2,2- polyr lene chlor tetraf	,3,3-Heptafluoro-3- loroethenyl)oxy]propane ner with otrifluoroethylene and luoroethylene	1-Propene,1,1,2,3,3,3- hexafluoro-polymer with 1,1- difluoroethylene and tetrafluoroethylene
PLC assessment criterion <sup>a</sup>	cbi	35560-16-8	116018-	J7-6	25190-89-0
					(Continued)

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		TABLE 4 (Continued)		
	Fluoroplastics			
Supporting Information Data: Chapter	4.6 FEVE	4.7 EFEP	4.8 CPT	4.9 THV
Structure	cbi	-(CH <sub>2</sub> -CH <sub>2</sub> ) <sub>n</sub> -(CF <sub>2</sub> -CF <sub>2</sub> ) <sub>m</sub> -[CF <sub>2</sub> - CF(CF <sub>3</sub> )] <sub>1</sub> -	-(CF <sub>2</sub> -CF <sub>2</sub> ) <sub>n</sub> -(CFCI-CF <sub>2</sub> ) <sub>m</sub> -(CF <sub>2</sub> - CF(OR <sup>4</sup> )] <sub>1</sub> -	-(CF <sub>2</sub> CH <sub>2</sub> ),-(CF <sub>2</sub> -CF-CF <sub>3</sub> ),- (CF <sub>2</sub> -CF <sub>2</sub> ) <sub>2</sub>
Polymer composition (must have C, H, Si, S, F, Cl, Br, or I covalently bound to carbon)	Yes	Yes	Yes	Yes
Molecular weight (Mn) <sup>b</sup> (Mn >1000 Da and oligomer content <1%)	7000-46 000	130 000	200 000-300 000	131 000
Molecular weight distribution Mw <sup>c</sup> ÷ number average M <sub>n</sub>	2.0-4.0	4	2–5	1.8
Wt% oligomer (<5% for <1000 Da oligomers, <2% for <500 Da oligomers)	Mn <1000 range of <3.5% and Mn <500 is <0.7%	Negligible; <0.1 wt% oligomer content	Negligible; <0.1 wt% oligomer content	wt.% <1000: None
Ionic character	Neutral	Neutral	Neutral	Neutral
Reactive functional groups (RFGs) <sup>d</sup> and functional group equivalent weight (FGEW)	None and N/A	None and N/A	None and N/A	None and N/A
Low molecular weight leachables	Negligible; cross- linked as final product	Negligible	Negligible	No active leachables by USP class VI (121 °C)
Residual monomers	0.12%–1.43% non- fluorinated	Negligible	Negligible	None detected
Ratio of residual monomers to molecular weight (typical value)	10 <sup>-7</sup> -10 <sup>-8</sup>	<10 <sup>-5</sup>	<10 <sup>-5</sup>	~10 <sup>-13</sup>
Structural similarities to RFG of concern	None	None	None	None
Reference standard		ASTM D7472	ASTM D7471	
				(Continued)

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	Fluoroplastics			
Supporting Information Data: Chapter	4.6 FEVE	4.7 EFEP	4.8 CPT	4.9 THV
Physical-chemical properties				
Water solubility and octanol/ water partition coefficient, K <sub>ow</sub>	Insoluble/practically insoluble and N/A	Insoluble/practically insoluble and N/A	Insoluble/practically insoluble and N/A	Insoluble/practically insoluble and N/A
Particle size (median mass aerodynamic diameter, MMAD, should be >5 µm)	Solution or flake 150 nm for emulsion	2–4 mm (pellets)	2–4 mm (pellets)	Pellets ~400–750 µm
Stability				
Hydrolysis, light (hv), oxidation, biodegradation (aerobic and anaerobic)	Stable	Stable	Stable	Stable
Thermal stability at normal foreseeable use maximum continuous temp. (°C)	220 °C	130 °C; low melting point 160 °C–190 °C and high decompositon temperature of 357 °C–380 °C	200 °C; low melting point 239 °C–251 °C and high decomposition temperature of >400 °C	Continuous use is expected ~room T. (<100 °C as host resin melts at 120 °C); No expected degradation; fluoropolymer degrades >350 °C by TGA
Meets <sup>a</sup> PLC criteria (Yes or No)	Yes	Yes	Yes	Yes
Fluorinated polymerization aid (PA) used? (Yes or No)	No	°Z	No	Yes and No
Recommended processing/ application (use) temperature (T°C)	180 °C–200 °C	Molding temperature: 200 °C-280 °C; Use max as noted above	Molding temperature: 310°C–330°C; Use max as noted above	Melt processing: <350 °C Application: <100 °C (in LLDPE)
Abbreviations: ECTFE, ethylene-chlorotrifluc <sup>a</sup> See OECD (2009) and BIO by Deloitte (20 <sup>b</sup> Molecular Weight is number average mole <sup>c</sup> Molecular weight is weight average molecu <sup>ample.</sup> <sup>d</sup> For definition of reactive functional group, USEPA (2010). See Supporting Information.	oroethylene; HFP, hexafluoropropyl 15) for details on characteristics of scular weight which is defined as th ular weight which is determined by , lists of low-, moderate-, and high-	ene; PCTFE, polychlorotrifluoroethylene; PLC, a "Polymer of Low Concern" and Supporting Ir te total weight of the polymer divided by the t summing the weights of all the chians and the concern functional groups and FGEW limits, se	polymer of low concern; PVDF, polyvinylidene rformation: Chapter 3. otal number of molecules. It is the mole fractic a dividing by the total number of chains. It is the e USEPA polymer exemption guidance manua	fluoride. n of molecules in a polymer sample. ne weight fraction of molecules in a polymer l, BIO by Deloitte (2015, pp. 191–192), and

TABLE 4 (Continued)

	Specialty fluoroplastics		Fluoroelastomers		
Supporting Information Data: Chapter	4.13 Amorphous	4.14 Ionomer	4.10 FEPM	4.11 FKM	4.12 FFKM
	Perfluoro(alkenyl vinyl) ether polymer	Sodium or potassium salts of perfluorosulfonic acid/TFE copolymer or perfluorocarbox- ylic acid/TFE copolymer	Tetrafluoroethylene- propylene copolymer	1-Propene,1,1,2,3,3,3- hexafluoro-polymer with 1,1-difluoroethylene copolymer and terpolymers	Tetrafluoroethylene- trifluoromethyl trifluorovinyl ether copolymer
PLC assessment criterion <sup>a</sup>	37626-13-4	9002-84-0, 1314-23-4, 409-21-2, 111173- 25-2	27029-05-6	9011-17-0, 26425-79-6, 25190- 89-0	26425-79-6
Structure	See Supporting Information	See Supporting Information	See Supporting Information	Supporting Information	-(CF2CF2)x -[CF2-CF (OCF3)]y-(Cure Site Monomer)z
Polymer composition (must have C, H, Si, S, F, Cl, Br, or I covalently bound to carbon)	Yes	Yes	Yes	Yes	Yes
Molecular weight <sup>b</sup> (Mn >1000 Da and oligomer content <1%)	150 000-300 000	>100 000	Various grades vary between 146 000–275 000	30 000340 000	10 000-1 000 000
Molecular weight distribution Mw <sup>c</sup> ⊹ number average M <sub>n</sub>	1.4-2.5	1.0-2.4	Various grades give various ratios from 1.4 to 3.3	1.2–2.4	1.2–3.5
Wt% oligomer (Figure MWD) (<5% for <1000 Da oligomers, <2% for <500 Da oligomers)	Negligible	Negligible	<0.01%	Negligible to <1%	Negligible
lonic character	Neutral	Neutral	Neutral	Neutral	Neutral
Reactive functional groups (RFGs) <sup>d</sup>	None and N/A	None and N/A	None and N/A	None and N/A	None and N/A
Functional group equivalent weight (FGEW; typical value)	>10 <sup>5</sup>	>10 <sup>5</sup>	>10 <sup>5</sup>	>10 <sup>4</sup> -10 <sup>5</sup>	>10 <sup>4</sup>
					(Continued)

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		TABLE 5 (Co	ontinued)		
	Specialty fluoroplastics		Fluoroelastomers		
Supporting Information Data: Chapter	4.13 Amorphous	4.14 Ionomer	4.10 FEPM	4.11 FKM	4.12 FFKM
Low molecular weight leachables	<1 ppm	<1 ppm	No active leachables	<0.4 ppm to <1 ppm	No active leachables
Residual monomers	<1 ppm	<1 ppm	No residual monomers Only cross-linking agent at <1 ppm	<50 ppt to <5 ppm	<50 ppb
Ratio of residual monomers to molecular weight (typical value)	>10 <sup>-5</sup>	>10 <sup>-5</sup>	10 <sup>-11</sup> -10 <sup>-12</sup>	>10 <sup>-10</sup> -10 <sup>-13</sup>	0.25 ppt as Mn = 10 <sup>5</sup> (for representative FKM)
Structural similarities to RFG of concern	None	None	None	None	None
Reference standard				ASTM D 1418	
Physical-chemical properties					
Water solubility and octanol/ water partition coefficient, K <sub>ow</sub>	Insoluble/practically insoluble and N/A	Insoluble/practically insoluble and N/A	Insoluble/practically insoluble and N/A	Insoluble/practically insoluble and N/A	Insoluble/practically insoluble and N/A
Particle size (median mass aerodynamic diameter, aerodynamic diameter, MMAD, should be >5μm)	Solution, sheet or pellets	<ul> <li>(1) Aqueous dispersion casting (as a film) followed by annealing or (2) Melt extrusion as a membrane (reinforced)</li> </ul>	Sheet or crumb	Sheet or block; powders 300-350 µm stability increased/enhanced when cross-linked	Sheet or block; or "crumb"
Stability					
Hydrolysis, light (hu), oxidation, biodegradation (aerobic and anaerobic)	Stable	Stable	Stable	Stable	Stable
					(Continued)

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	Specialty fluoronlastics		Fluoroalactomarc		
Supporting Information Data: Chapter	4.13 Amorphous	4.14 Ionomer	4.10 FEPM	4.11 FKM	4.12 FFKM
Thermal stability at normal foreseeable use maximum continuous Temp (°C)	>250 °C	Sulfonic acid polymer: maximum operating temperature of 175 °C under anhydrous conditions, 220 °C -240 °C in aqueous systems carboxylic acid polymer: use below 120 °C	200 °C	180°C	200 °C300 °C
Meets <sup>a</sup> PLC criteria (Yes or No)	Yes	Yes	Yes	Yes	Yes
Fluorinated polymerization aid (PA) used? (Yes or No)	Yes and No	Yes and No	No	Yes and No	Yes and No
Recommended processing/ application (use) temperature (T°C)	<280 °C	Sulfonic acid polymer: maximum operating temperature of 175 °C under anhydrous conditions, 220 °C–240 °C in aqueous systems carboxylic acid polymer: use below 120 °C	-60 °C-204 °C (AFLAS Technical Document)	Melt processing: <300 °C 160 °C-320 °C (cross- linking temperature)	160 °C320 °C (cross-linking temperature)
Abbreviations: FEPM, trifluoroethylene-prop: <sup>a</sup> See OECD (2009) and BIO by Deloitte (201 <sup>b</sup> Molecular weight is <i>number</i> average molec <sup>c</sup> Molecular weight is weight average molecu <sup>d</sup> For definition of reactive functional group, USEPA (2010). See Supporting Information.	ylene copolymer; FKM, HFP-VF2 <sub>F</sub> 5) for details on characteristics of ular weight. lar weight. lists of low-, moderate-, and high-	olymer and HFP-VF2-TFE polym a "Polymer of Low Concern." concern functional groups and Fi	ers; FFKM, TFE-PMVE perfluoroel GEW limits, see USEPA polymer e	astomer; PLC, polymer of low concern. exemption guidance manual, BIO by Deloitt	:te (2015, pp. 191–192), and

until all data cells in the tables cited above were backed up with a narrative, a testing method, and/or references where publicly available.

- Where several companies have provided data on the same fluoropolymers, the table data presented provide a multicompany compilation and assessment along with appropriate methods and references.
- Individual companies supplying data are identified as authors, but there is no direct attribution regarding which company supplied which data for this study.

#### PLC ASSESSMENT RESULTS

This study was conducted on commercial fluoropolymer products using the PLC criteria to characterize their potential hazard. Figure 1 illustrates the PLC criteria used (BIO by Deloitte, 2015; Henry et al., 2018). The pictured criteria encompass structure, physicochemical property, and stability criteria evaluated in the study. Data informing structure criteria, MW, Mn, and MW distribution (MWD), physicochemical property criteria, water and lipid solubility and  $K_{ow}$ , and stability criteria are presented in Tables 4 and 5. The study also gathered structural data on (a) residual monomers, (b) ratio of residual monomers to MW, (c) structural similarities to reactive functional groups (RFGs) of concern, and (d) thermal stability at normal foreseeable maximum continuous use temperatures. Brief descriptions of PLC criteria are provided in Table 3 with additional details, including references for each criterion in Supporting Information: Chapter 3. An additional data point gathered was whether the fluoropolymer(s) presented utilized a fluorinated polymerization aid (PA) during manufacture. The study results are presented in Tables 4 and 5 and summarized below.

Polymer composition: Each of the fluoroplastics, specialty fluoroplastics, and fluoroelastomers assessed in this study met the criterion of polymer composition whereby either fluorine (F) and/or chlorine (Cl) must be covalently bound to the carbon-only polymer backbone.

MW and MWD: All fluoroplastics, specialty fluoroplastics, and fluoroelastomers in the study met the criteria for MW (Mn >1000 Da) and MWD (1-3). The data demonstrate the fluoroplastics, specialty fluoroplastics, and fluoroelastomers in the study are high-MW solid polymers with fairly narrow MWD and negligible to low wt% oligomer content. The MW for fluoroplastics in Table 4 and specialty fluoroplastics in Table 5 ranged from 50 000 to 300 000, and the MWD ranged from approximately 1.4 to 3. We note that FEVE was measured in its uncured state and that, upon curing, its MW increased significantly. The MW and MWD were determined in a variety of ways depending on the fluoropolymer and its solubility (or insolubility) in various solvents. The MW and MWD data for fluoroelastomers and specialty fluoroplastics in the study are presented in Table 5. The MW and MWD varied because of the various grades of fluoroelastomers ranging from 100 000 to 250 000 with some less than (down to 10 000) and greater than (up to 500 000). MWD was on the order of 1.4 to 3.5. Fluoroelastomer MW is lower for uncured fluoroelastomer versus cured fluoroelastomer. Cured fluoroelastomer is the form used in many formed-use applications (e.g., gaskets and o-rings). The methods and references for MW and MWD data are presented in the Supporting Information: Chapter 4 with the specific chapter noted in Tables 4 and 5. Methods included size exclusion chromatography (SEC), gel permeation chromatography (GPC) along with osmotic pressure, and parallel plate rheometry methods.

Weight % oligomer: The criteria for wt% oligomer are less than 5% oligomer content for Mn less than 1000 Da, and less than 2% oligomer content for Mn less than 500 Da (BIO by Deloitte, 2015; Henry et al., 2018; see also the Supporting Information). All fluoroplastics, specialty fluoroplastics, and fluoroelastomers in the study met the wt% oligomer criteria. Many polymers in the study were reported as "negligible" for oligomers based on analyses conducted. Polymers in the study not cited as negligible have reported numerical data presented in Tables 4 and 5. In addition to SEC and GPC, analytical methods employed included a weight loss upon heating method and the FDA 21 CFR 177.1380 method. The methods and references for wt% oligomer are presented in the Supporting Information: Chapter 4 with the specific chapter noted in Tables 4 and 5.

*Ionic character*: The fluoroplastics, specialty fluoroplastics, and fluoroelastomers in the study are neutral polymers, either containing no ionic groups or may contain anionic at the terminus of their high MW polymer chains as noted in the prior study of fluoropolymers (Henry et al., 2018). Notably different are fluorinated ionomers, which have neutralized (salts) sulfonic acid or carboxylic acid groups pendant to the polymer backbone and as such are neutral and not ionically charged in their polymeric solid form and are low in toxicity and not dermally irritating on skin contact (USEPA, 1997). None of the evaluated polymers in the study have cationic nature. The methods and references for ionic character are presented in the Supporting Information: Chapter 4 with the specific subchapter noted in Tables 4 and 5.

RFG, functional group equivalent weight (FGEW) and structural similarities to RFG of concern: All fluoroplastics, specialty fluoroplastics, and fluoroelastomers in the study met the RFG and FGEW criteria. The polymers in this study do not contain the reactive functional groups set forth in the PLC criteria (e.g., acrylates, alkoxysilanes, amines, aziridines, carbodiimides, and so forth; see Supporting Information: Chapter 3). Given that the polymers in this study have no RFGs, the FGEW values in Tables 4 and 5 are very large numbers (such as  $>10^4-10^5$ ) or the value given is not applicable due to the lack of RFGs altogether. Even the polymers with some functional groups present (e.g., fluorinated ionomers) are not reactive. For example, the FEVE polymerization process leads by design to a polymer with neutral and/or anionic end groups. FEVE resins do contain a small amount of hydroxyl and carboxyl functional groups. These functional groups are classified as low concern RFG by the USEPA (1997) and OECD (2009). There are no RFG structural similarities across the polymers in this study.

Low MW leachables (MW < 1000 Da): All fluoroplastics, specialty fluoroplastics, and fluoroelastomers in the study met the low MW leachable PLC criteria, which has been widely discussed (see Supporting Information: Chapter 3 for references). Many of the study polymers report no active leachables, whereas the rest cite values less than 1 ppm (Tables 4 and 5). For FEVE, it is reported that some nonfluorinated polymer PA may well remain in the uncured polymer resin. The methods and references for low MW leachables are presented in the Supporting Information: Chapter 4 with the specific chapter noted in Tables 4 and 5. The data presented in Tables 4 and 5 were determined for each of the respective polymers in this study using techniques such SEC and GPC as the predominant analytical methods along with the use of USP Class VI testing. Additional methods included 21 CFR 177.2600 (USCFR, 2022) and the USEPA's toxicity characteristic leaching procedure (TCLP; SW-846 Test Method 1311; USEPA, 1992).

Residual monomers and ratio of residual monomers to typical MW: PLC criteria of equal interest to the low MW leachables are the residual monomers and the ratio of residual monomers to typical MW (see Supporting Information: Chapter 3 for references). All fluoroplastics, specialty fluoroplastics, and fluoroelastomers in the study met the residual monomers and ratio of residual monomers to typical MW PLC criteria. The study data presented in Tables 4 and 5 show the polymers in this study have residual monomers ranging from less than 50 ppb for several fluoropolymers and up to less than 0.1% for PCTFE based on the methods utilized. Fluoroelastomers in this study have residual monomers ranging from less than 50 ppb up to less than 5 ppm. Residual monomers were determined in several ways including dynamic and static headspace gas chromatography/mass spectrometry (GC/MS) at 150 °C. The monomers used in most cases have very low boiling points and are thus readily volatilized (and captured or destroyed) during polymer manufacture processing and drying steps. The methods and references for residual monomer determination are presented in the Supporting Information: Chapter 4 with the specific chapter noted in Tables 4 and 5. Given the very low residual monomer levels reported, the ratio of residual monomers to polymer MW range from  $10^{-11}$  to  $10^{-13}$  for the study polymers.

Water solubility and octanol/water partition coefficient ( $K_{ow}$ ): The fluoroplastics, specialty fluoroplastics, and fluoroelastomers in this study are solids that are hydro- and oleophobic, practically insoluble in both water and noctanol. Therefore, a  $K_{ow}$  cannot be computed and is not applicable to these substances. It is worth noting that the practical lack of solubility in water (<10 mg/L) and n-octanol indicate the inability for the study fluoropolymers to actively or passively cross cell membranes. This does mean there is no indication that these polymers can bioaccumulate or bioconcentrate in biota (Henry et al., 2018 and this study). The methods and references for solubility are presented in the

Supporting Information: Chapter 4 with the specific chapter noted in Tables 4 and 5.

Particle size: To meet the PLC assessment criteria for particle size, a powder must be 5  $\mu$ m or greater in size (median mass aerodynamic diameter [MMAD]). All fluoroplastics, specialty fluoroplastics, and fluoroelastomers in the study met the particle size PLC criterion. As shown in Tables 4 and 5, the fluoroelastomers in this study are provided in sheets, blocks, pellets, or "crumb," and the fluoroplastics and specialty fluoropolymers in this study are provided in the form of powders, pellets, sheets, flake, or in dispersions. References and additional information regarding the form of the study polymers is provided in the Supporting Information: Chapter 4.

Stability: All fluoroplastics, specialty fluoroplastics, and fluoroelastomers in the study met the PLC criteria for hydrolysis, light stability, oxidative stability, and aerobic and anaerobic biodegradability (e.g., breakdown into species with Mn <1000 Da). Public literature has abundant thermal, chemical, and biological stability data for the polymers in this study as stability is a hallmark property for these polymers (Ebnesajjad, 2017). For biodegradation, the assessments were largely made based on property data of the study polymers demonstrating they are insoluble and stable in environmental media and thus are not expected to be bioavailable and therefore not biodegrade.

Additionally, published literature reports (Drobny, 2016; Ebnesajjad, 2017; Grot, 2013; Henry et al., 2018; Polymer Industry Association [PIA], 2019) that the study polymers are stable at foreseeable maximum continuous use temperatures presented in Tables 4 and 5. All polymers, including fluoropolymers can degrade when misused or when heated above their recommended use temperatures (Fluoropolymer Products Group of Plastics Europe [FPG], 2012; PIA, 2019). Of course, users are expected to follow guidance for use provided by manufacturers. Hence, the recommended temperatures for reasonably foreseeable use for the study substances are presented in Tables 4 and 5. References and additional information regarding the stability of the study polymers is provided in the Supporting Information: Chapter 4.

Fluorinated PA: If a fluorinated PA was used in the manufacture of the polymer, it was reported for each fluoropolymer in this study. Nine of the 14 fluoropolymers in the study were reported *not* to have used a fluorinated PA in their manufacture. It is industry practice to use fluorinated PAs when it is necessary to obtain specific end-use property or performance requirements generally related to very high-polymer MWs (see also Supporting Information: Chapter 7). For five study polymers, THV, FKM, FFKM, fluorinated ionomers, and amorphous fluoropolymers, a response of "Yes and No" was provided indicating that for some polymer grades a fluorinated PA is used, but not for others. See Supporting Information: Chapter 4 for additional information.

*Results summary*: This study examined three fluoroelastomers, nine fluoroplastics, and two specialty fluoroplastics: ionomers and amorphous. Data for each were gathered from the author companies and assessed by the PLC criteria applicable to the polymer itself "in use" (BIO by Deloitte, 2015; Henry et al., 2018; OECD, 2009). All fluoroplastics, specialty fluoroplastics, and fluoroelastomers in the study met the PLC criteria based on the data presented in Tables 4 and 5 with additional details provided describing methods and references in the Supporting Information: Chapter 4.

Including the four fluoroplastics in the prior study (Henry et al., 2018), data for 18 fluoropolymers have been provided for PLC assessment. These polymers have a wide range of compositions and structures and represent most of the global commercial fluoropolymer market (see additional text in the Discussion). These 18 fluoropolymers represent the major fluoropolymers manufactured and are used worldwide in innumerable critical end-use products and applications. Tables 1 and 2 highlight examples of the enduse markets as well as critical functionality and benefits these polymers provide.

Each of the assessed polymers in this study are insoluble in both water and n-octanol, and thus  $K_{ow}$  is not applicable. This lack of solubility in water and octanol confirms that fluoropolymers are not mobile in the environment and are not bioaccumulative and not able to bioconcentrate. The stability studies reported here on each of the study fluoropolymers reveal their stability in terms of light, hydrolysis, heat, oxidation, and biodegradation. When coupled with the lack of solubility, these fluoropolymers are most often characterized as relatively inert materials in the environment. Like any other chemical material or product, it is important to follow the fluoropolymer manufacturer's recommended use and temperature conditions. Tables 4 and 5 describe these recommendations for each fluoropolymer. As reported, the physical forms of the fluoropolymers are largely pellets, blocks, crumb, sheets, some powders (all with MMAD >5 µm). The solid fluoropolymers are not nanoparticles, and concerns related to nanoparticles do not apply during normal product use. Due to the properties described above for the assessed fluoropolymers-large molecules with no water solubility-the fluoropolymers are biologically inert without the practical ability to cross cell membranes.

During the evaluation of the study fluoropolymers, there was a conscious focus on several core PLC parameters: MW, low MW leachables, % oligomers, and residual monomers, which are direct outcomes related to fluoropolymer manufacturing. In addition to what is reported here in Tables 4 and 5 for the fluoropolymers themselves, industry efforts to manage emissions during manufacturing are discussed below.

#### DISCUSSION

Fluoropolymers have substantial, unique societal value: Fluoropolymers possess a remarkable combination of properties and functional characteristics, as shown in Tables 1 and 2, that make them valued materials of choice in a broad range of industries and applications critical to life

and a sustainable environment in the 21<sup>st</sup> century. Their unparalleled combination of properties and performance characteristics deliver functionality to a wide variety of products and systems critical to achieving important societal goals (Amcham, 2020c; FPG, 2021a; Wood, 2020b). They are strategically important to innovation in vital sectors of the global economy requiring high-speed, high-volume data transmission, miniaturization, or operations in extreme temperatures. Moreover, they are crucial to achieving important societal goals such as decarbonization, renewable energies, and/or competitiveness in the digital transition (FPG, 2021a). Fluoropolymers are indispensable for critical applications in the chemical, electronic, semiconductor, healthcare, and transport sectors and the deployment of 5G networks (FPG, 2021a). For many critical applications, fluoropolymers are the material of choice because alternatives are unable to provide the full complement of performance and functionality required. As such, there are currently no viable commercial alternatives to fluoropolymers in virtually every critical application in which they are used (FPG, 2021a, 2017; PFP, 2020).

Commercial fluoropolymers in this study meet the PLC criteria: Widely used by regulators, PLC criteria have been established around the world and documented by OECD expert groups as an appropriate hazard assessment methodology for polymers in-use and can effectively identify low risk fluoropolymers to help prioritize regulatory action (BIO by Deloitte, 2015; OECD, 1993, 2009). Here, we present PLC data, for hazard assessment, that define a group of fluoropolymers' "in-use" properties. PLC is not a comprehensive life-cycle assessment tool. Full life-cycle assessments consider all phases of product "life" including creation (manufacturing) and end-of-life (disposal). Information on manufacture and end-of-life is provided later in this study. Recently, polymers have been under increased regulatory scrutiny. In 2019, the industry-led European Centre for Ecotoxicology and Toxicology of Chemicals (ECETOC) developed a Conceptual Framework for Polymer Risk Assessment ("CF4Polymers"; ECETOC, 2019). CF4Polymers provides guiding elements to be considered in assessing potential ecological and human health hazards and risks posed by polymer substances. CF4Polymers also considers specific life-cycle stages of polymer products and their associated routes of exposure. The authors of the CF4Polymers framework support the PLC approach as a means to accomplish polymer risk assessment. They specifically support the findings of Henry et al. (2018) and state that they are "unaware of scientific evidence to justify generally assigning fluoropolymers the same level of regulatory concern as other PFAS" (ECETOC, 2019). In 2020, the European Commission contracted a study to propose criteria to identify PRR under REACH (Wood, 2020a). The report states that the authors consider fluoropolymers meeting the criteria to be considered PLC, "following the recommendations of Henry et al. (2018)."

The properties and characteristics of fluoropolymers are anchored in the strength of the carbon–fluorine bond, which

render them highly stable (thermally, chemically, and biologically), inert, and durable-long lasting in use-under exacting and high-performance conditions. Physical, chemical, thermal, and biological stability are important criteria for a polymer to be considered a PLC. The data presented in Tables 4 and 5 demonstrate that commercial fluoropolymers from the author companies meet the criteria to be considered PLC. The PLC criteria for physicochemical properties reflect the state of the polymers in this study, solids, as well as their inertness and stability. None of the fluoropolymers assessed in this study were soluble in water or octanol. They are biologically inert, insoluble in water and octanol, and not expected to move in or between environmental media. Fluoropolymers are also twice as dense as water. These properties and water insolubility mean fluoropolymers are not mobile in the environment and therefore would not be expected to be found in sources of drinking water. Fluoropolymers are neither bioavailable nor bioaccumulative. These solid polymers cannot be absorbed through a cell membrane via passive or active transport and do not bind or interact with the cell surface (see also Supporting Information: Chapter 8). In addition, whereas aquatic and mammalian toxicology studies of fluoropolymers may be desirable for some, they are technically difficult for insoluble, solid, high-MW polymers. The OECD test guidelines reiterate this in many cases. This is confirmed for example in REACH Annex VII guidance, which repeatedly states toxicity is unlikely to occur "if a substance is highly insoluble in water or the substance is unlikely to cross biological membranes" (see Supporting Information: Chapter 9).

Finally, structure criteria including MW, MWD, residual monomer(s), oligomers, and other synthesis by-products, as represented by low MW extractables and leachables have been determined for the fluoropolymers presented and meet values established for the PLC criteria and regulated uses (e.g., USP). The concentrations in the fluoropolymer that have been evaluated are extremely low, reflective of effective manufacturing processes that minimize these compounds complemented by capture and/or destruction systems for such materials. For additional information, see the section below discussing responsible manufacturing. This study and prior work (Henry et al., 2018) provide a guide for other global fluoropolymer manufacturers to gather and present data on additional commercial fluoropolymers to determine if they too meet the PLC criteria.

Fluoropolymer stability, aka persistence, is not an intrinsic hazard: Fluoropolymers are stable, inert, solid materials. Fluoropolymers resist degradation by acids, bases, oxidants, reductants, photolytic processes, microbes, and metabolic processes; for this reason, they are thermally, chemically, and biologically highly inert. Fluoropolymer stability was presented in the introduction and is further considered in the Supporting Information: Chapters 4 and 5. Fluoropolymers are not expected to degrade under environmental conditions or normal use and processing conditions (Wood, 2020a). They are stable and remarkably durable and are therefore persistent. However, persistence alone does not imply that there is a present or future risk to human health or the environment (Rüdel et al., 2020). Persistence itself is not an intrinsic hazard, as it does not in itself imply or inform the potential for an adverse effect (aka toxicity). There is no language in REACH supporting the notion that persistence alone justifies risk-management measures. REACH has regulated persistence in combination with other properties that do inform potential hazards. In fact, REACH combines persistence with bioaccumulation and toxicity (or "very persistent" with "very bioaccumulative/very mobile" vPvB/ vPvM) to justify designation as a substance of very high concern (SVHC) and consideration of potential riskmanagement measures for uses associated with unacceptable risk. Therefore, persistence on its own does not justify the need for specific risk-management measures. Fluoropolymers themselves are persistent, but they are not bioaccumulative, not mobile, and not toxic and therefore not SVHCs from a regulatory perspective (Ruwona and Henry, 2021).

PFAS grouping and segmentation—Scope of regulatory measures: The OECD definition of PFAS is based only on chemical structure (OECD, 2021). It describes a universe of fluorinated organic substances with vastly different physical, chemical, and biological properties, including polymers and nonpolymers; solids, liquids, and gases; highly reactive and inert substances; soluble and insoluble substances; and volatile and involatile substances and is too broad to allow effective, science-based assessment and regulation of chemical compounds as an entire group (Amcham 2020a; BDI, 2021; Buck et al., 2021; Orgalim, 2021; Wallington et al., 2021). A 2021 OECD report states: "it is highly recommended that such diversity be properly recognized and communicated in a clear, specific and descriptive manner" and "the term 'PFASs' does not inform whether a compound is harmful or not, but only communicates that the compounds under this term share the same trait for having a fully fluorinated methyl or methylene aliphatic carbon moiety" (OECD, 2021).

In this context, the available property data (Tables 4 and 5) reveal that fluoropolymers have distinctly different properties from nonpolymeric PFAS and from SCFPs that have a polymeric backbone that does not contain C-F bonds directly attached to it. The perfluoroalkyl moiety in SCFPs is found in a side-chain connected via a functional group to the polymer backbone and "can potentially lead to the formation of nonpolymer PFAS as a result of degradation" (Fluoropolymer Products Group of Plastics Europe [FPG], 2021b; Wood, 2020a; see Supporting Information: Chapter 6). Segmentation that clearly differentiates the broad PFAS family according to their properties, rather than using a structure-based classification alone (OECD, 2021), is needed for a scientifically sound, risk-based regulatory approach. Regulating all PFAS as one homogenous group (ECHA, 2020) absent consideration of their properties, particularly when the properties are so demonstrably different, neglects basic scientific consideration of these properties, which are the foundation of substance differentiation. The USEPA does not consider all PFAS to have

similar risk profiles and therefore they are following a categorical grouping approach based on information about similarities in structure, physicochemical properties, and existing test data on the toxicity of PFAS (USEPA, 2021b). Therefore, segmentation based on properties should be conducted before performing any grouping-based risk assessment, placing stable, nonhazardous fluoropolymers that meet the criteria to be considered PLC in a separate category (see also Supporting Information: Chapter 6).

Fluoropolymer market perspective: The commercial fluoropolymer global market sales have been reported to be approximately 230 000 MT (Dams & Hintzer, 2017). Given the expected fluoropolymer market growth, ranging from approximately 4%-5% to 7%-8% (Allied Market Research [AMR], 2022; Future Market Insights [FMI], 2022; FPG, 2021a; Globe Newswire, 2021), a pro forma market table was created for 2021 using a 5% growth rate. Adding ionomers as well as updated amorphous market information (company data) to the above, the total commercial fluoropolymer market sales is estimated to be approximately 330 000 MT in 2021 (see Supporting Information: Chapter 10). Four fluoropolymers: PTFE, FEP, PFA, and ETFE, were the focus of the first fluoropolymer PLC paper (Henry et al., 2018) and account for approximately 64% of fluoropolymers sold globally in 2021 (pro forma basis). The sales volume of these four fluoropolymers is represented by the first four bars in Figure 10.1 in Supporting Information: Chapter 10. This study discusses 14 fluoropolymers representing an additional 32% (pro forma basis) of the global fluoropolymer market. Therefore, this study, in combination with Henry et al. (2018), presents PLC data from the cited manufacturers of commercial fluoropolymers representing approximately 96% of the global commercial fluoropolymer market that meet the criteria to be considered PLC. The projected 2021 sales volume of the major types of commercial fluoropolymers covered in this study (PVDF, FKM, FEPM, amorphous, ionomers, THV, ECTFE, PCTFE, and FFKM, EFEP, CTP, and FEVE) are also represented in Figure 10.1 in Supporting Information: Chapter 10. As noted, estimated market volumes were provided for the sum of FEPM, CPT, EFEP, and FEVE as well as a small "others" category. The fluoropolymer polyvinyl fluoride (PVF) was not covered by these two papers but is also shown in Figure 10.1 in Supporting Information: Chapter 10. Other fluorinated polymers, perfluoropolyethers, and SCFPs are not addressed in this study (see Supporting Information: Chapter 6).

#### FLUOROPOLYMER LIFE-CYCLE CONSIDERATIONS

This study focuses on the properties of the 14 selected commercial fluoropolymers themselves in-use providing data that demonstrate they meet the criteria to be considered PLC. Additionally, the life-cycle stages of fluoropolymer creation (manufacturing) and disposal at the end of industrial or consumer use (end-of-life) are important to consider. The primary focus in these life-cycle stages is generally nonpolymer PFAS from the manufacturing process or fluoropolymer degradation in end-of-life disposal (ECHA, 2020; FPG, 2021a; Guelfo et al., 2021; Lohmann et al., 2020).

The long-established life-cycle assessment approach to environmental protection and risk management first considers the extent of emissions, their toxicity, and their exposure potential (Guinee et al., 2011). When emissions are sufficiently large in scope, toxicity, and exposure potential, emissionmanagement methods are then considered, including process input changes and emission controls to reduce or eliminate the risk of the emissions. Fluoropolymer manufacturing and disposal life-cycle stages were discussed in the paper that first presented fluoropolymer PLC data (Henry et al., 2018). Here we provide an update and current perspective.

Responsible manufacturing: As corroborated by the data presented here and in prior work (Henry et al., 2018), a large volume percentage and number of commercial fluoropolymers are manufactured that meet the criteria to be considered PLC. Emissions from fluoropolymer manufacture are a key product life-cycle focus. The main focus during the manufacturing phase is not directly related to fluoropolymers but from emissions. Emissions of concern may include nonpolymer PFAS such as fluorinated PAs, unreacted monomers, oligomers, or other unintended by-products formed during manufacturing. It is important to note that, although some high-MW fluoropolymers require use of a fluorinated PA in manufacturing (see also Supporting Information: Chapter 10), it has been reported that at least 50% of commercial fluoropolymers are made without one (Pro-K Fluoropolymer Group, 2021).

Recently, a group of fluoropolymer member companies of FPG voluntarily committed to responsible manufacturing principles through the commissioning of a Regulatory Management Option Analysis, developed by independent consulting firm Chemservices (FPG, 2021a). Member companies of this group are working on individual projects and joint projects at the trade association level with third-party experts. Specifically, companies have committed to continuously improving and/or developing the best available techniques in the manufacturing process, managing environmental emissions, developing R&D programs for the advancement of technologies allowing for the replacement of nonpolymer PFAS PAs and/or working with downstream users to increase the recyclability and reuse of its products in line with the objectives of circular economy (FPG, 2021a). Implementation of this voluntary industry initiative to address concerns relating to fluoropolymers will strengthen already ongoing efforts performed by the fluoropolymer industry promoting responsible manufacturing practices. In addition, member companies are committed to working with EU authorities to establish and implement technical actions to guarantee adequate control of the risks derived from the manufacture and use of fluoropolymers to mitigate such risks wherever possible. This will be done following transparency principles and agreements to monitor progress. For example, important emission reduction has been demonstrated by major fluoropolymer manufacturers including fluorinated PA recovery for reuse, 99% removal of fluorinated PA in wastewater treatment, and 99.99% capture and destruction efficiency of gaseous emissions routed to a thermal oxidizer (Chemours, 2021c), as well as 99–99.9 plant emission reductions (Daikin, 2021c, 2022). Four other companies have reported replacement of fluorinated PAs with nonfluorinated PAs (Arkema, 2008, 2021b; Chemours, 2022; Gujarat Fluorochemicals Limited, 2022; Solvay, 2022). These are substantial efforts toward mitigating emissions associated with fluoropolymer manufacturing being worked on by fluoropolymer manufacturers. This study and the prior study (Henry et al., 2018) provide a guide for other global fluoropolymer manufacturers to gather and present data on their commercial fluoropolymers in-use demonstrating that they meet the PLC criteria.

End-of-use: At the end of industrial or consumer use, fluoropolymers may be disposed via the following routes: landfill, incineration (e.g., waste-to-energy [WTE] facilities), or reuse/ recycling. There is considerable data demonstrating that fluoropolymers such as PTFE do not degrade in the environment or release substances of toxicological or environmental concern (FPG, 2021a; Hintzer & Schwertfeger, 2014). FPG member companies are working with the industry and end users on this subject and are engaged in a research project aimed at identifying conditions required for proper disposal (incineration) of fluoropolymers (FPG, 2021a).

Fluoropolymers are chemically, thermally, and biologically stable (Henry et al., 2018; this study) and therefore are not expected to transform to dispersive nonpolymeric PFAS when disposed of in a landfill. A recent study presented results from OECD guideline biodegradation studies demonstrating that PTFE is stable and does not degrade under environmentally relevant conditions (Ruwona and Henry, 2021). Further, fluoropolymers that meet the criteria to be considered PLC, such as those in this study and prior work (Henry et al., 2018), have negligible leachables, unreacted monomers, and oligomers most likely destroyed in fluoropolymer use processing and would therefore not be expected to significantly contribute to landfill leachate (Ruwona and Henry, 2021).

Available data reveal that fluoropolymers are mineralized (i.e., all C-F bonds broken, hydrofluoric acid generated, and scrubbed to calcium fluoride) under commercial WTE incineration operating conditions (Aleksandrov et al., 2019; Bakker et al., 2021; DEC, 2021; Giraud et al., 2021a, 2021b). In recent pilot scale studies representative of full-scale WTE facilities, the most common form of end-of-life destruction conducted on PTFE found that combustion converted the fluorine into controllable hydrogen fluoride gas and that, of the 31 PFAS studied, no fluorine-containing products of incomplete combustion were produced above background levels (Aleksandrov et al., 2019). Further, a recent study investigating the presence of PFAS in waste incinerator flue gas stated: "based on a literature review, RIVM expects that most of the PFASs will largely degrade during the incineration process and then be removed when the flue gases are cleaned. The remaining PFASs are expected to be removed during the recovery of the carbon dioxide" (Bakker et al., 2021). The RIVM report affirmed that PTFE is the most stable fluorine-containing polymer. For PTFE, the RIVM report concluded that complete thermal decomposition is achieved at a temperature of approximately 800 °C. It was therefore assumed that other fluorine-containing polymers also thermally decompose completely at a temperature of 800 °C. Temperatures at the pyrolysis front and the combustion front in the waste-burning bed range from 900 °C to 1100 °C (Asthana et al., 2006; Ménard et al., 2006), which is well above 800 °C, the temperature at which the complete thermal decomposition of PTFE is achieved (Bakker et al., 2021). Studies for additional fluoropolymers and those with additional pilot and/or full-scale fluoropolymer studies would contribute to this body of data and further affirm their results. The PFP and FPG currently have joint projects working on these potential contributions.

Recycling of fluoropolymer products and articles containing fluoropolymers is difficult because separation of the fluoropolymer from the end products is not always possible (FPG, 2021a; Hintzer & Schwertfeger, 2014; Pro-K Fluoropolymer Group, 2018). This is because fluoropolymers are used predominantly in small components of larger finished articles involving a wide variety of materials. There are several options to recycle fluoropolymer products. In primary recycling, solid fluoropolymer waste is ground and later fed back into the manufacturing cycle of some fluoropolymer products. Recycled fluoropolymers may be used in high-end applications when correctly collected, cleaned, and reprocessed. In secondary recycling, solid fluoropolymer waste is ground, followed by degradation to approximately 1% of the original degree of polymerization by using electron beams, gamma rays, or thermomechanical degradation. The recovered material can be used in the manufacturing of new fluoropolymer products. Lastly, in tertiary recycling or upcycling, solid fluoropolymer is ground, then decomposed into the starting monomers at temperatures higher than 600 °C (pyrolysis) to obtain the same chemical components from which the fluoropolymer was manufactured; monomers, such as tetrafluoroethylene, are purified by distillation, and can then be reused to manufacture new fluoropolymer (3M, 2021; Schlipf & Schwalm, 2014). For the primary and secondary schemes, recycling treatments can be undertaken by the manufacturers of fluoropolymers themselves (onsite), or at a larger scale, mainly by specialist recycling companies. The upcycling needs to be colocated to a fluoropolymer manufacturing plant that can use tetrafluoroethylene.

Primary and secondary recycling is limited because of the presence of fillers, colorants, and other materials in the composition of their final articles. Further, recycling might not work for all end-of-life components, as they are used predominantly in small components of larger finished articles involving a wide variety of materials. Therefore, collecting and dismantling for recycling might not be feasible for all products (FPG, 2021a; Hintzer & Schwertfeger, 2014; Pro-K Fluoropolymer Group, 2018). However, it should be noted that upcycling treatment is applicable to some articles containing fluoropolymers, such as pipe liners in chemical plants, as well as other plant components such as pumps, tank liners, seals, hoses, compensators, and many other fluoropolymer

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This study has described the composition, uses, performfluoroplastics and ORCID REFERENCES Brochure\_EN.pdf JP-FN-F019

components and systems. These are the products for which the high quantities of fluoropolymers are used offering significant recycling potential.

#### **SUMMARY**

ance properties, and functionalities of 14 commercially availfluoropolymers, including able fluoroelastomers. Fluoropolymers are the preferred material of choice because of their unique combination of properties, which are not achievable from other materials or via other functions. As a result, fluoropolymers have become a critical mainstay for society and are useful to modern living, as they provide vital, reliable functionality to a broad range of industrial and consumer products. Further, the study has presented data demonstrating the subject fluoropolymers satisfy the widely accepted polymer hazard assessment criteria to be considered PLC. The data presented demonstrate the fluoropolymers in the study are thermally, biologically, and chemically stable, negligibly soluble in water, nonmobile, nonbioavailable, nonbioaccumulative, and nontoxic, and contain low levels of impurities. These results further demonstrate that the fluoropolymer class should be considered distinctly different and should not be grouped with other PFAS for hazard assessment or regulatory purposes. When combined with earlier work (Henry et al., 2018), the study demonstrates that commercial fluoropolymers are available that meet the criteria to be considered PLC, which represent approximately 96% of the global fluoropolymer market. Lastly, emissions from fluoropolymer manufacture and disposal at end-of-use are a product life-cycle focus. Emissions may include nonpolymer PFAS such as fluorinated PAs, unreacted monomers, oligomers, or other unintended byproducts formed during manufacturing. Fluoropolymer manufacturers recently committed voluntarily to responsible manufacturing principles by continuously improving and/or developing the best available techniques in the manufacturing process, managing environmental emissions, developing R&D programs for the advancement of technologies allowing for the replacement of fluorinated PAs, and/or increasing recyclability and reusing fluoropolymers in line with the objectives of circular economy.

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#### CONFLICT OF INTEREST

The authors are employed by companies that commercially manufacture fluoropolymers. SHK is an independent fluorotechnology consultant working on behalf of AGC Chemicals Americas Inc. and principal of BeachEdge Consulting LLC.

#### DATA AVAILABILITY STATEMENT

Data gathered for this paper is presented in the paper itself and the Supporting Information: Data file provided. Additional data are available upon request from the corresponding author Stephen Korzeniowski (shkorzo@gmail.com).

#### SUPPORTING INFORMATION

The Supplement contains a glossary of terms as well as additional information on the study of fluoropolymers properties and functionalities, polymer of low concern (PLC) background and criteria, references and methods for the PLC data for the study of fluoropolymers, benefits, features and alternatives assessment for the study of fluoropolymers, the differences between fluoropolymers and side-chain fluorinated polymers, fluoropolymer bioavailability and toxicity studies, fluoropolymer global market information, fluoropolymer socioeconomic analyses and risk-management options analysis (RMOA).

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# Fluoropolymers: The Safe Science That Society Needs

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Fluoropolymers are high value chemicals that provide a wide variety of properties in key industrial sectors. These chemicals are indispensable to guarantee the adequate functioning of modern society, with key contributions in safety, decarbonization, and high-tech development. Due to their chemical composition and structure, fluoropolymers match the definition of the PFAS group of substances. However, such definition was originally not intended for regulatory purposes. Indeed, this group of substances is currently under heavy pressure due to the fact that some other chemicals in the group have led to environmental concerns in the past. However, fluoropolymers show clearly differentiated properties from other PFAS, and the vast majority of these polymers have been identified as matching the definition of Polymer of Low Concern. Fluoropolymers are not expected to degrade during normal use or at their end of life, and the main concerns related to their manufacture are being successfully addressed by industry, with innovative developments in both safer designs and improvement of abatement techniques to control emissions.

#### I. Introduction

For several years, per-and polyfluoroalkyl substances (PFAS) have been on the radar of regulators, scientists, non-governmental organizations, and consumers globally, because some chemicals pertaining to this very wide group of substances have been found to be persistent, bioaccumulative, and toxic to human health and the environment. For some of these substances, this concern is justified and their (eco)toxic effects are well known. This is the case, for example, with perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS), for which regulatory controls have been implemented in major economic regions where they were used extensively. Regulators in these countries are now concerned about other PFAS substances where data on (eco) toxicity is not available and hence they could a potential risk in the future specially because they are likely to be persistent owing to strong C-F bond. However, the broad group of

\* Jaime Sales, Regulatory Advisors Chemservice Iberia S.L., Castellón, Spain. Francisco Hernández, Regulatory Advisors Chemservice Iberia S.L., Castellón, Spain. Deepak Kapoor, Gujarat Fluorochemicals GmbH, Regus Centre Watermark, Hamburg, Germany. Marcel van den Noort, Gujarat Fluorochemicals GmbH, Regus Centre Watermark, Hamburg, Germany. For correspondence <j.sales@chemservice-group.com>. PFAS also includes groups of substances - which exhibit clearly differentiated properties compared to other substances in the PFAS group, particularly related to their expected impact on humans and the environment, degradation potential to PFAS of concern and specific applications of use. One of such unique group is fluoropolymers. This paper highlights the differences that can be established between fluoropolymers and other substances in the PFAS group and provides arguments to justify that these chemicals should be regulated separately from other PFAS.

Fluoropolymers are high molecular weight substances structurally characterised by having fluorine atoms directly attached to their carbon-only backbone. This differentiates fluoropolymers from other substances typically included in the PFAS group of chemicals. In fact, they can also be further differentiated from other polymeric fluorinated substances, such as side-chain fluorinated polymers (SCFPs) or perfluoropolyethers (PFPEs).

The main fluoropolymers meet criteria to be identified as Polymers of Low Concern (PLC) as developed by the Organisation for Economic Co-operation and Development (OECD). Existing scientific data demonstrates that, because of their unique set of properties, such as negligible solubility in water or high molecular weight, fluoropolymers cannot enter or accumulate in the human tissue, and they cannot degrade into other PFAS under intended conditions of use or under ambient environmental conditions. Therefore, it is considered that fluoropolymers do not pose a significant risk to water quality, human health, or the environment. Finally, potential indirect situations that may generate concerns related to PFAS emissions, such as the need to use fluorinated polymerisation aids in the fluoropolymer manufacturing process, are being addressed by industry, with significant progress made over the last years. Furthermore, the End-of-Life (EOL) phases of applications related to fluoropolymers are not expected to be of concern.

However, since fluoropolymers meet the OECD definition of PFAS, they are included in the scope of the restriction proposal that 5 Competent Authorities from Member States of the European Economic Area have announced on the broad PFAS group of chemicals under the REACH Regulation<sup>1</sup>. Therefore, fluoropolymers could face market restrictions in Europe if their differentiated properties are not clearly highlighted in the restriction proposal. This could even lead to a ban on the uses of these high value materials in different applications in which they are used.

This paper argues for an exemption of the Fluoropolymer group from the PFAS restriction proposal.

#### II. Societal Importance of Fluoropolymer Applications

Fluoropolymers are used in a wide variety of highly critical applications due to their valuable properties, mainly by industrial actors.<sup>2</sup> In the case that the use of fluoropolymers would be banned in Europe, a number of critical sectors would be significantly impacted, which could result in severe damage to the European society. The list below covers just a selection of examples of industries that could be damaged because of this.

Renewable Energy: fluoropolymers are key components in solar panels and wind turbines, where they protect against weather impacts of equipment exposed to e.g., rain and environmental contaminants. In photovoltaic cells, fluoropolymers improve electrical insulation. Furthermore, these materials are critical and absolutely necessary for optimal performance of lithium-ion batteries and hydrogen fuel cells. Without fluoropolymers,

these devices will not work efficiently, and the goals of the European Green Deal would be seriously compromised.

- Semiconductors: fluoropolymers provide properties that are essential in this use, such as resistance to harsh chemicals that need to be used in the manufacturing process while providing an environment completely free of impurities. No fluoropolymers available will mean that the semiconductor industry will not be able to produce the high-tech microchips that allow for the development of modern (and reduced in size yet powerful) devices such as mobile phones, laptops and many other hightech equipment.
- Chemical process industry: due to their unmatched properties in terms of resistance to chemical attack and optimum performance under wide variations of temperature, fluoropolymers are the only available set of products on the market that allow for adequate performance of many chemical processes. While other materials could be used for handling chemical streams, these would need continued maintenance and replacement and what is worse, they would significantly increase the risk of failure and accidents, leading to higher probability of operators and the environment being unexpectedly exposed to highly hazardous chemicals. Fluoropolymers can be found in all kinds of tubing and industrial equipment, as well as joints and gaskets to secure operation and containment of chemicals.
- Transport: fluoropolymers contribute to both fuel efficiency (as key components in combustion engines) and safety, playing a key role in systems such as brakes in cars or wing flaps in aircrafts. They are also the best option available (due to their high resistance but also high flexibility) to protect electrical cables in aircrafts, where high reliability of such cables, which can be exposed to thermal as well as chemical pressure, is fundamental.
- Food and water treatment: wherever high purity is required, fluoropolymers play an irreplaceable role. These materials are present in water filtration systems (which avoids the need to use chem-

<sup>1</sup> Regulation (EC) No 1907/2006

<sup>2</sup> Fluro Council, 'Understanding FluoroTechnology' (2017) <https://fischerpaperproducts.com/wp-content/uploads/2017/02/Understanding-Fluorotechnology-FluoroCouncil.pdf> accessed 24 October 2022.

icals for water treatment) and also in food processing systems to guarantee adequate sanitary conditions and avoid contamination which could otherwise reach consumers.

Pharmaceutical and medical devices: medical implants that are intended to be used in the human body (catheters, implants) due to their biological compatibility and inertness. Certainly, materials that are used for this purpose are not toxic for human health and, due to their high durability, can last for many years in the body without replacement. Furthermore, the production of medicines and vaccines by the pharma industry require as well ultra purity conditions which can only be achieved with equipment based on fluoropolymer materials.

#### III. Fluoropolymers Inside the Broad PFAS Group

PFAS are a group of 4,730 different highly fluorinated synthetic (man-made) substances<sup>3</sup>, both polymeric and non-polymeric, although other sources increase the number to approximately 9,000 chemi-

6 Ibid.

- 8 Interstate Technology Regulatory Council (ITRC), 'Naming Conventions and Physical and Chemical Properties of Per- and Poly-fluoroalkyl Substances' (2020) <a href="https://pfas-1.itr-cweb.org/fact\_sheets\_page/PFAS\_Fact\_Sheet\_Naming\_Conventions\_April2020.pdf">https://pfas-1.itr-cweb.org/fact\_sheets\_page/PFAS\_Fact\_Sheet\_Naming\_Conventions\_April2020.pdf</a>> accessed 24 October 2022.
- 9 IUPAC, 'What are polymers? International Union of Pure and Applied Chemistry' (2022) <a href="https://iupac.org/polymer-edu/what-are-polymers/">https://iupac.org/polymer-edu/whatare-polymers/</a>> accessed 24 July 2022.
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- 11 (n 3).

cals.<sup>4</sup> They are grouped together in accordance with a common definition based on chemical structure<sup>5</sup>: "PFASs are defined as fluorinated substances that contain at least one fully fluorinated methyl or methylene carbon atom (without any H/Cl/Br/I atom attached to it), i.e., with a few noted exceptions, any chemical with

*fluorinated methylene group (–CF2–) is a PFAS.*" It should be noted that such definition was originally not intended to be used for regulatory purposes.<sup>6</sup> This has been highlighted recently in a publication by an independent panel of experts on the topic, which generally concluded that all PFAS should not be grouped together for the purpose of assessing human health risks, and that the definition of appropriate subgroups can only be defined on a case-by-case manner.<sup>7</sup>

at least a perfluorinated methyl group (-CF3) or a per-

Due to the large number of chemicals pertaining to this group, and the wide variability of composition and properties, PFAS can be divided in different families. A summary of the structure of the PFAS group is displayed in **Figure 1**.<sup>8</sup>

As seen in Figure 1, fluoropolymers are part of the PFAS group by definition. However, they are different to other PFAS due to their polymeric nature. A polymer is defined as a molecule of high relative molecular mass (macromolecule), the structure of which essentially comprises the multiple repetitions of units derived from molecules of low relative molecular mass, known as monomers.<sup>9</sup> In the case of fluoropolymers, this macromolecule is a long chain (backbone) of thousands of connected carbon atoms to which fluorine atoms are bound.<sup>10</sup> For this reason, this family of synthetic polymers can be easily differentiated from the non-polymeric PFAS, which are also based on chains of carbon atoms, but which are much shorter than those of polymers (chain length between 2 and 13 carbon atoms).

According to the bibliography, out of the 4,730 substances included in the PFAS category,<sup>11</sup> only 256 are commercially relevant.<sup>12</sup> In the case of fluoropolymers, only 38 substances are currently available on the market, out of the 267 compounds that are currently identified. This means that commercial fluoropolymers only represent 0.8% of the PFAS universe, but they represent 14.8% of the PFAS with commercial relevance. This is a good illustration of how important fluoropolymers are in modern society, due to the unique properties of these materials and their superior performance in many applications.

<sup>3</sup> OECD, 'Toward a new comprehensive global database of per- and polyfluoroalkyl substances (PFASs)' (2018) Series on Risk Management, 39.

<sup>4</sup> The National Institute for Occupational Safety and Health (NIOSH), 'Per- and polyfluoroalkyl substances (PFAS)' (2022) <https://www.cdc.gov/niosh/topics/pfas/default.html> accessed 24 October 2022.

<sup>5</sup> OECD, 'Reconciling Terminology of the Universe of Per- and Polyfluoroalkyl Substances: Recommendations and Practical Guidance' (2021) Series on Risk Management, 61.

<sup>7</sup> J k Anderson et al, 'Grouping of PFAS for human health risk assessment: Findings from an independent panel of experts' (2022) Regulatory Toxicology and Phamacology, 134.

<sup>12</sup> R C Buck et al, 'Identification and classification of commercially relevant per- and poly-fluoroalkyl substances (PFAS)' (2021) Integrated Environmental Assessment and Management 17, 1045–1055.



Figure 1: Structure of families in the PFAS Group

#### IV. Fluoropolymers are Non-Toxic, Polymers of Low Concern

Existing scientific data demonstrates that, because of their unique characteristics such as the negligible solubility in water or the high molecular weight, fluoropolymers cannot enter or accumulate in the human bloodstream. Therefore, fluoropolymers are do not pose a significant risk to human health, or the environment.<sup>13</sup> This allows to conclude that fluoropolymers meet the criteria to be identified as PLC. While the PLC criteria are not completely agreed worldwide, basic consensus exists around the following:<sup>14</sup>

- High molecular weight, based on the Number-average molecular weight (Mn): an Mn of ≥1,000 Da is a generally accepted Mn range for a PLC.
- Content of low molecular weight, oligomeric species (no common levels accorded among global regulations).
- Presence (or absence) of specific reactive functional groups (RFGs) in the polymer: these are functional groups that are known to be associated with toxicity of polymers and include cationic species that are known to result in aquatic environmental toxicity.
- Solubility (in water and other solvents): polymers with water solubilities <10 mg/L showed generally low health concern.

 Other criteria: stability of the polymer, chemical class (or polymer class), residual monomer content and human health hazard classification.

In order to establish if fluoropolymers meet these conditions, research was originally conducted on a set of 4 specific polymers: polytetrafluoroethylene (PTFE), ethylene- tetrafluoroethylene copolymer (ETFE), tetrafluoroethylene-hexafluoropropylene copolymer (FEP), and tetrafluoroethylene-perfluoroalkyl trifluorovinyl ethers copolymer (PFA). The evaluation of these fluoropolymers<sup>15</sup> shows that they satisfy the widely accepted assessment criteria to be considered PLCs. All of them are high molecular weight polymers, stable against hydrolysis, light, oxidation, and biodegradation, and thermally stable in the range of 150 °C to 260 °C.

<sup>13</sup> B J Henry et al, 'A Critical Review of the Application of Polymer of Low Concern and Regulatory Criteria to Fluoropolymers' (2018) 14 Integrated Environmental Assessment and Management 3, 316–334. S H Korzeniowski et al, 'Critical Review of the Application of Polymer of Low Concern Regulatory Criteria to Fluoropolymers II: Fluoroplastics and Fluoroelastomers' (2022) Integrated Environmental Assessment and Management.

<sup>14</sup> OECD, 'Data analysis of the identification of correlations between polymer characteristics and potential for health or ecotoxicological concern' (2009) <http://www.oecd.org/chemicalsafety/riskassessment/42081261.pdf> accessed 24 July 2022; Deloitte, 'Technical assistance related to the review of REACH with regard to the registration requirements on polymers' (2015) Final report prepared for the European Commission (DG ENV), in collaboration with PIEP.

<sup>15 (</sup>n 13).

Also, they are practically or completely insoluble in water and not soluble in octanol. As solubility in octanol is predictive of lipid solubility, it can be expected that fluoropolymers do not dissolve in cell membrane lipids to gain access to cellular contents. Because these fluoropolymers cannot enter the cells, they are not capable of bioaccumulation or bioconcentration in aquatic life.

More recent research has expanded these conclusions to cover 14 additional fluoropolymers.<sup>16</sup> The new data confirms the same conclusions as originally established by Henry et al. in 2018, for the original set of 4 fluoropolymers; it is confirmed that all the fluoropolymers evaluated (covering approximately 96% of the global fluoropolymer market) fulfill the PLC criteria, and can therefore be expected to be negligibly soluble, not mobile, not bioavailable, not bioaccumulative, and not toxic.

#### V. Fluoropolymers are Different From Other Polymeric PFAS

As discussed in **Section II**, fluoropolymers can be clearly differentiated from short-chain or long-chain non-polymeric PFAS. But fluoropolymers are also different from the other families of polymeric PFAS, such as SCFPs or PFPEs, on the basis of their nature, structure, uses, and applications, as well as from the point of view of safety and expected environmental impacts.

Attending to the structure of the macromolecules, the polymeric PFAS can be grouped in the following three main categories:<sup>17</sup>

- Fluoropolymers: have a carbon polymer backbone with fluorine atoms directly attached to carbon atoms in the backbone.<sup>18</sup>
- PFPEs: have a polyether polymer backbone, in which repeating monomer contains a carbon-oxygen bond, with fluorine atoms directly attached to carbon atoms in the backbone.
- SCFPs: have a carbon polymer backbone with fluorinated side chains directly attached to carbon atoms in the backbone. In this case, fluorine atoms are not directly attached to carbon atoms in the backbone. In the final structure, the fluorinated side chains are attached to the polymer backbone by a spacer moiety and a linking group.<sup>19</sup>

The different groups of polymeric PFAS based on their structure are displayed in Figure 2 (Wahlström et al., 2021).

These differences in the structure of the polymeric PFAS have consequences in their properties. Fluoropolymers are solid materials known for exhibiting material properties (i.e., intrinsic to the material), whereas SCFPs, marketed as liquids, greases, or dispersions in water, have surface properties, which means that they act in direct contact with products to which they are applied. This fact has implications in the downstream uses of these materials. For example, fluoropolymers are not used in firefighting foams, which is a classical application of SCFPs. In general, while fluoropolymers are used mainly in industrial applications, such as chemical processing industries, renewable energy, telecommunications, electronics and semiconductors, automotive and aerospace, food and water processing, architecture and building, and medical devices,<sup>20</sup> SCFPs are typically used in consumer applications, such as surface protectors to provide water, oil, and stain repellence to textiles, apparel, leather, carpets, nonwovens, and paper, and soil release properties.<sup>21</sup> In relation to PF-PEs, while these are mainly used as lubricants in specific industrial sectors, certain consumer applications related to surface protection are also relevant.<sup>22</sup>

Finally, fluoropolymers are substantially different from the other polymeric PFAS in terms of potential emissions due to degradation into small PFAS molecules during intended use or under environmental conditions and, for this reason, they have no environmental impact. Fluoropolymers have a high molecular weight, little to no water solubility and volatility, therefore they are not expected to degrade to low-

<sup>16 (</sup>n 12).

<sup>17</sup> European Commission, 'Scientific and technical support for the development of criteria to identify and group polymers for Registration/Evaluation under REACH and their impact assessment' (2020).

<sup>18 (</sup>n 13).

<sup>19</sup> H Fiedler, 'A critical review of a recommended analytical and classification approach for organic fluorinated compounds with an emphasis on per- and polyfluoroalkyl substances' (2020) 17 Integrated Environmental Assessment and Management 2, 331–351.

<sup>20</sup> J Glüge J, 'An overview of the uses of per- and polyfluoroalkyl substances (PFAS)' (2020) Environmental Science: Processes & Impacts 22, 2345; S Banerjee, 'Poly(fluoroacrylate)s with tunable surface hydrophobicity via radical copolymerization of 2,2,2trifluoroethyl acfluoroacrylate and 2-(trifluoromethyl)acrylic acid' (2017) Polymer Chemistry 8, 1978.

<sup>21 (</sup>n 20) Glüge et al; (n 2).

<sup>22 (</sup>n 19).



Figure 2: Types of Polymeric PFAS Based on Their Structure

er molecular weight PFAS.<sup>23</sup> Also, they are not expected to lead to the formation of long-chain PFAS as a result of degradation.<sup>24</sup> PFPEs exhibit a similar behaviour to fluoropolymers,<sup>25</sup> because the repeating units of the PFPEs contain only 2 or 3 perfluorinated carbon atoms per oxygen atom, and their degradation cannot lead to the formation of long-chain PFAS.<sup>26</sup>

However, the linking group in the structure of the SCFPs can be susceptible to cleavage, depending on the structure of each material, resulting in loss of the fluoroalkyl side chain. Thus, SCFPs can ultimately be a source of perfluoroalkyl acids (PFAAs), such as PFOA, PFOS, perfluorobutanoic acid (PFBA), perfluorohexane sulfonic acid (PFHxS), or perfluorohexane carboxylic acid (PFHxA), unless there is stability data to prove otherwise. This means that, under environmental conditions, SCFPs can degrade to these non-polymer PFAS, which are well known due to their negative effects on the environment.

#### VI. Use of PFAS as Polymerisation Aids in the Production of Fluoropolymers

The main concerns that have been typically flagged in relation to fluoropolymers are not based on these materials as such, but on the use of other PFAS substances in the manufacturing process of fluoropolymers. Under certain conditions, the use of short-chain PFAS as polymerisation aids (surfactants) is necessary to achieve the final fluoropolymer substance. This may result in emissions of PFAS from the fluoropolymer manufacturing process. In addition, residuals of these fluorinated surfactants may be carried over with the final fluoropolymer substance down the supply chain, which may also result in additional PFAS emissions from fluoropolymer products during the life cycle. The production process can also involve the generation of unintended fluorinated oligomers or lower molecule polymers during the process.

All the above items of concern have been raised by researchers (Lohmann et al., 2020) and regulators. The fluoropolymer industry is committed to addressing these issues, and improvements in the fluoropolymer manufacturing process continue to be investigated. Furthermore, the fluoropolymer industry in Europe, via the Fluoropolymer Products Group (FPG) of Plastics Europe, recently commissioned a Regulatory Management Option Analysis (RMOA) on fluoropolymers. The objective of the RMOA was to evaluate the possible Regulatory Management Options (RMOs) that could be applicable to fluoropolymers, and to identify the most appropriate one in terms of

<sup>23</sup> Ibid; The Danish Environment Protection Agency, 'Survey of PFOS, PFOA and other perfluoroalkyl and polyfluoroalkyl substances' (2013) Environmental Project No 1475.

<sup>24 (</sup>n 17).

<sup>25 (</sup>n 17); (n 19).

<sup>26 (</sup>n 12).

different parameters, such as effectiveness and proportionality. As a conclusion of this RMOA (Plastics Europe, 2022),<sup>27</sup> the fluoropolymer industry in Europe has established a commitment to make efforts to address the existing concerns related to the use of fluorinated polymerisation aids (FPAs) in the manufacture of fluoropolymers, and to work on minimizing emissions of low carbon chain fluorinated byproducts.

Several fluoropolymer manufacturers have recently announced important achievements in the development of manufacturing processes that do not require the use of FPAs.<sup>28</sup> These achievements, which result in technically equivalent fluoropolymer grades with no presence of unintended fluorinated by-products, are expected to have significant impact in future trends of fluoropolymer manufacture, as they should lead towards a clear reduction of the use of such fluorinated surfactants. In this regard, it is worth mentioning that, according to IHS and Chemical Economic Handbook (CEH) reports, it is estimated that 55.2% of fluoropolymer production does not require the use of FPAs.<sup>29</sup> The global production of fluoropolymers is estimated at approximately 320,000 tonnes per year. Table 1 shows information from sources related to total volume of the main substances in the fluoropolymer family, according to the sources.

With the full implementation of these new achievements as announced by industry, it is expected that close to 83% of the global production will not require the use of short-chain PFAS. It is to be noted that the three main fluoropolymers by volume (PTFE,

PVDF and FKM) will shortly be manufactured fully without the use of FPAs, reaching only with this three fluoropolymers almost 80% of global volume (and this number is expected to grow, with expected increased volumes for some of those polymers, such as PVDF in the electric vehicle industry). Still, industry continues to make efforts on research and development to completely remove the use of fluorinated surfactants from the manufacture of fluoropolymers. While it is difficult to anticipate a date when 100% production will be possible without the use of FPAs, key industrial players expect that within 10 years they will be at or very close to that objective.

In parallel to this, it is worth highlighting that industry has also made significant progress in the development of abatement techniques that currently allow for close to or even above 99% recovery of any PFAS emissions that could be related to the manufacturing process of fluoropolymer.<sup>30</sup> Coupled with the continued efforts to remove FPAs from the manufacturing process, it is expected that the production (and continued use) of fluoropolymers will be performed under conditions that will not generate any significant risks to human health or the environment in terms of exposure to PFAS.

#### VII. Fluoropolymers Do Not Generate Significant Concerns During Endof-Life

An additional reason of concern to regulators and researchers related to fluoropolymers is the EOL stage of products manufactured with these polymers, due to uncertainties in the fate of these persistent polymers if landfilled, or to potential generation of additional PFAS during incineration.

It is relevant to note that, precisely because fluoropolymers are used in specific industrial applications, the waste phase for many of those sectors of use is already significantly regulated and therefore waste containing fluoropolymers will be adequately managed, in many cases via specific legislation (e.g., electronics). In addition to this, it needs to be taken into account that fluoropolymers have a very longlife span in their applications of use (in many cases going above 30 years). This means that the rate of generation of fluoropolymer waste is significantly lower compared to other polymers (plastics). Indeed, based on recent studies that have evaluated available

<sup>27</sup> Plastics Europe, 'Regulatory Management Option Analysis for Fluoropolymers' (2022) <https://fluoropolymers.plasticseurope.org/index.php/fluoropolymers/irreplaceable-uses-1/reports-policy-documents/rmoa> accessed July 24 2022.

<sup>28</sup> Chemours, 'Chemours Announces Process Innovation with New Viton™ Fluoroelastomers Advanced Polymer Architecture (APA) Offering' (2022) <https://www.chemours.com/en/news-media-center/all-news/press-releases/2022/chemours-announces-process-innovation-with-new-viton-fluoroelastomers-advanced-polymer-architecture> accessed 24 August 2022; Solvay, 'Producing new fluoropolymers without fluorosurfactants' (2022) <https://www.solvay.com/en/article/eliminating-pfas> accessed August 24 2022; GFL, 'Company Announcement' 2022 <https://www.gfl.co.in/up-load/pages/ebce5fed9030753d0ee651bf1f48d0a0.pdf> accessed August 24 2022.

<sup>29</sup> IHS Markit, 'Chemical Economics Handbook' (2016) <a href="https://ihs-markit.com/products/fluoropolymers-chemical-economics-handbook.html">https://ihs-markit.com/products/fluoropolymers-chemical-economics-handbook.html</a>> accessed 24 October 2024.

<sup>30</sup> R Dams and K Hintzer, 'Industrial Aspects of Fluorinated Oligomers and Polymers, in Fluorinated Polymers' (2016) Polymer Chemistry Series Volume 2: Applications, 1-31; (n 28) Chemours.

Fluoropolymers	Volume (tonnes)	% of total volume	Use of FPAs	% volume that does not require the use of FPAs	% volume that will not require the use of FPAs
PTFE Total	169,759	53%			
PTFE Suspension	84,879.5	26.5%	N	26.5%	26.5%
PTFE Emulsion	84,879.5	26.5%	Y		26.5%
PVDF (Homopolymer + Copolymer)	51,248	16%	N	16%	16%
FKM	35,000	10.9%			
FKM Copolymer	25,000	7.8%	Ν	7.8%	7.8%
FKM Terpolymer	10,000	3.1%	Y/N	1.6%	3.1%
FEP	32,030	10%	Y		
PVF	6,406	2%	Y		
PFA	3,203	1%	Y		
ETFE	3,203	1%	Y		
THV	800	0.3%	Y		
ECTFE (Copolymer + Ter- polymer)	2,200	0.3%	Ν	0.3%	0.3%
PCTFE	8,600	2.7%	N	2.7%	2.7%
Others	7,851	2.5%			
TOTAL	320,300			54.8%	82.9%

Global production of fluoropolymers and use of FPAs.

data from 2020,<sup>31</sup> it is anticipated that less than 0.01% by weight of fluoropolymers entered relevant waste streams in Europe. This is significantly lower to other plastics that are estimated at about 4.8%. In that year, the majority of fluoropolymers waste (83.5%) was either incinerated or thermally destructed. About 13% of the waste was landfilled, in an operation that is expected to result in no significant environmental concern.

Pilot studies of the most common form of EOL destruction, which is municipal incineration, of the most common fluoropolymer, which is PTFE, found that the combustion converted the fluorine into controllable hydrogen fluoride gas and that of the 31 PFAS species studied, no fluorine containing products of incomplete combustion were produced above background levels.<sup>32</sup>

<sup>31</sup> Conversio, 'Fluoropolymer waste in Europe 2020 – End-of-life (EOL) analysis of fluoropolymer applications, products and associated waste streams' (2022).

<sup>32</sup> K Aleksandrov, 'Waste incineration of Polytetrafluoroethylene (PTFE) to evaluate potential formation of per- and Poly-Fluorinated Alkyl Substances (PFAS) in flue gas' (2019) Chemosphere 226.

Related to the incineration, in 2021 the National Institute for Public Health and the Environment of the Netherlands carried out a literature study to investigate presence of PFAS in waste incinerator flue gases.<sup>33</sup> It was investigated to what extent and under what conditions PFAS, including fluoropolymers, are thermally degraded and what kind of incineration byproducts are formed. In this research, PTFE was found to be the most stable fluorine-containing polymer. For PTFE, it was concluded that complete thermal decomposition is achieved at a temperature of about 800°C. It was therefore assumed that other fluorine-containing polymers also thermally decompose completely at a temperature of 800°C. Temperatures at the pyrolysis front and the combustion front in the waste-burning bed range from 900 to 1100°C,<sup>34</sup> which is well above the temperature of 800°C at which the complete thermal decomposition of PTFE is achieved.

Landfills that receive fluoropolymers containing wastes also effectively contain any fluorinated compounds that might leach from the fluoropolymer waste through their leachate collection systems. The European landfill directive defines the different categories of waste (municipal waste, hazardous waste, non-hazardous waste, and inert waste), and it applies to all landfills, defined as waste disposal sites for the deposit of waste onto or into land. Typically, fluoropolymer waste is chemically inert. Therefore, fluoropolymers disposed in landfills are not expected to pose any threat to human health and environment.

For certain applications like non-stick frying pans, industry is working on suitable labelling for proper collection and recycling of used pans.

#### VIII. Fluoropolymers Are Used in High Value Industrial Applications

Fluoropolymers are extremely stable, solid specialty materials that have unique physicochemical proper-

ties which render them specialty plastics that are virtually chemically inert, non-wetting, non-stick, and highly resistant to temperature variability, fire, and weather, and exhibit low flammability. They also display features such as low coefficient of friction, dielectric strength, and flexibility. The exceptionally strength of the carbon-fluoride bond in fluoropolymers generates these high value properties.<sup>35</sup>

These properties, and particularly the joint combination of all of them in single products, make them irreplaceable in many applications, and it is commonly accepted that their unique set of properties cannot be matched by alternative materials, particularly in the wide range of operability they offer. In fact, fluoropolymers are frequently the high-cost option in many industries, being the material of choice only when other products are known to fail to provide the required combination of properties for the desired application.

The industrial sectors in which fluoropolymers are typically used are chemical processing industries, transport (e.g., automotive, aerospace), electronics (semiconductors, data transmission cables, electrical cables), food and water processing, pharmaceutical, medical devices, or construction.<sup>36</sup> In most of these applications, fluoropolymers are used when the material of choice needs to withstand very harsh conditions in relation to e.g., chemical environment, very high or very low temperatures (sometimes involving wide temperature variations), usually combined with other required properties such as high flexibility, barrier properties, biocompatibility, electric properties, or flame retardancy, to name a few.

Frequently the value that fluoropolymers provide to these applications are strongly related to critical areas such as:

- Safety of human health or the environment, providing safe equipment required to handle harsh chemicals in many industries thus avoiding releases of hazardous materials (chemical industries, food processing, pharmaceuticals), or providing protection to a wide range of systems (data transmission, electric cables in automobiles or aircrafts, protecting passengers from failure events.
- Clean water, providing efficient filtration systems for water treatment and replacing outdated and environmentally aggressive processes.
- Green energy production, playing a key role in the efficient development of lithium-ion batteries or hydrogen fuel cells.

<sup>33</sup> Rijksinstituut voor Volksgezondheid en Milieu, 'Per- and polyfluorinated substances in waste incinerator flue gases' (2021).

<sup>34</sup> A Asthana et al, 'A 2-D mathematical model of on-grate municipal solid waste combustion' (2006) Sohn International Symposium Advanced Processing of Metals and Materials; A Asthana et al, 'A 2-D mathematical model of on-grate municipal solid waste combustion' (2006) Sohn International Symposium Advanced Processing of Metals and Materials.

<sup>35 (</sup>n 20).

<sup>36 (</sup>n 2).

 Semiconductors, where the use of fluoropolymers is irreplaceable for the purpose of ensuring the technology that is currently required to produce modern reduced electronic devices.

It is worth noting that in many cases, fluoropolymers were the innovative solution that was introduced to solve previous issues in terms of safety or performance. For example, fluoropolymer-based gaskets were implemented in the chlor/alkali process years ago, and they are still considered the Best Available Technology to replace asbestos gaskets due to obvious health concerns related to carcinogenicity potential of this material).<sup>37</sup> Furthermore, it is relevant to highlight that in some applications, products could still be manufactured without fluoropolymers, but not at the level of technological development that modern society demands. This is the case of semiconductors, which could indeed be manufactured if fluoropolymers were not available, but under technical conditions dating back many years, impacting for example on the size of microchips. This would make it factually impossible to produce modern gadgets (e.g., laptops, mobile phones) at sizes that are typical in modern society. In summary, in the absence of fluoropolymers, many EU industrial sectors would face a technological leap backwards of 50+ years, which would force Europe to lose its technological independence in front of other regions.

According to the bibliography, out of the 4,730 substances included in the PFAS category,<sup>38</sup> only 256 are commercially relevant.<sup>39</sup> In the case of fluoropolymers, only 38 substances are currently available on the market, out of the 267 compounds that are currently identified. This means that commercial fluoropolymers only represent 0.8% of the PFAS universe, but they represent 14.8% of the PFAS with commercial relevance. This is a good illustration of how important fluoropolymers are in modern society, due to the unique properties of these materials and their superior performance in many applications.

#### **IX.** Conclusions

Fluoropolymers are part of the PFAS group by OECD definition. For this reason, fluoropolymers are included in the scope of the restriction proposal that is being developed in the European Economic Area. However, because of their different chemical struc-

ture and properties, they need to be considered as a separate family within the broad PFAS group, clearly distinct not only from the non-polymeric PFAS, but also from the other polymeric PFAS. These differences are relevant not only in terms of grouping but more importantly also in relation to the risk for human health and the environment that will be derived from their manufacture and use.

The main differences between fluoropolymers and the other members of the large PFAS group of chemicals are the following:

- Structural differences, which render them a unique and clearly differentiated family of chemicals within the broad PFAS group, both from nonpolymeric as well as from other polymeric PFAS.
- Safety and environmental considerations, since they meet the PLC conditions, due to their high molecular weight and negligible solubility in different fluids, and are thus not toxic, not bioavailable, not bioaccumulative, not mobile, and have insignificant human health or environmental impacts.
- Limited expected potential to degrade into small PFAS molecules during the intended use or under ambient conditions in the natural environment.
- Unique combination of properties, frequently related to the enhancement of safety of workers, population and the environment, as well as to the development of green energy solutions and high technological applications. This makes fluoropolymers extremely valuable and irreplaceable in extremely demanding uses in a wide variety of industrial sectors.

In parallel, industry has placed significant efforts to address the concerns that have been raised on fluoropolymers, related to the use of other PFAS as polymerisation aids in the manufacturing process that may result in emissions through the life cycle. Relevant achievements on this topic have been announced over the last months from different suppliers, as well as on the improvement of abatement techniques to control emissions.

<sup>37</sup> Joint Research Centre, 'Best Available Techniques (BAT) Reference Document for the Production of Chlor-alkali' (2014) <a href="https://pub-lications.jrc.ec.europa.eu/repository/handle/JRC91156">https://pub-lications.jrc.ec.europa.eu/repository/handle/JRC91156</a>> accessed 24 August 2022.

<sup>38 (</sup>n 3).

<sup>39 (</sup>n 12).

The value that fluoropolymers provide to downstream applications is strongly related to critical areas such as:

- Safety of human health or the environment, providing safe equipment required to handle harsh chemicals in many industries thus avoiding releases of hazardous materials (chemical industries, food processing, pharmaceuticals), or providing protection to a wide range of systems (data transmission, electric cables in automobiles or aircrafts, protecting passengers from failure events.
- Clean water, providing efficient filtration systems for water treatment and replacing outdated and environmentally aggressive processes.
- Green energy production, playing a key role in the efficient development of lithium-ion batteries or hydrogen fuel cells.
- Semiconductors, where the use of fluoropolymers is irreplaceable for the purpose of ensuring the

technology that is currently required to produce modern reduced electronic devices.

Based on all the data available, including recent positions expressed by different experts on the topic, it appears evident that fluoropolymers should not be grouped with other PFAS for risk assessment or regulatory purposes. If fluoropolymers are to be included in the upcoming PFAS restriction under the REACH Regulation, the most reasonable and proportionate decision would be to include a broad derogation to ensure continued use of these highly valuable, PLC materials. Such derogation could be conditioned to the continued replacement of fluorinated polymerization aids from the manufacturing process of fluoropolymers, which is ultimately the only reason for concern that could be justified for these chemicals, and not the intrinsic properties of fluoropolymers.

# Low-temperature mineralization of perfluorocarboxylic acids

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Per- and polyfluoroalkyl substances (PFAS) are persistent, bioaccumulative pollutants found in water resources at concentrations harmful to human health. Whereas current PFAS destruction strategies use nonselective destruction mechanisms, we found that perfluoroalkyl carboxylic acids (PFCAs) could be mineralized through a sodium hydroxide-mediated defluorination pathway. PFCA decarboxylation in polar aprotic solvents produced reactive perfluoroalkyl ion intermediates that degraded to fluoride ions (78 to ~100%) within 24 hours. The carbon-containing intermediates and products were inconsistent with oft-proposed one-carbon-chain shortening mechanisms, and we instead computationally identified pathways consistent with many experiments. Degradation was also observed for branched perfluoroalkyl ether carboxylic acids and might be extended to degrade other PFAS classes as methods to activate their polar headgroups are identified.

er- and polyfluoroalkyl substances (PFAS) are anthropogenic substances containing multiple C-F bonds. PFAS are used as omniphobic surfactants in many industrial processes and products, including in poly(tetrafluoroethylene) production; as water-, oil-, and stain-resistant barriers for fabrics and food service containers; and as components of aqueous film-forming foams for fire suppression (1). As a result of their widespread global use, environmental persistence, and bioaccumulation, PFAS contamination is pervasive (2) and affects drinking water, surface waters, livestock, and agricultural products around the world (3). This persistent environmental contamination is alarming because chronic exposure to even low levels of these compounds is associated with negative health effects such as thyroid disease, liver damage, high cholesterol, reduced immune responses, low birth weights, and several cancers (4). Many of these effects have been obscured by PFAS manufacturers for decades (5). The growing focus on removing parts-perbillion to parts-per-trillion levels of PFAS contamination from drinking water supplies has produced several PFAS-removal approaches, including established adsorbents such as activated carbon and ion-exchange resins, as well as emerging materials such as cross-linked polymers (6, 7). Adsorbents or membrane-based

separation processes create PFAS-contaminated solid or liquid waste streams but do not address how to degrade these persistent pollutants. PFAS destruction is a daunting task because the strong C-F bonds that give PFAS their desirable properties also make these compounds resistant to end-of-life degradation. Harsh PFAS degradation methods include incineration (8), ultrasonication (9, 10), plasmabased oxidation (11), electrochemical degradation (12, 13), supercritical water oxidation (14), ultraviolet-initiated degradation using additives such as sulfite or iron (15-19), and other combinations of chemical and energy inputs (20) (table S1). Leveraging the reactivity of perfluoroalkyl species might, however, offer milder alternatives to address the PFAS contamination problem.

The opportunity to degrade PFAS at high concentrations in nonaqueous solvents has recently been developed using PFAS adsorbents that can be regenerated using a simple solvent wash. This development enables the destruction of these compounds after they have been removed from water resources, which broadens suitable degradation conditions beyond dilute aqueous environments. Here, we accessed reactive perfluoroalkyl anions that are mineralized under mild conditions by decarboxylating perfluorocarboxylic acids (PFCAs), one of the largest classes of PFAS compounds, at low temperatures in dipolar aprotic solvents (Fig. 1). PFCAs of various chain lengths undergo efficient mineralization in the presence of NaOH in mixtures of water and dimethyl sulfoxide (DMSO) at mild temperatures (80 to 120°C) and ambient pressure. Under these conditions, perfluorooctanoic acid (PFOA, 1) is completely degraded with >90% defluorination and minimal formation of fluorocarbon by-products. Experimental observations and density functional theory (DFT) calculations offer strong evidence for degradation pathways distinct from the single-carbon-chain shortening processes proposed in prior PFAS degradation studies (*11, 16, 18, 21–23*). This reactivity mode is immediately promising for PFCA destruction and may prove generalizable to other PFAS classes as methods to activate their polar groups are identified.

## Decarboxylation and defluorination of PFCAs in polar aprotic solvent

Perfluoroalkylcarbanions are easily accessed by decarboxylating PFCAs in dipolar aprotic solvents. In a solution of DMSO and H<sub>2</sub>O (8:1 v/v) at 120°C, PFOA decarboxylates to form perfluoro-1H-heptane 2, which phase separates from solution as an oil. <sup>1</sup>H, <sup>13</sup>C, and <sup>19</sup>F nuclear magnetic resonance (NMR) spectroscopy of the isolated oil confirmed the formation of the decarboxylated product in high purity (figs. S1 to S4). This decarboxylation reaction is consistent with those reported by Kong et al., who found that most carboxylic acids decarboxylate reversibly in dimethylformamide (24). Zhou et al. (25) studied the origins of this reversible carboxylation computationally and determined that the lower barrier to decarboxylation was fully induced by solvent effects from the polar aprotic solvent (figs. S45 and S58). Such reactivity has also been observed as a complication for analytical standards (26, 27). We found that when the same PFOA solution in DMSO/ H<sub>2</sub>O was subjected to the decarboxylation conditions but in the presence of NaOH (30 equiv), PFOA instead degraded to a mixture of fluoride, trifluoroacetate ions, and carboncontaining by-products (Fig. 2A). Degradation also occurred in other polar aprotic solvents such as dimethylacetamide and sulfolane but did not proceed in pure water (fig. S20 and table S3). <sup>19</sup>F NMR spectroscopy of reaction aliquots collected over 24 hours indicated that resonances corresponding to PFOA were no longer detectable within 14 hours. Unexpectedly, no resonances corresponding to perfluoroalkyl groups containing between four and seven carbons were observed. Resonances corresponding to sodium perfluoropropionate (CF<sub>3</sub>CF<sub>2</sub>CO<sub>2</sub>Na) at -81.5 and -118.2 ppm were observed just above the baseline within spectra of aliquots collected at reaction times shorter than 24 hours but were absent in spectra of later aliquots (fig. S10). The only prominent fluorine resonance in the aliquot sampled at 24 hours corresponds to sodium trifluoroacetate (CF<sub>3</sub>CO<sub>2</sub>Na, -73.6 ppm; Fig. 2B). Integration of this resonance indicated that its intensity plateaued at ~4 to 24 hours, corresponding to only 7% of the F content and 9% of the C content relative to the initial PFOA concentration (Fig. 2, A and C). The resonance from CF<sub>3</sub>CO<sub>2</sub>Na ions eventually decreased in intensity and presumably degraded into fluoride, albeit much more slowly than the rate of PFOA disappearance (Fig. 2C, inset). This resonance disappeared over 300 hours, which we confirmed

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**Fig. 1. Overview of degradation pathways identified in this study.** Heating PFCAs in polar aprotic solvents such as DMSO decarboxylates them to 1H-perfluoroalkanes. When this reaction was performed in the presence of NaOH, the PFCA mineralized to fluoride, sodium trifluoroacetate, and nonfluorinated carbon-containing products. The 1H-perfluoroalkane underwent the same degradation process at even lower temperatures. Computational studies identified the corresponding perfluoroalkenes as likely intermediates, and an authentic standard of the seven-carbon perfluoroalkene was competent for the degradation.

by subjecting an authentic sample of sodium trifluoroacetate to the same reaction conditions (fig. S24). PFOA degradation is thus rapid and forms  $CF_3CO_2Na$  and trace  $CF_3CF_2CO_2Na$  as the only identifiable perfluoroalkyl-containing liquid-phase by-products, each of which continues to degrade over extended reaction times. Subjecting perfluorooctane sulfonate ions to the basic decarboxylation conditions did not result in decreasing perfluoroalkyl <sup>19</sup>F NMR integrations or fluoride formation (fig. S19 and table S3), indicating that decarboxylation to the reactive anion intermediate is the key first step of the defluorination process for PFCAs.

Ion chromatography (IC) indicated that  $90 \pm 6\%$  of the fluorine atoms originating from the PFOA were recovered as fluoride ions after 24 hours of reaction at 120°C (fig. S29). Control experiments showed that the fluorinated polytetrafluoroethylene reaction vessels did not contribute an appreciable amount of fluoride to fluoride recovery (table S3). Fluoride analyses performed by IC at shorter reaction times indicated that fluoride increased proportionally to the decrease in [PFOA] observed by <sup>19</sup>F NMR spectroscopy. This high fluoride recovery indicates that most of the perfluoroalkyl fluorines were defluorinated and mineralized rather than being transformed to smaller-chain PFAS or being lost as volatile fluorocarbons.

## Degradation of varied PFAS and by-product analysis suggest a complex mechanism

PFCAs with different chain lengths (two to nine carbons) were degraded, providing fluoride recoveries between 78% and quantitative at 24 hours for all PFCAs with four or more carbons (Fig. 2D). Although the longer-chain ( $C \ge 4$ ) PFCAs had a degradation profile similar to that of PFOA in that their perfluoro-

alkyl peaks disappeared from the <sup>19</sup>F NMR spectra (fig. S22) and  $CF_3CO_2^-$  was formed (Fig. 2D and fig. S23), the destruction of shorterchain PFCAs (C = 2, 3) was slower and appeared to occur by different mechanisms. For trifluoroacetate (C = 2), degradation is slow (>6 days; fig. S24), likely because the instability of the  $CF_3^-$  anion (28) hinders decarboxylation, such that destruction occurs either more slowly or by a different mechanism. The carbanion corresponding to perfluoropropionic acid (PFPrA) (C = 3) decarboxylation is similarly unstable (28), resulting in degradation faster than trifluoroacetate but slower than the longer PFCAs (fig. S22). Although the PFPrA <sup>19</sup>F NMR peaks disappeared completely over 3 days, fluoride recovery was lower than in other PFCAs (3.9  $\pm$ 1.6%; Fig. 2D). PFPrA, unlike others in the series, decarboxylates to form a volatile product; in the <sup>19</sup>F NMR for PFPrA degradation, peaks corresponding to CF<sub>3</sub>CF<sub>2</sub>H can be identified (figs. S11 and S12). Headspace gas chromatographyelectron-impact mass spectrometry (MS) also detected the  $CF_3CF_2^{+}$  fragment in the gas phase of the reaction (fig. S40). This finding was corroborated by atmospheric pressure chemical ionization-MS of a liquid aliquot of the reaction that had a prominent peak corresponding to CF<sub>3</sub>CF<sub>2</sub><sup>-</sup> (compare fig. S39 with figs. S38 and S40). It appears to be more favorable to produce volatile CF<sub>3</sub>CF<sub>2</sub>H than for the C = 3 PFCA to proceed down the destruction pathway; as discussed below, this supports our proposal that a  $\gamma$ -carbon is necessary for the major defluorination pathway to occur. Previous PFAS degradation studies have suggested that PFCAs (or other PFAS that are PFCA precursors) degrade through a decarboxy lation-hydroxy lation-eliminationhydrolysis (DHEH) pathway in which each PFCA is shortened by one carbon each cycle, producing successively shorter PFCAs (11, 16, 18, 21–23). However, the nonconformal degradation of the three-carbon acid and the products observed in the <sup>19</sup>F NMR spectra of degradation reactions of PFCAs containing four or more carbons in the present study indicated that degradation instead occurs through distinct, non-single-carbon shortening mechanisms under these conditions.

The hypothesis that degradation does not occur by iterative one-carbon shortening was further supported by quantifying the carboncontaining by-products formed when PFOA was degraded for 24 hours. We examined a combination of solution <sup>1</sup>H and <sup>19</sup>F NMR spectroscopy and quantitative <sup>13</sup>C NMR spectroscopy of the precipitate isolated from the reaction and dissolved in D<sub>2</sub>O. We also performed ion chromatography on the combined solution and precipitate by adding water to the reaction mixture until the precipitate redissolved. These measurements accounted for the complete carbon balance of the PFOA degradation  $(107 \pm 8 \text{ mol}\% \text{ C} \text{ relative to the } [PFOA]_0;$ table S4 and fig. S30). Other than the residual CF<sub>3</sub>CO<sub>2</sub><sup>-</sup> ions described above, which continued to degrade at longer reaction times, no other organofluorine compounds were detected. Instead, one-, two-, and three-carbon products lacking C-F bonds were identified and quantified. Formate ions were found in solution (fig. S9) and in the precipitate, corresponding to  $2.5 \pm 0.3$  mols formate ions/mol PFOA, as determined by combining the formate concentrations measured in the solution and precipitate by NMR spectroscopy. This amount is consistent with ion chromatography of the reaction mixture and redissolved precipitate, which provided  $2.1 \pm 0.2$  mols formate/mol PFOA. Formate formation and the varying amounts of formate produced by PFCAs of other chain lengths inspired a deeper mechanistic study (see below). Carbonate ions were detected exclusively in the precipitate, corresponding to  $2.1 \pm 0.3$  mols/mol PFOA. The most likely source of carbonate ions was from the initial decarboxylation step, along with other downstream processes that generate carbon dioxide or single-carbon products at the same oxidation state. Two-carbon products, glycolate ions ( $0.6 \pm 0.1 \text{ mol/mol PFOA}$ ) and oxalate ions ( $0.7 \pm 0.1 \text{ mol/mol PFOA}$ ), were found in the precipitate, along with three-carboncontaining tartronate ions (0.2  $\pm$  0.1 mol/mol PFOA). The glycolate and oxalate ions were identified by 13C NMR spectroscopy and comparison with authentic standards. Tartronate ions were identified by a combination of <sup>13</sup>C and <sup>1</sup>H NMR spectroscopy, which were consistent with literature reports (29) and showed the expected correlations in two-dimensional NMR experiments (figs. S31 and S32). Finally, a small amount of the PFOA carbon balance was found in an unknown product, which

## Fig. 2. Overall reaction scheme, experiments monitoring PFOA and $\rm CF_3CO_2^-$ concentrations over the course of the reaction, and summary of degradation products from a series of PFCAs

of different lengths. (A) Heating 0.089 M PFOA in 8:1 DMSO:H<sub>2</sub>O with 30 equiv NaOH allowed 90% of the initial fluorine to be recovered as inorganic fluoride and residual trifluoroacetate with few other organofluorine by-products. Formate ions (26 mol %) and several other nonfluorinated by-products were identified (107  $\pm$  8 mol %). (**B**) <sup>19</sup>F NMR spectra from 0 to 24 hours. Peaks corresponding to PFOA perfluoroalkyl fluorines between -115 and -126 ppm, as well as at -80 ppm, disappeared in less than 24 hours. Trifluoroacetate (-73.6 ppm) appeared and disappeared (disappearance shown in inset of panel C) more slowly over the course of the reaction. (C) Amount of PFOA (purple, solid line) and sodium trifluoroacetate (gray, dashed line) in the reaction over time. Error bars correspond to the standard deviation of three experiments. (D) Fluoride recovery was calculated as mols fluoride after reaction as detected by ion chromatography per mol fluorine in PFCA reactant. Formate/PFCA was calculated as mols formate as detected by IC after reaction per mol PFCA reactant. CF<sub>3</sub>CO<sub>2</sub><sup>-</sup>/PFCA was determined as mols CF<sub>3</sub>CO<sub>2</sub><sup>-</sup> as calculated from <sup>19</sup>F NMR spectroscopy after 24 hours of reaction per mol PFCA reactant. All measurements are expressed as the average of three trials unless specified otherwise, and error is expressed as a standard deviation. All reaction times are 24 hours unless specified otherwise. "a," 286 hours, single measurement; "b," 63% ± 12% of PFPrA starting material degraded after 24 hours. (E) Structures of the identified carbon-containing by-products.

we designated as a secondary degradation product derived from the reaction of glycolate ions with other intermediates because it was formed in greater amounts when glycolic acid was included at the beginning of the PFOA degradation reaction. Identifying and quantifying these carbon products has important implications for PFOA degradation. First, the high recovery of products with no C-F bonds, along with the high fluoride ion recovery, confirms that these conditions efficiently mineralize PFCAs. Furthermore, identifying multiple two- and three-carbon by-products further implicates mechanisms more complicated than iterative one-carbon shortening processes.

PFCAs of different lengths degraded by different pathways, as indicated by the distinct patterns in their formate and  $CF_3CO_2^-$  formation. If the chain-shortening DHEH mechanism were operative, then we would expect that resonances belonging to chain-shortened



0.89 ± 0.01

species would appear transiently in the  $^{19}\mathrm{F}\,\mathrm{NMR}$ spectra as longer-chain PFCAs speciated into a distribution of shorter-chain PFCAs. Instead, only <sup>19</sup>F NMR peaks corresponding to CF<sub>3</sub>CO<sub>2</sub><sup>-</sup> and trace amounts of CF<sub>3</sub>CF<sub>2</sub>CO<sub>2</sub><sup>-</sup> were detected, and the following by-product patterns emerged. PFCAs containing four or fewer carbons did not produce any CF<sub>3</sub>CO<sub>2</sub>, but all PFCAs containing more than four carbons produced roughly the same substoichiometric amount of CF<sub>3</sub>CO<sub>2</sub><sup>-</sup>: ~0.3 equivalents of CF<sub>3</sub>CO<sub>2</sub><sup>-</sup>/mol PFCA. PFCAs containing fewer than six carbons did not produce substantial amounts of formate (Fig. 2D), but PFCAs containing six or more carbons produced increasing amounts of formate, with C = 6 and 7 producing ~1 equivalent of formate per PFCA, C =  $8 \sim 2$  equivalents, and C =  $9 \sim 2.5$ equivalents. These observations indicate that CF<sub>3</sub>CO<sub>2</sub><sup>-</sup> and formate production occur by distinct pathways.

ONH

80.8 ± 3.3

Experiments conducted at near-ambient temperatures showed that decarboxylation

fluorination and chain-shortening steps can occur at near-ambient temperature, giving experimental insight into the possible mechanism. Substantial defluorination still occurred when the isolated PFOA degradation product (perfluoro-1H-heptane 2) was subjected to degradation conditions but heated to only 40°C (table S3). PFCAs have historically been decarboxylated by heating PFCA salts in ethylene glycol at 190 to 230°C to yield perfluoro-1Halkanes (30) or by pyrolyzing PFCA salts at 210 to 300°C to yield perfluoro-1-alkenes (31), but dipolar aprotic solvent-assisted degradation enabled decarboxylation at only 80 to 120°C, which can be followed by an even lower-temperature defluorination. When 2 was subjected to the basic degradation conditions, both fluoride and chain-shortened PFCAs were observed by IC and <sup>19</sup>F NMR at short reaction times (5 min at 120°C) and low temperatures (25 min at 40°C), in contrast to

0.26

is the rate-limiting step and subsequent de-

tartronate



Fig. 3. Proposed PFCA degradation mechanism with activation energies ( $\Delta G^{\ddagger}$ , kcal/mol) for each step as calculated at the M06-2X/6-311+G(2d,p)-SMD(DMSO) level. Cycle AD shows a three-carbon shortening of the original PFCA of *n* carbons ("1," red, top) with one carbon lost as CO<sub>2</sub> (converted to  $CO_3^{2-}$  under basic conditions) and two carbons lost to fluoroacetic acid, which readily degrades under these reaction conditions. Pathway B shows the reaction that results from the 1,2 addition of hydroxide to the carboxyl carbon of INT6. Proposed pathways for the conversion of INT14 to INT30, along with pathways for nonfluorinated, carbon-containing by-products, are described in fig. S50. The alkene INT30 becomes protonated and proceeds through a similar pathway as pathway A. At INT35, the aldehyde analog of acid fluoride INT6, 1,2 addition to the carboxyl carbon leads to the formation of formate by elimination in pathway C, whereas 1,4 addition to the  $\beta$  carbon leads back to pathway D. All energies are expressed in units of kilocalories per mole.

reactions starting from the carboxylated PFOA at the same conditions, in which no fluoride or short-chain PFCAs were formed at short reaction times or at low temperatures (table S3). Degradation of 2 at 40°C for 48 hours showed 57% defluorination (table S3). Although the insolubility of the polyfluoroalkane standard in the DMSO and water solvent precluded accurate measurements of its concentration by NMR spectroscopy, the presence of the CF<sub>3</sub>CO<sub>2</sub><sup>-19</sup>F NMR peak (fig. S13) indicated that the decarboxylated material likely followed a similar degradation pathway. In this lowtemperature experiment, intermediates that were not observed in the higher-temperature experiments became evident; at around -210 ppm, a triplet with J = 48 Hz appeared, which corresponds to the fluoroacetate ion (CH<sub>2</sub>FCOO<sup>-</sup>; fig. S13). The fluoroacetate peak did not appear in the higher-temperature degradations because it degrades rapidly at those temperatures, as confirmed by the degradation of a pure standard. Temperature-dependent studies of the original PFOA degradation reaction showed that the reaction slowed slightly when the reaction was conducted at 100°C (time to [PFOA] = 0 is ~100 hours compared with 16 hours for 120°C; figs. S21 and S25 to S27) and slowed substantially when lowered to 80°C (>290 hours; figs. S21 and S28). Therefore, significant defluorination of 2 was unexpected at 40°C, suggesting that the steps after the decarboxylation were low-barrier or barrierless. These observations further indicate that degradation does not proceed by successive chain shortening through iterative decarboxylation steps.

#### Computational studies reveal steps in defluorination mechanism with negligible barriers

DFT was used to determine the mechanism of this degradation reaction. These studies predicted that decarboxylation is the rate-limiting step of the degradation and that a series of low-barrier or enthalpically barrierless reactions can lead to levels of defluorination consistent with experimental observations. DFT calculations were performed at the M06-2X/ 6-311+G(2d,p)-SMD(DMSO) level (see the supplementary materials for details) and used PFOA as the starting point for the calculations. This mechanism should also be valid for the degradation of straight-chain PFCAs of other lengths. After the initial decarboxylation of PFOA (compound 1; Fig. 3) at an activation energy of about 28 kcal/mol, calculations indicated that the resulting anion INT1 would eliminate a fluoride to become perfluoroalkene INT2 (Fig. 3 and fig. S44). Unlike previous PFCA degradation mechanisms in the literature predicting that the perfluoroalkyl fragment will hydroxylate after decarboxylation (11, 16, 18, 21-23), these computational results point to the formation of an alkene followed by an enthalpically barrierless hydroxylation of the activated electrophilic alkene. Hydroxylation of the alkyl fragment INT1, as postulated in previous studies, was calculated to have an activation energy of 29.7 kcal/mol under our study's conditions after protonation of the fragment (fig. S46), whereas formation of the alkene INT2 had a barrier of 19.5 kcal/mol, followed by a hydroxylation with no enthalpic barrier ( $\Delta G = -44.3$  kcal/mol). The highly exothermic nature of this alkene hydroxylation step played a leading role in driving the degradation, consistent with observations that the defluorination and chain-shortening steps of the reaction neither have high energy barriers nor lead to the formation of successively shorter PFCAs. Accordingly, when perfluoro-1-heptene 3 (INT2) was subjected to degradation conditions (table S3), it also degraded to similar products even at 40°C, corroborating the computational prediction and indicating that the alkene is likely on the degradation pathway. Further, calculations also suggested that the hydroxylation is specifically favored at the terminal position, because addition on the internal side of the alkene had a barrier of 8.9 kcal/mol (fig. S47). After this alkene hydroxylation (INT4), calculations suggested that a series of low- or no-barrier reactions occurred, as shown in Fig. 3 and fig. S44. The enol can then eliminate another fluoride, forming  $\alpha$ , $\beta$ -unsaturated acyl fluoride INT6 through retro 1,4-conjugate addition.

This resulting  $\alpha$ , $\beta$ -unsaturated acid fluoride INT6 has two plausible reaction pathways that are consistent with the experimental findings: a 1,4-conjugate addition that leads to  $CF_3CO_2^-$  formation (pathway D) or a 1,2 addition (pathway B) that can lead to formate formation (pathway C), which together explain

the experimentally observed by-product distribution. Calculations indicated that neither option had enthalpic barriers and thus very low free energies of activation, indicating that both reactions occurred to some extent (fig. S48). In the enthalpically barrierless 1,4-conjugate addition (Fig. 3, pathway D, X = F) that leads to the formation of shorter PFCAs such as  $CF_3CO_2^-$ , the hydroxide adds to the  $\beta$  carbon of  $\alpha$ , $\beta$ -unsaturated acyl fluoride INT6, followed by an enthalpically barrierless fluoride elimination to form 1,3-diketone compound INT8. Hydroxide again adds to this intermediate on the ketone carbonyl side to generate INT9, which is more favorable than the addition on the acyl fluoride side (fig. S49). Finally, fragmentation occurs to generate an equivalent of PFCA three carbons shorter than the initial carboxylic acid and an equivalent of fluoroacetic acid, which was observed in the experiments conducted at 40°C (figs. S13 and S16). As an example, if five-carbon PFCA perfluoropentanoic acid (PFPeA) went through this cycle, it would produce an equivalent of carbon dioxide (1 carbon), an equivalent of trifluoroacetic acid (2 carbons), and an equivalent of fluoroacetic acid (2 carbons) by this pathway. However, from the experimental results, only about 0.3 equiv of CF<sub>3</sub>CO<sub>2</sub><sup>-</sup> were produced from PFPeA (Fig. 2D), indicating the PFCA degradation does not proceed quantitatively by this process. This pathway also does not account for the substantial amounts of formate produced in reactions from longer PFCAs.

Formate ion production is explained by a pathway stemming from the favorable 1,2hydroxylation product, which provides an  $\alpha,\beta$ -unsaturated PFCA (pathway B). As with INT6, there are multiple possible sites for hydroxide addition to INT14, either to the  $\alpha$ (13.6 kcal/mol) or  $\beta$  (12.0 kcal/mol) carbons. Possible pathways propagating from both of these processes, along with the formation of oxalate and other carbon by-products, are described in the supplementary materials (figs. S50 to S54). Although both of these pathways for the conversion of INT14 to INT30 are plausible and supported by computation, the possibility of other active mechanisms cannot be ruled out. However, both of these hydroxylations are more favorable than decarboxylating the  $\alpha$ , $\beta$ -unsaturated perfluoroacid (22.3 kcal/ mol), and both lead to the formation of perfluoroalkene anion INT30. The chain length of the alkene depends on which hydroxylation pathway the substrate follows, either four carbons shorter than the original chain (1,3 addition) or five carbons shorter than the original chain (1,4 addition). Calculations showed that perfluoroalkene anion INT30 is protonated rather than eliminating a fluoride to generate the alkyne (figs. S55 and S56). After the protonation, hydroxide adds to the alkene, much like

the first postdecarboxylation step in the first proposed pathway. Likewise,  $\alpha$ ,  $\beta$ -unsaturated aldehyde INT35, an analog to the  $\alpha$ , $\beta$ -unsaturated acid fluoride INT6, is generated through retro-1,4 addition. At this point, the intermediate again faces a bifurcation, with opportunities for both the 1,4-conjugate addition and the 1,2 addition of the hydroxide to the  $\alpha$ , $\beta$ unsaturated aldehyde. Similar to the addition to the  $\alpha$ , $\beta$ -unsaturated acyl fluoride, both of these reactions were calculated to have no enthalpic barrier (fig. S57). Through the 1,4-conjugate addition (Fig. 3, pathway D, X = H; figs. S59 and S60), the 1,3-diketone compound generated will be attacked by hydroxide, followed by the same fragmentation as noted before. That is, a PFCA and a fluoroacetic aldehyde are formed, the latter of which can be transformed into fluoroacetic acid or be rapidly hydrolyzed. However, if INT35 undergoes 1,2 addition of hydroxide to the  $\alpha$ , $\beta$ -unsaturated aldehyde (Fig. 3, pathway C; figs. S55 and S60), the resulting aldehyde (INT36) cannot eliminate a hydride, whereas its acid fluoride counterpart INT13 can eliminate a fluoride. Instead, INT36 can eliminate the entire perfluoroalkyl chain, creating an equivalent of formate and a one-carbon-shorter alkene anion that can either exit the cycle through 1,4-conjugate addition or proceed through the cycle again to form more formate, thus giving rise to the trend of increased formate formation by PFCAs of longer chain length.

## Experimental support for the computationally determined mechanism

Our calculations affirmed that decarboxylation is the rate-determining step of the degradation, and the calculated activation energy of ~28 kcal/mol is consistent with the experimentally determined value of 30.0 kcal/mol (see the supplementary materials, page 6 and table S2). The proposed mechanism is also supported by experimental observations of  $CF_3CO_2^{-}$  and the formate distribution shown in Fig. 2D. By this mechanism, CF<sub>3</sub>CO<sub>2</sub><sup>-</sup> was produced as a nonstoichiometric by-product, in accordance with the observation that only ~0.3 to 0.4 equivalents of  $CF_3CO_2^-$  were formed per mol PFCA for all PFCAs with  $C \ge 5$ . This proposed mechanism also explains why fourcarbon perfluorobutanoic acid (PFBA) did not produce CF<sub>3</sub>CO<sub>2</sub><sup>-</sup>, whereas the five-carbon PFPeA did, because PFBA that has gone through cycle AD would create FCOO<sup>-</sup>, which will decompose spontaneously to carbon dioxide and fluoride (32) or hydrolyze from INT8 to form tartronate. This two-cycle mechanism also explains why five-carbon PFPeA produced CF<sub>3</sub>CO<sub>2</sub><sup>-</sup> but no formate, because the carbon chain is not long enough to go through pathway C. The mechanism predicts that the amount of formate will increase as the length of the initial PFCA carbon chain increases; this was also affirmed by experimental results for PFCAs of six to nine carbons (Fig. 2D). The formation of carbonaceous by-products such as oxalate, glycolate, and tartronate is also consistent with this mechanism (figs. S50 to S54). Furthermore, when conducting reactions with protodecarboxylated perfluoro-1H-heptane 2 or perfluoro-1H-hexane S1 (figs. S5 to S8) at 40°C, the formation of intermediate products containing five- or four-carbon fluorous chains was observed (figs. S14 and S17), respectively, which likely correspond to INT8/INT9 (figs. S15 and S18), the intermediate with the highest activation energy (25.6 kcal/mol) in this pathway. The peaks corresponding to this intermediate disappeared as peaks corresponding to the five- and four-carbon PFCAs appeared. These PFCAs that are shortened by three carbons are the logical products of a singlepathway AD cycle from their respective starting materials. The experimental observations confirm that the computed mechanism provides a complete model to describe the observations made experimentally about this complex degradation. We also performed calculations to test proposed difluorocarbene (fig. S62), perfluoroalkyl hydroxylation (fig. S46), and  $\alpha$ -lactone (33, 34) (fig. S61) mechanisms that had been proposed for such degradations, but these were found to have barriers too high to be compatible with the experimental conditions.

## Generalization of the PFCA destruction method to perfluoroalkyl ether carboxylates

Branched perfluoroalkyl ether carboxylic acids, another major class of PFAS contaminants, are also mineralized by perfluoroalkyl anion intermediates. The ammonium salt of hexafluoropropylene dimer acid (ammonium perfluoro (2-methyl-3-oxahexanoate; also known as FRD-902, the trade name GenX, or HFPO-DA in its acid form) is a perfluoroalkyl ether carboxvlic acid that was introduced as an industrial replacement for PFOA. This compound now contaminates water sources such as the Cape Fear River, which serves as the primary drinking water source for >350,000 residents of North Carolina (35). For this compound, the decarboxylation and branched CF3 chain defluorination occurred at 40°C, an even lower temperature than for the PFCAs (fig. S35). This finding is consistent with computational results indicating that the barrier for GenX decarboxylation is only 20.4 kcal/mol (fig. S63). However, because of the presence of the ether oxygen in place of the  $\gamma$ -carbon, the structure was unable to eliminate a  $\gamma$ -fluorine and instead formed perfluoroalkyl ether carboxylic acid intermediate 5 through hydrolysis (Fig. 4), which built up in solution and was observed by both  $^{19}\mathrm{F}\,\mathrm{NMR}$  and electrospray ionization MS (figs. S33, S35, and S42). Further degradation occurred at elevated temperatures (80°C;



Fig. 4. Proposed mechanism for branched perfluoroalkyl ether carboxylic acid degradation. Pathway A (blue) shows the branched CF<sub>3</sub> defluorinating in the same manner as PFCAs in Fig. 3. The lack of  $\gamma$ -fluorines forces formation of **5** through pathway E (orange), as observed by NMR and MS. Calculations show the hydroxide-mediated  $S_N2$  that eliminates the perfluoroalkoxide tail in pathway F (purple), leading to the formation of a PFCA that is degraded according to the mechanism described in Fig. 3. All energies are expressed in units of kilocalories per mole.

fig. S35). Calculations showed that the decarboxylation of this intermediate was unfavorable (figs. S65); rather, a hydroxide-mediated  $\rm S_N2$  with a barrier of 21.9 kcal/mol occurred in which the perfluoroalkoxide tail was eliminated (fig. S66). This perfluoroalkoxide formed a carboxylic acid ( $\Delta G^{\ddagger}$  = 21.9 kcal/mol) with the same number of carbons as the original perfluoroether tail. Because GenX contains a three-carbon tail, it produced the C3 PFCA (PFPrA), the degradation of which led to incomplete defluorination (41%; Fig. 2D) and the formation of CF3CF2H (figs. S37, S40, and S41). These observations are consistent with those of the direct degradation of PFPrA (Fig. 2D and figs. S11, S12, S39, and S40). The experimental observations showed that temperatures of 40°, 80°, and 120°C are necessary to form intermediate 5, to form the PFCA analog, and to initiate PFCA degradation, respectively. These temperature steps correspond to the calculated energy barriers of 20.4, 21.9, and 27.7 kcal/mol, respectively (figs. S35, S63, and S64). Degradation of a longer perfluoroalkyl ether carboxylic acid with a five-carbon perfluoroalkyl tail (compound 4; figs. S34, S36, S40, and S43) proceeded by a similar mechanism as that of GenX and gave fluoride recoveries consistent with those obtained from the five-carbon PFCA PFPeA. These findings indicate that perfluoroalkyl ether carboxylates also degrade through perfluoroalkyl anionbased processes. Intermediates in the degradation of 4, as observed by atmospheric pressure chemical ionization-MS (fig. S43), corroborated the proposed mechanism (Fig. 4).

#### Conclusions

The perfluorocarbon reactivity that we have described here leverages low-barrier defluorination mechanisms to mineralize PFAS at mild temperatures with high rates of defluorination and low organofluorine side-product formation. In contrast to other proposed PFAS degradation strategies, the conditions described here are specific to fluorocarbons, destroy concentrated PFCAs, give high fluoride ion recovery and low fluorinated by-product formation, and operate under relatively mild conditions with inexpensive reagents. The proposed mechanism is consistent with both computational and experimental results, provides insight into the complexity of PFAS mineralization processes, and may be operative but unrecognized in other PFAS degradation approaches. This demonstration of the reactivity of perfluoroalkyl anions, and the ability to access such intermediates efficiently from PFCAs, may inform the development of engineered PFAS degradation processes and facilitate expanding this reactivity mode to PFAS with other polar head groups.

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K.N.H., W.R.D. **Competing interests:** Northwestern University has filed a provisional patent (63/261,772) that describes methods to degrade PFCAs on behalf of inventors B.B.T. and W.R.D. W.R.D. is a founder and equity holder in Cyclopure, Inc., which is commercializing technologies related to PFAS detection and remediation. Cyclopure is uninvolved in the research described in this manuscript. The remaining authors declare no competing interests. **Data and materials availability:** All data are available in the manuscript or the supplementary materials. **License information:** Copyright © 2022 the authors, some rights reserved; exclusive licensee American Association for the Advancement of Science. No claim to original US government works. https://www.science.org/about/science-licenses-journal-article-reuse

#### SUPPLEMENTARY MATERIALS

science.org/doi/10.1126/science.abm8868 Materials and Methods Supplementary Text Figs. S1 to S66 Tables S1 to S4 Data S1 References (*36–57*)

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### Application of Supercritical Water Oxidation to Effectively Destroy Per- and Polyfluoroalkyl Substances in Aqueous Matrices

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atures ≥450 °C destroy perfluorinated carboxylic acids, but temperatures of ≥575 °C are necessary to destroy perfluorosulfonic acids. A continuous 5-log reduction in concentration of PFAS (99.999% destruction) is demonstrated for 3 h at steady-state operation. The destruction efficiency is not impacted by the addition of cocontaminants such as petroleum hydrocarbons, and volatile organic compounds. The treated effluent is largely composed of complete combustion products including carbon dioxide, water, and the corresponding anion acids; hence, the treated liquid can be released back into the environment after neutralization.

**KEYWORDS:** supercritical water, oxidation, per- and polyfluoroalkyl substances, defluorination, AFFF, SCWO, PFAS

#### INTRODUCTION

Per- and polyfluoroalkyl substances (PFAS) are man-made fluorinated hydrocarbons used in many applications since the 1940s due to their unique physical and chemical properties including being hydrophobic and oleophobic and having a low surface tension.<sup>1</sup> In addition, the presence of strong carbonfluorine bonds provides extremely high chemical and thermal stabilities.<sup>1,2</sup> PFAS are widely used for commercial and industrial applications, including in aqueous film-forming foam (AFFF) for fire-training and fire-fighting operations in emergency response, manufacturing facilities for surface coatings, and mist suppressants in metal-plating operations, among others.<sup>1</sup> Due to their extensive applicability, PFAS have been ubiquitously detected in environmental media, human serum, and biota. $^{3-7}$  The bioaccumulation of these compounds has gained global attention due to potential health risks such as a decline in thyroid levels, decreased vaccine antibody response, and organ toxicity.<sup>8–18</sup> This has led to some PFAS being listed as persistent organic pollutants (POPs) under the Stockholm Convention.<sup>19</sup>

temperature and flowrate of the system, finding that reactor temper-

Considering the chronic health risks associated with perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS), the United States Environmental Protection Agency (U.S. EPA) established a preliminary remediation goal

of 70 ng/L (or parts per trillion, ppt) in December 2019 for PFOS and PFOA in groundwater that is used as a source of drinking water.<sup>16</sup> In May 2022, the U.S. Environmental Protection Agency (EPA) announced the addition of five new PFAS to the list of regional screening levels (RSLs). These include PFOS, PFOA, perfluornonanoic acid (PFNA), perfluorohexane sulfonic acid (PFHxS), and hexafluoropropylene oxide dimer acid (HFPO-DA). These PFAS are in addition to perfluorobutane sulfonic acid (PFBS), which was added to the RSLs in 2014 and updated in 2021.<sup>20</sup> Multiple U.S. states have recently published or are proposing PFAS levels for monitoring, notification, and/or cleanup at or below 70 ppt.<sup>21-23</sup>

Neutralization Fluid (NaOH)

Recently, the EPA proposed to designate PFOA and PFOS, including their salts and structural isomers, as hazardous substances under the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) to

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facilitate cleanup of contaminated sites and to reduce human exposure to these chemicals.<sup>24</sup> To meet this goal, studies have evaluated a variety of conventional and advanced technologies for PFAS removal from and/or degradation in water. Conventional remediation techniques, such as oxidation using peroxide or persulfate and bioremediation, have had limited effectiveness.<sup>25–30</sup> Application of conventional granular activated carbon adsorption and ion exchange resin are a challenge due to differing chemical and physical properties of distinct PFAS, as shorter chain PFAS tend to break through faster which necessitates the faster change out or regeneration of the sorbents.<sup>31</sup> Several effective PFAS treatment methods are being developed, but most have only been tested at the laboratory scale with few field applications.<sup>32</sup> Some technologies under development include sorption using carbonbased materials (biochars and nanotubes) and/or other novel sorbents, removal by ion exchange, advanced oxidation processes (AOPs; electrochemical oxidation, photolysis, photocatalysis, activated persulfate oxidation, and ultraviolet (UV)induced oxidation), advanced reduction processes (ARPs; potassium iodide (KI) combined with UV), thermal (thermal chemical reaction, microwave hydrothermal, and incineration), chemical/electrical treatment (sonochemistry, electrical discharge plasma, and high-voltage electric discharge), and microbial treatments.<sup>28,32-43</sup> Many of these technologies have been shown to produce short-chain PFAS as byproducts or exhibit selective destruction of only perfluorinated carboxylates (PFCAs) and partial mineralization of perfluorinated sulfonates (PFSAs).<sup>37,38,44,45</sup> Reductive methods reported in the literature for the destruction of PFAS have been shown to follow defluorination mechanisms by the cleavage of carbon-fluoride bonds. Due to the high reduction potential of hydrated electrons (-2.9 V), reductive defluorination involving hydrated electrons has been shown to be effective for PFAS destruction.<sup>46-49</sup> Reductive methods have been shown to be generally more efficient than oxidative methods, requiring very little energy to initiate breakage of the carbon-fluoride bond. This efficiency makes reductive methods attractive compared to energy-intensive oxidative methods such as SCWO; however, reductive methods are not consistently showing degradation of all PFAS compounds to ppt concentrations.<sup>50,5</sup> Degradation was slow and incomplete for perfluorinated sulfonates (PFHxS and PFOS), and most of these reported methods are laboratory scale with many limitations to the fullscale application of these processes. Hydrated electrons are short lived and require anoxic conditions. The presence of oxygen and water chemistry (bicarbonates, nitrates, chloride ions, and humic acids) in environmental aqueous matrices quenches the hydrated electrons generated and hence results in suppression of PFAS destruction.46,50-52 Recent interim guidance released by the U.S. EPA for the planned research and development on destruction and disposal technologies for PFAS and PFAS-containing materials mentions supercritical water oxidation (SCWO) as one of the promising innovative technologies for the destruction of PFAS in AFFF.<sup>5</sup>

SCWO involves oxidation of aqueous organic compounds at temperatures and pressures above the critical point of water in the presence of oxygen.<sup>54,55</sup> This technology has shown rapid and near-complete destruction of several recalcitrant organic contaminants including polychlorinated biphenyls, radioactive waste, and certain nerve agents.<sup>54,56,57</sup> The SCWO process involves reacting the dissolved organic contaminant with an oxidant in water at a temperature and pressure above the

supercritical point of water (374 °C and 3205 pounds per square inch [psi]). At these conditions, the water and organics become miscible and form a uniform homogeneous mixture, which results in changes in their properties and provides a single fluid phase of a water-oxygen-organic mixture. The reaction of organic molecules with oxygen generates environmentally benign end products, such as water, carbon dioxide, and inorganic salts.<sup>58</sup> These benefits promote SCWO as a promising technology to treat PFAS despite the unique chemical and physical properties of these compounds.<sup>44,57,59</sup> SCWO is an energy-intensive process, which operates at high temperature and high pressure. Continuous operation under high oxidizing conditions poses challenges such as salt plugging and corrosion of the reactor construction materials. However, these challenges can be managed by taking special consideration while choosing the construction materials capable of withstanding oxidizing environments to mitigate corrosion and special reactor designs to handle the salt formation and prevent salt plugging.<sup>60</sup> The continued development of effective technologies, such as SCWO, for the complete destruction of PFAS is critical to meet the recent U.S. EPA guidance and state regulations.53

In this study, the operating conditions and destruction performance of a SCWO continuous reactor (hereafter referred to as PFAS Annihilator) were evaluated and found to have several benefits for environmental remediation and waste management industries. The PFAS Annihilator consistently achieves near-complete destruction of PFAS, bringing the concentrations down to non-detect for most target PFAS, and consistently down to less than 70 ppt for all PFAS in under 30 s. This technology can be used to treat material contaminated with PFAS and other substances such as petroleum hydrocarbons or chlorinated solvents, which are also readily oxidized.<sup>55</sup> Moreover, SCWO can be applied to a variety of PFAS-impacted liquids such as AFFF, landfill leachate, and investigation-derived waste (IDW) due to its non-targeted carbon-fluorine bond destruction.44,59 The treated effluent is largely composed of the products of complete combustion including carbon dioxide and water and the corresponding anion acids; hence, the treated liquid can be released back into the environment after neutralization.50

#### MATERIALS AND METHODS

Chemicals and Reagents. Laboratory-prepared feeds were spiked with technical-grade PFOA (98% purity), and PFOS (98% purity), along with lower amounts of PFBA, PFPeA, PFHxA, PFHpA, PFDA, PFUnDA, PFDoDA, 8:2 FTS, N-MeFOSAA, N-EtFOSAA, L-PFBS, and PFBS (Synquest Laboratories [Alachua, FL], Sigma-Aldrich [St. Louis, MO] and Wellington Laboratories [Ontario, Canada]) (Table S1). Volatile organic compounds (VOCs; 1,1-dichloroethene, benzene, tetrachloroethene, toluene, and trichloroethene) (SPEX CertiPrep, Metuchen, NJ) and diesel fuel (Turkey Hill, OH) were added as co-contaminants. Final concentrations in the inlet feed were determined through PFAS, total organic carbon (TOC), and VOC analysis. The full lists of PFAS and organic compounds evaluated are shown in Tables S1 and S2, respectively, but only detected compounds are presented in the figures for visual clarity. Optima grade methanol (≥99.9% purity) (Sigma-Aldrich) and certified American Chemical Society grade acetone (≥99.5% assay) and ammonia (7 N solution in methanol) (Fisher Scientific

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Figure 1. PFAS Annihilator process flow diagram showing flow paths, sample heating, reactor location, and sample cooling prior to collection of the effluent samples at the sampling port.

[Pittsburgh, PA]) were used to clean the reactor between trials. Hydrogen peroxide  $(H_2O_2)$  from Sigma-Aldrich was used as the oxygen source, and monobasic sodium hydroxide (NaOH) from Sigma-Aldrich was added to the process to neutralize the effluent stream. Deionized (DI) water was produced in house via a two-tank deionizing system in parallel, installed, and maintained by AmeriWater (Dayton, OH).

SCWO Reactor. The bench-scale PFAS Annihilator is comprised of a tubular reactor heated by an Accurate Thermal Systems (Hainesport, NJ) sand bath. A tube-in-tube heat exchanger was used to preheat the feed and recover heat after the reaction. Additional cooling of the reactor effluent was performed using a cooling drum supplied with potable water. A custom-designed gas-liquid separator was used to separate the treated aqueous effluent from the generated vapor. The feeds, oxidant, and neutralization solutions were pumped through the PFAS Annihilator utilizing Shimadzu (Columbia, MD) LC 20-AP preparative pumps. Pressure was monitored throughout the system with inline Swagelok (Solon, OH) 6000 psi pressure gauges. Pressure was maintained in the system utilizing a Tescom (Elk River, MN) 4000 psi back pressure regulator. Effluent pH was measured using a Sensorex (Garden Grove, CA) TX100 inline pH meter. Temperatures were measured with inline Type K thermocouple probes (Omega, Norwalk, CT). A schematic of the PFAS Annihilator used to evaluate the destruction of PFAS is shown in Figure 1. The temperature readings were output to a BrainChild PR20 data logger (CAS Dataloggers, Chesterland, OH). Due to the high temperatures and pressure operating conditions and the generation of hydrofluoric acid, a high nickel alloy (Alloy 625) that is highly resistant to corrosion was used for all hot and pressurized components of the system. No glassware or other laboratory ware is used anywhere in the system or in the handling of samples destined for PFAS analysis to mitigate the potential for PFAS loss to glassware as is well documented.<sup>61,</sup>

**Laboratory Samples.** Laboratory-prepared inlet samples were composed of PFAS, petroleum hydrocarbons, and/or VOCs prepared in DI water, followed by sonication for at least 1 h.

Field Samples. Upon receipt, all field samples were analyzed for PFAS, VOCs, TOC, and anions as described in

sample analysis. The TOC and PFAS concentrations were used to calculate an appropriate oxidant dosing for the field sample. The field sample detailed in this report was run through the PFAS Annihilator without any preprocessing or preparation.

Article

**SCWO Operating Conditions.** At the beginning of each run, the SCWO reactor was allowed to reach its equilibrium temperature ( $\pm 10$  °C) running DI water at 3500 psi ( $\pm 200$  psi). The oxidant solution was prepared to achieve  $\geq 100\%$  excess oxygen in the system, calculated assuming complete combustion of the TOC and/or total target PFAS in the feed. Either the liquid oxidant ( $H_2O_2$ ) or the dissolved gaseous oxygen was pumped via a secondary Shimadzu LC-20AP preparative pump into the system upstream of the reactor at 3500 psi along with the feed/sample stream. A neutralization solution (NaOH) was prepared such that an effluent pH of 5 to 7 was achieved while ensuring the neutralization flow did not exceed 7% of the total system flowrate.

The feed and oxidant were introduced into the PFAS Annihilator at their specified flowrates after the system temperature stabilized. The vapor stream, primarily consisting of carbon dioxide and excess oxygen, was separated from the aqueous stream in a gas—liquid separator and sampled by C18 cartridges and impingers prior to being discharged into the laboratory hood. The liquid effluent samples were collected from the sampling port as labeled in Figure 1.

After each run was completed, the system was immediately flushed with DI water and/or low-concentration oxidant. After cooling, the system was rinsed with DI water, methanol, and then again with DI water. For runs with a high concentration of PFAS or where operating conditions were not optimal for PFAS destruction, ammonia in methanol and/or acetone was also used to clean the system.

**Sample Analysis.** All samples were analyzed for PFAS at Battelle's accredited laboratory, using isotope dilution liquid chromatography tandem mass spectrometry (LC/MS/MS). Transformation byproducts formed during SCWO were analyzed using a Waters Acuity I-class UPLC Sample Manager coupled to a Quadrupole time-of-flight mass spectrometer, TripleTOF/MS 5600 (AB Sciex, Framingham, MA) at Battelle's Laboratory. The aqueous influent, effluent, and equipment blanks, and gaseous effluents (methanol extracts of

C18 cartridges and impinger) were investigated for transformation byproducts. Details of all analytical methods for PFAS are described in the Supporting Information. To characterize fluorine changes, influent and effluent samples were analyzed using <sup>19</sup>F-nuclear magnetic resonance (NMR) spectroscopy at Battelle's Laboratory. The <sup>19</sup>F NMR spectra were obtained with a Bruker AVANCE NEO 500 MHz NMR spectrometer equipped with a broadband observe probe with gradients in a mixture of water and deuterium oxide as the solvent. Chemical shifts were reported relative to CFCl<sub>3</sub> (0 part per million [ppm]). Fluoride was also commercially evaluated by anion analysis using U.S. EPA Method 300. TOC and VOCs were commercially analyzed using U.S. EPA Methods 9060A and 8260C, using samples collected in volatile organic analysis vials preserved with phosphoric acid and hydrochloric acid, respectively.

**Data Analysis.** The relative change of PFAS, fluoride, TOC, and VOCs was determined by comparing the inlet and effluent concentrations of the system. Equations for percent destruction and defluorination can be found in eqs 1 and 2. This analysis assumes that little, if any, accumulation of compounds occurred in the SCWO system for accurate representation of compound destruction/production. The reported effluent concentrations are those directly measured exiting the reactor without correcting for dilution from the addition of the oxidant or neutralization solutions. This provides an accurate representation of the reactor discharge. Since the feed sample is diluted by less than 15% when using  $H_2O_2$  as the oxidant, the concentration changes reported are representative of the reactor performance and are not due to significant dilution of the feed stream.

%destruction

$$= \frac{\text{effluent concentration of PFAS}\left(\frac{ng}{L}\right)}{\text{inlet PFAS concentration as organofluorine}\left(\frac{ng}{L}\right)} \times 100$$
(1)

%defluorination

$$= \frac{\text{effluent inorganic fluoride}\left(\frac{ng}{L}\right)}{\text{inlet PFAS concentration as organofluorine}\left(\frac{ng}{L}\right)} \times 100$$
(2)

To simplify the data presentation when the concentration of many PFAS are being reported, the PFAS are classified as PFCAs, PFSAs, and precursors/intermediates as defined in Table S1, and the raw concentration values of each measured PFAS compound are then tabulated in the Supporting Information.

#### RESULTS AND DISCUSSION

Using the laboratory-spiked inlet samples, the effects of oxidant type, temperature, and residence time on the SCWO destruction of PFAS were evaluated.

Impact of the Oxidant Type on PFAS Destruction. Two oxidant sources, dissolved oxygen in water and  $H_2O_2$ , were used to provide at least 100% excess oxygen in independent tests. In the initial investigation,  $H_2O_2$  provided equivalent or superior destruction of all measured PFAS, including PFCAs (PFBA, PFPeA, PFHxA, PFHpA, and PFOA) and PFSAs (PFBS, PFPeS, PFHxS, PFHpS, and PFOS) compared to dissolved oxygen as the oxidant source when operating at 3500 psi and 600  $^{\circ}$ C (Figure 2). Both



Figure 2. PFAS destruction with  $H_2O_2$  as the oxidant is equivalent or superior to the PFAS destruction when using dissolved oxygen as the oxidant. System operating at 600 °C, 3500 psi, and 50 mL/min.

oxidants caused a similar 4 to 6 log reduction in the concentration of the total effluent PFAS relative to the total inlet concentration of 11.3 ppm. In both cases, only the two compounds having the highest concentrations in the inlet (PFOA and PFOS) were still present at over 100 ppt in the effluent; The other measured compounds were not detected or were detected at less than 3 ppt.  $H_2O_2$  has about 1000× higher oxygen density than oxygen dissolved in water at 100 psi, dramatically reducing the required volume of oxidant added to the feed stream and reducing the combined reactor volumetric flowrate by  $\sim$ 5×. This greatly reduces the volume of water that must be heated when operating the reactor, reducing energy requirements and cost of operation. Other researchers have also observed accelerated oxidation performance with H<sub>2</sub>O<sub>2</sub> compared to oxygen on organic contaminants.<sup>55,63</sup> This is due to the high activation energy of O2 oxidation and the slow conversion of O<sub>2</sub> and H<sub>2</sub>O that requires three steps to produce OH radicals as shown in eq 3 through eq 5.63 Alternatively, the decomposition of  $H_2O_2$  to OH radicals is direct (eq 5).<sup>63</sup> Due to the equivalent or improved destruction of PFAS when using  $H_2O_2$  in this study and in the literature,  $H_2O_2$  is used as the oxidant source for the remaining tests.

$$CF_3(CF_2)_n RH + O_2 \rightarrow CF_3(CF_2)_n R + HO_2$$
 (3)

$$CF_3(CF_2)_nRH + HO_2 \rightarrow CF_3(CF_2)_nR + H_2O_2$$
(4)

$$H_2O_2 \rightarrow 2OH^{-1}$$
 (5)

Impact of Residence Time and Temperature on Performance. The combination of elevated temperature and residence time provides enough energy to overcome the activation energy to cleave the carbon-fluorine bond to degrade PFAS to produce carbon dioxide  $(CO_2)$  and hydrofluoric acid (HF). A generic reaction is shown in eq 6 using PFOA as an exemplar PFAS.

$$C_8HF_{15}O_2 + 7H_2O_2 \rightarrow 15HF + 8CO_2$$
 (6)

To determine the optimal operating conditions, influent and effluent concentrations of PFAS were measured at four flowrates in 25 °C increments from 450 to 625 °C. At least 85% of total PFAS were destroyed under all tested conditions. Between the operating temperatures of 450° and 525 °C, the reactor operated in this  $\geq$ 85% destruction efficiency regardless of flowrate. A similar observation was made by other

researchers studying the batch-scale reactions of PFOS, where the highest PFAS destruction was observed at 500 °C, and the reaction at this temperature was independent of the residence time; therefore, it was concluded that temperature is the key parameter for PFAS destruction.<sup>44</sup> However, the current study expanded to higher temperatures using a flow through system. This setup shows that further elevated temperatures allowed the reaction to destroy >99% of PFAS. Destruction of PFAS is inversely dependent on residence time or indirectly dependent on the reactor flowrate.

At temperatures  $\geq$ 525 °C, slower flowrates show improved PFAS destruction. A slower flowrate also achieves maximum destruction at lower temperatures compared to reactions run at higher flowrates. At 550 °C, the slowest tested flowrate (60 mL/min) showed an additional 1- to 2-log reduction in the effluent PFAS concentration than seen at any of the other tested flowrates (100, 140, and 190 mL/min). At 575 °C, the 60 mL/min flowrate achieves the maximum PFAS destruction (about 5–6 log reduction). Increasing flowrates at this operating temperature (575 °C) reduced PFAS destruction efficiency. Further increasing the temperature allowed higher flowrate streams to also achieve the maximum PFAS destruction. However, the reactor was unable to maintain a temperature of 625 °C at 190 mL/min due to the energy transfer required to heat the high influent flowrate. Figure 3



Figure 3. Effect of temperature and residence time on PFAS destruction.

summarizes these data. The concentration of all 24 PFAS from each of two sequential samples collected at each set of conditions is shown in Table S4. Interestingly, the nonsulfonated PFAS (PFCAs) showed complete defluorination at all temperatures and flowrates evaluated, while the sulfonated acids (PFSAs) required a higher temperature and residence time to be defluorinated. The degradation of the PFCAs makes up nearly all the destruction seen at temperatures  $\leq$ 500 °C.

Estimated Reaction Kinetics. The reactor flowrates were converted to residence times to estimate the reaction kinetics for the degradation of PFAS within the reactor. The residence time at each data point shown in Figure 3 is unique because under supercritical conditions, the reaction temperature has a notable impact on density, leading to variable residence times for a consistent volumetric flowrate. The reaction rates were estimated using the PFAS compounds whose concentrations were above the limit of quantitation (LOQ) for all four tested residence times, which only included PFSAs (all PFCAs were destroyed under all test conditions). A reactor operating temperature of 575 °C was used for these calculations because it shows the greatest disparity in the destruction efficiency of PFAS over the tested flowrate range. At lower or higher temperatures, the reaction is either not at all impacted by the residence time, or there is only one data point that is not at

either the maximum  $(C_t/C_0 \cong 1 \times 10^{-5})$  or minimum  $(C_t/C_0 \cong 1 \times 10^{-1})$  destruction, meaning that there are not sufficient data points sampled to properly estimate the kinetics at those temperatures. Figure 4 indicates first-order reaction kinetics at 575 °C and provides rate constants (*k*) of 0.51, 0.49, and 0.48 for PFOS, PFHxS, and PFHpS, respectively.



Figure 4. Natural logarithmic ratio in the effluent PFAS concentrations at four residence times.

The first-order reaction equation for PFSA destruction is shown in eq 7. Although not shown in Figure 4, shorter chain PFSAs and all PFCAs proceeded to non-detect (ND) quickly, which prevented an accurate rate calculation for those compounds (Table S4).

$$\ln(A) = \ln(A_0) - kt \tag{7}$$

Steady-State Operation. To determine the startup and steady-state operation of the PFAS Annihilator, the system was operated for 3 h with effluent samples collected every 20 min. These samples were analyzed to measure the loss of target PFAS and the generation of inorganic fluoride. The concentration of PFAS in the effluent decreased by ~4 orders of magnitude within 20 min of introducing the feed solution, while the effluent fluoride concentration increased dramatically. The concentration of PFAS was reduced by another order of magnitude after another 20 min of operation, while the fluoride remained at nearly the same level (Figure 5). This is expected as there is a diminishing return in total generated fluoride as the concentration of PFAS undergoes further log reductions. The large increase in fluoride concentration in the effluent suggests mineralization of PFAS by defluorination during the SCWO treatment. In addition, <sup>19</sup>F NMR analysis of influent and steady-state effluent samples further supports this finding. There is an increase in the inorganic F peak in effluent spectra, and disappearance of organofluorines (F attached to carbons) resulting from defluorination of PFAS (Figure S1). Although <sup>19</sup>F NMR spectra represent a qualitative analysis, disappearance of the organofluorine peaks further demonstrates the complete defluorination of PFAS.

The reactor showed a slight 15 °C decrease in the effluent temperature for the first 40 min of operation, which was recovered and even slightly elevated by 60 min of continuous operation. By 60 min of continuous operation, all measured parameters had reached a steady value and remained constant for the remaining 120 min of testing, suggesting about a 1-h time to steady state for the PFAS Annihilator (Figure 5). Additionally, the status of the reactor is well summarized by the temperature reading; When the reactor effluent temperature temperature reading.

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**Figure 6.** Measured PFCAs, PFSAs, PFSAs precursors/intermediates, and co-contaminants in treatments (A) lab Sample, (B) lab sample with cocontaminants spiked at low level, (C) lab sample with co-contaminants spiked at high level, and (D) field sample. The concentrations of all PFAS compounds in the stream were less than 75 ppt after passing through the SCWO reactor.

ature has re-equilibrated after the introduction of a sample, the SCWO system is operating at steady state and is achieving optimal PFAS destruction.

Throughout this steady-state period, the total effluent PFAS concentration remained below 50 ppt, which is six orders of magnitude lower than the total inlet PFAS concentration of 22.8 ppm (99.9998% destruction). The most concentrated compound in the inlet (PFOA) was decreased by nearly seven orders of magnitude from 12.3 ppm to 3.83 ppt. The inlet and effluent concentrations for fluoride and for all 24 measured PFAS are provided in Table S5.

Comparing the total inlet and effluent fluorine, a total of 72.6% of the total inlet fluorine (largely contained in the

PFAS) is detected and quantified in the effluent as ionic fluoride. While this may indicate that some fluorine is accumulating within the reactor, the reactor was rinsed with water after testing to collect any fluorine sorbed onto the reactor surfaces. While some fluoride was detected (0.77 mg/L), this totaled less than 0.5% of the total inlet fluorine, suggesting that the reaction byproducts are not accumulating within the reactor. The total target PFAS measured in the postrun water rinse was also low (27.0 ppt), further suggesting that undestroyed PFAS is not adhering to or building up on the reactor walls. These data suggest that neither PFAS nor the reaction product, fluorine, are accumulating within the reactor. In addition, the reactor surface residuals were collected and

analyzed via energy-dispersive spectroscopy (EDS) and X-ray diffraction (XRD) and show that there is no fluorine detected on these surfaces, further supporting the idea that PFAS are destroyed rather than accumulated or sorbed onto the reactor surfaces (Figure S2). Additional effort is underway to better understand the movement of fluorine through the reactor.

Effect of Co-contaminants on PFAS Annihilation. The PFAS Annihilator has been demonstrated to greatly reduce the concentration of PFAS in laboratory-spiked samples (Figures 2, 3, 5); However, environmental samples are much more complex and can have a number of additional co-contaminants. In many of the Department of Defense (DoD) sites impacted by AFFFs due to fire-fighting or fire-training activities, it is common to find VOCs and total petroleum hydrocarbons (TPH) commingled with PFAS contamination.<sup>64</sup> To evaluate the practicality of applying this technology to environmental remediation, a laboratory-spiked sample was prepared consisting of PFAS, TPH (low and high concentration), and VOCs (low and high concentrations). The low-concentration spiked sample was found to contain ~1200 ppt of total organic contaminants, and the high-concentration spiked sample was found to contain ~7,400,000 ppt of total organic contaminants. The measurable TOC concentrations are shown in the bottom row of Figure 6, and detailed data of all analytes are provided in Table S6. The results show that the destruction of PFAS is largely unaffected by the addition of organic cocontaminants when compared to the laboratory sample that was only spiked with PFAS (Figure 6A) and that the total concentration of co-contaminants also decreases (Figure 6B,C). This proves that SCWO is effective for co-contaminant treatment along with PFAS destruction. The total PFAS concentrations and the sum of PFOA and PFOS measured in the low-concentration effluent sample (Figure 6B) and the PFAS-spiked lab sample (Figure 6A) were 15.72 and 1.23 ng/ L, respectively, compared to 31.46 and 28.37 ng/L in the absence of co-contaminants. Overall, the destruction efficiency of PFCAs, PFSAs, and PFAS precursors was not affected by the presence of co-contaminants (Figure 6 and Table S6). This confirms that complexity of the feed stream does not alter the destruction efficiency of PFAS, and the results demonstrate effective destruction of co-contaminants in the PFAS-impacted IDW streams. The effluent vapor was similarly analyzed for PFAS. This analysis yielded no detectable levels of any of the 24 target PFAS, confirming that the influent compounds are being destroyed rather than escaping the system as a gas.

The individually detectable co-contaminants were found to decrease to undetectable levels in both the low- and high-concentration spiked samples (Figure 6B,C), and all target organic compounds (and TOC when detected) decreased. This is an expected result as SCWO processes are not specific to breaking carbon-fluorine bonds. Carbon–carbon bonds are also expected to oxidize under the operating conditions of the PFAS Annihilator.<sup>55</sup>

**Demonstration on an AFFF-Impacted IDW Sample.** As a final proof of concept test, an AFFF-impacted IDW sample was run through the PFAS Annihilator. The field-collected sample with an initial total target PFAS concentration of 4.9 ppm was run directly through the SCWO reactor without any preprocessing, and a similar destruction efficiency of PFAS was achieved as the laboratory PFAS-spiked sample (Figure 6D). The resultant effluent total PFAS concentration was 10.2 ppt and the sum of PFOA and PFOS measured at 1.5 ppt showing six orders of magnitude reduction in PFAS (Table S6), demonstrating the PFAS Annihilator as a viable technology to destroy high concentrations of PFAS in AFFF-impacted IDW. Although there was a slight increase in the measured concentration of two VOCs from the influent to the effluent, both concentrations are below the method quantitation limit and may not be accurate. Another interesting finding was a decrease in dissolved fluoride as the field sample passed through the reactor (Table S6). This may be associated with the dramatic change in ion solubilities as water transitions from the sub to supercritical state. Methods to collect this precipitating material are underway and will allow further evaluation of this hypothesis.

In all trials (PFAS spiked, PFAS and co-contaminants spiked, and field sample), PFCA, PFSA, and PFAS precursors/ intermediates show a similar level of destruction regardless of the complexity of the feed (Figure 6A–D). The total summation of measured PFAS concentration in the effluent sample of each of the laboratory and field samples was  $\leq$ 75 ppt (ng/L) with no individual PFAS analyte concentration remaining higher than 70 ppt for any collected effluent sample. The influent and effluent PFAS concentrations for each of the samples presented in Figure 6 are tabulated in Table S6, which highlights the similarities in the effluent PFAS concentration that are achieved by the PFAS Annihilator from disparate inlet samples, demonstrating that the complexity of the feed stream does not alter the destruction of PFCAs, PFSAs, PFAS precursors/intermediates, or organic co-contaminants.

Although no pretreatment was required for any of the tested samples and no clogging was observed in these tests, the underlying tubular reactor may be prone to clogging from samples with high concentrations of dissolved solids. The built-in pressure and flow monitors would have deviated from their steady-state operational conditions if appreciable build up were occurring. During long-term operations, processing much larger samples for weeks at a time, the potential reactor clogging could be mitigated with the use of inline devices (e.g., a supercritical salt trap<sup>65</sup>) or modified reactor designs<sup>66,67</sup> to remove salts and other compounds that precipitate out of solution at supercritical conditions.

**Identification of Byproducts.** Aqueous influent, effluent, and equipment blanks, and gaseous effluents (methanol extracts of C18 cartridges and impinger) were investigated for transformation byproducts using LC-qToF/MS analysis. Greater than 99% destruction of PFOA and PFOS was achieved in the effluent; hence, no longer chain PFAS were detected in the samples analyzed.

Some unidentified short-chain byproducts were formed (Table S7 and Figure S3) and found to elute early on the total ion chromatography (TIC) chromatogram (Figure S3). These are very low-level findings relative to the targeted compounds, which were unquantifiable without analytical standards and were not consistently seen on every run. These data suggest that SCWO completely destroyed PFAS, instead of partial mineralization, which agrees with our previous data from the liquid effluents and reactor surfaces.

**Environmental Implications.** The PFAS Annihilator tested here is demonstrated as a promising technology for the destruction of PFAS and other common co-contaminants typically found at AFFF-impacted fire-training sites. This research presents optimization of the reaction conditions for the complete destruction of PFAS. The oxidant type (O<sub>2</sub> and H<sub>2</sub>O<sub>2</sub>), temperature (450–625 °C), flowrate (60–190 mL/min), and time to reach steady-state conditions were studied.

The best operating conditions (≥600 °C and ≤100 mL/min or 625 °C and  $\leq$ 140 mL/min) using H<sub>2</sub>O<sub>2</sub> as the oxidant destroyed PFAS in laboratory-spiked solutions with initial concentrations ranging from 5 to 50 ppm to below 70 ppt levels in the resultant effluent. The optimized technology was then applied to three inlet sources (PFAS spiked with and without co-contaminants and a field sample) where it successfully reduced PFAS of different chemistries, chain lengths, and precursor presence by up to 6 orders of magnitude. These preliminary data and the impact of operational changes are valuable in upscaling SCWO systems for the destruction of PFAS in contaminated sources for environmental remediation. These data suggest that the destruction of PFAS using SCWO is independent of the oxygen source used in the reactor and that higher temperatures can be used to maintain destruction efficiency while increasing throughput.

Many technologies for the treatment of PFAS-impacted IDW rely on separation techniques, which transfer PFAS from one media to another and therefore generate PFASconcentrated secondary waste streams (e.g., sorbents and ion exchange regenerated solvent concentrate, reverse osmosis reject, nanofiltration) that require further treatment or disposal. Incineration poses several challenges such as off-site transportation, concerns on the incomplete combustion of byproducts, high-energy requirements, immediate release of combustion products into the environment, and cost of operation.<sup>68</sup> As no destruction methods are readily available for the long-term effective management of PFAS-impacted IDW and these secondary waste streams, SCWO provides an effective approach. SCWO is an energy-intensive process, but much of the expended energy can be recaptured through heat exchangers in a well-designed system. SCWO is also not appropriate for thick slurries (>50% solids) as they do not pump well through a reactor. The SCWO process demonstrated here is capable of directly processing a PFAS-impacted field sample, and the effluent can be released to the environment after confirmatory analysis. Further demonstration is on-going to prove pilot- and full-scale field deployments of the PFAS Annihilator at AFFF-impacted sites, landfill leachate, as well as the destruction of stockpiled AFFF concentrates.

#### ASSOCIATED CONTENT

#### **G** Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsestwater.2c00548.

Description of sample preparation and analytical methods; Figures of <sup>19</sup>F NMR spectra; EDS/XRD characterization of reactor surface residual; and TIC overlay spectra; tables of listed PFAS analytes and other co-contaminants measured, their analytical methods; concentrations of PFAS and other co-contaminants measured entering and exiting the PFAS Annihilator SCWO reactor at different reactor operating temperatures and flowrates; and list of SCWO transformation byproducts and their respective fragments identified from PFOS and PFOA destruction and raw tabulated data (PDF)

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Article

# ANNEX IV

Memorandum Legal Observations Gujarat Fluorochemicals GmbH



#### Memorandum Martin Ahlhaus Dipl.-Verwaltungswirt (FH) Rechtsanwalt Date 22.03.2023 Provinostraße 52 86153 Augsburg Martin Ahlhaus Author T: +49 (0) 821 899823-20 Dr. Dominik Strobl F: +49 (0) 821 899823-99 M: +49 (0)160 88 678 04 ahlhaus@produktkanzlei.com То **European Chemicals Agency**

Legal Observations

# Proposal for a restriction of Per- and polyfluoroalkyl substances (PFAS) according to Regulation (EC) No. 1907/2006 (REACH)

submitted by

- BAuA, Federal Institute for Occupational Safety and Health
- Bureau REACH, National Institute for Public Health and the Environment (RIVM)
- Swedish Chemicals Agency (KEMI)
- Norwegian Environment Agency
- The Danish Environmental Protection Agency

Version 2.0 Date: 22.03.2023

prepared for and on behalf of

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Amtsgericht Augsburg · HRB 34009

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### A. Executive Summary

- (1) The legal basis for the Proposal is Article 68(1) REACH. This provision requires, that an unacceptable risk to human health or the environment, arising from the manufacture, use or placing on the market of the substance(s) within the intended scope is demonstrated. The Proposal substantially deviates from applicable legal prerequisites and principles. It is, therefore, flawed from a factual, technical and legal perspective as far as Fluoropolymers are included in the scope.
- (2) The scope of the Proposal, in essence, is based on the OECD definition of PFAS established in 2021. This definition also includes Fluoropolymers.
- (3) Insofar, however, the Proposal does not meet the requirements for a grouping approach under REACH. This would require that all substances within the scope share the key property in combination with the exposure that causes the risk leading to the proposal of a restriction. The Proposal is based on the assumption that all PFAS qualify as persistent and do have other hazard properties in addition to their persistence. The Proposal, however, lacks a mandatory risk assessment to demonstrate that Fluoropolymers share the same or similar hazard properties with other PFAS. In particular it needs to be noted that Fluoropolymers do not meet the criteria for being bioaccumulative, mobile or toxic. It follows already from scientific evidence that Fluoropolymers should not be included in the grouping approach.
- (4) Furthermore, the Proposal fails to demonstrate that there is an unacceptable risk to human health or the environment with respect to Fluoropolymers. Insofar, any proposal for a restriction needs to be based on a hazard assessment. Mere reference to the OECD PFAS definition is not sufficient as the definition is not established on the assessment whether a compound is harmful or not. Moreover, the assumption that all PFAS qualify as persistent is not sufficient, as persistence as such does not even qualify as a hazard criterion, which is already acknowledged by the Proposal.
- (5) Restricting Fluoropolymers as supported by the Proposal does also not align with the precautionary principle. A correct application of that principle presupposes identification of the potentially negative consequences of the proposed use of Fluoropolymers as well as a comprehensive assessment of the associated risks based on the most reliable scientific data available and the most recent results of international research. The Proposal lacks sufficient evidence in this regard and is based on a mere hypothesis rather than on a scientifically substantiated risk assessment. This specifically holds true for Fluoropolymers, for which no respective hazard and, consequently, no corresponding risk can be identified.
- (6) Moreover, the Proposal breaches the principle of proportionality with respect to Fluoropolymers. Due to the fact that any emission in connection with the entire life-cycle of Fluoropolymers from manufacturing to use until the end-of-life stages are to be consid-

ered *de minimis* if fluorinated polymerisation aids are restricted, a restriction of Fluoropolymers as such would not be necessary at all against the background of the principle of proportionality.

- (7) In addition, the Dossiers Submitters erroneously have chosen the restriction procedure under REACH for an intended approach which, in fact, is structured with significant similarity to an authorisation proceeding. The contemplated process to accept potential applications and to decide on potential for exemptions or derogations basically establishes a requirement for stakeholders to provide any and all evidence to substantiate a corresponding request within a unreasonable short time period and, therefore, shifts the burden of proof to stakeholders contrary to the legal perquisites defined in Article 68 REACH.
- (8) All in all, and irrespective further concerns on the Proposal demonstrating infringements of e.g. the principle of good administrative behaviour or the right to be heard and the right to comment, Fluoropolymers manufactured without the use of fluorinated polymerisation aids should be exempted from the scope of the Proposal. Without a corresponding exemption or derogation significant market distortion are to be expected as critical products, technologies or applications will no longer be available if removed from the market due to the contemplated restriction.

# B. Starting Point

# I. Gujarat Fluorochemicals Limited

- (9) Gujarat Fluorochemicals Limited (hereinafter referred to as "**GFL**") is an Indian Chemicals Company with over 30 years of expertise in Fluorine Chemistry. GFL holds domain expertise in Fluoropolymers, Fluorospecialities, Refrigerants and Chemicals, catering to the material requirements of modern world. GFL leverages its competencies in Fluorinebased products through product innovation and customer partnerships in diverse enduse markets. Impacting mobility, telecommunications, healthcare and architecture, GFL constantly challenges itself to find solutions to some of the most demanding applications.
- (10) GFL is committed to sustainable operations and corporate social responsibilities. Focus on clean processes, continuous development of new applications, customised solutions and consistent services make GFL one of the reliable strategic partners for our clientele globally.

#### II. Background

- (11) GFL commissioned Produktkanzlei Ahlhaus Handorn Niermeier Schucht Rechtsanwaltsgesellschaft mbH (hereinafter referred to as "Produktkanzlei") to assess the proposal for a restriction of Per- and polyfluoroalkyl substances (individual substances and/or the group of substances hereinafter referred to "PFAS", unless explicitly specified otherwise) according to Regulation (EC) No. 1907/2006 (hereinafter referred to as "REACH") as submitted by the German Federal Institute for Occupational Safety and Health (hereinafter referred to as "BAuA"), the Dutch Bureau REACH, National Institute for Public Health and the Environment (hereinafter referred to as "RIVM"), the Swedish Chemicals Agency (hereinafter referred to as "KEMI"), the Norwegian Environment Agency and the Danish Environmental Protection Agency (hereinafter jointly referred to as the "Dossier Submitters").
- (12) This memorandum summarizes the findings of the legal assessment with a special focus on general legal concerns as well as legal implications due to the fact that the intended restriction shall, in general, also cover Fluoropolymers.
- (13) The legal assessment is based on the aforementioned proposal as submitted on 13 January 2023 and initially published by the European Chemicals Agency (hereinafter referred to as "ECHA") on 7 February 2023. As the Dossier Submitters provided an updated version of the proposal, i.e. Version 2.0, as of 22.03.2023 (hereinafter referred to as "Proposal"), only this version is considered.
- (14) Following the prerequisite according to Article 69(6) REACH, ECHA has started the public consultation on the Proposal on 22 March 2023. Submissions can be made until 25 September 2023.

- (15) This legal assessment of the Proposal is drafted to supplement a broader submission of GFL within the public consultation. Produktkanzlei explicitly confirms that GFL is entitled to use this memorandum for this purpose.
- (16) We respectfully request to consider this submission in connection with the further proceeding to avoid further procedural flaws. We understand that the process to develop opinions at level of the Committee for Risk Assessment ("**RAC**") and the Committee for Socio-Economic Analysis ("**SEAC**") will be initiated already prior to the end of the period granted for submissions in the public consultation. While we further understand that the time period for opinion development as established in Articles 70, 71(1) REACH does require immediate action at committee level, we submit that any and all submissions need to be taken into consideration. The mere fact that opinion development has been initiated prior to the end of the consultation period should not result in a scenario that substantial submissions are not sufficiently considered. Therefore, we respectfully request ECHA, RAC, SEAC and the Dossier Submitters to consider the concerns raised with this submission of GFL to avoid procedural shortcomings which might give rise to further legal concerns.

### C. Legal Assessment

(17) From a legal perspective, it needs to be assessed whether the Proposal meets the applicable requirements for restrictions according to Title VIII of REACH from a procedural, scientific and legal perspective taking into account the scope of the Proposal as well as the underlying justification. Insofar, the following submissions need to be made on the Proposal.

#### I. Fluoropolymers in the restriction proposal

- (18) In general, we understand that Fluoropolymers qualify as PFAS within the (new) OECD definition on PFAS and would, therefore, be within the scope of a restriction according to the Proposal.
- (19) This is already acknowledged in the Proposal insofar as Fluoropolymers are explicitly addressed, including but not limited by means of specific derogations for Fluoropolymers and the related use of polymerisation aids as set out in Nos. 5a), 6, 7 and 8 (cf. Proposal, p. 4 et seqq.).
- (20) This notwithstanding, the proposal also underpins the fact that the Dossier Submitters consider Fluoropolymers to be a distinct group of PFAS. This view is supported by many sections of the Proposal in which Fluoropolymers are discussed separately, which indicates their independent and distinct position within the group of PFAS.
- (21) The proposed restriction following Restriction Option 2 (cf. Proposal, p. 4) contains a specific series of time-limited derogations for certain uses of Fluoropolymers in Column 2, No. 6. According thereto, the restriction shall not apply to Fluoropolymers and per-fluoropolyethers for the use in food contact materials for the purpose of industrial and professional food and feed production until 6.5 years after entry into force ("EiF"); implantable medical devices (not including meshes, wound treatment products, tubes and catheters) until 13.5 years after EiF; tubes and catheters in medical devices until 13.5 years after EiF; protonexchange membrane (PEM) fuel cells until 6.5 years after EiF and fluoropolymer applications in petroleum and mining industry until 13.5 years after EiF.
- (22) Furthermore, according to the proposed entry in Column 2, No. 8, importers and downstream users of Fluoropolymers and perfluoropolyethers making use of any of the derogations shall establish a site-specific management plan which shall include information on the identity of the substances and the products they are used in, a justification for the use and details on the conditions of use and safe disposal. Additionally, the management plan shall be reviewed annually and kept available for inspection by enforcement authorities upon request.
- (23) Of the many other sections in the proposal where specific reference is made to Fluoropolymers, the most important one is, that Fluoropolymers are the only group of PFAS

for which a separate assessment is provided within the environmental hazard assessment set out in Annex B to the Proposal (cf. Proposal, Annex B, p. 219 et seqq.).

#### II. Objections against the inclusion of Fluoropolymers

- (24) Even if one were to assume that the Proposal and the underlying aims and purposes are reasonable, the Proposal fails to demonstrate that the inclusion of Fluoropolymers would meet the requirements according to Article 68(1) REACH and general principles of law which need to be adhered to in connection with the introduction of a restriction under REACH.
- (25) First of all, it needs to be noted that Article 68(1) REACH establishes the prerequisites for a restriction under REACH as follows:

"When there is an unacceptable risk to human health or the environment, arising from the manufacture, use or placing on the market of substances, which needs to be addressed on a Community-wide basis, Annex XVII shall be amended in accordance with the procedure referred to in Article 133(4) by adopting new restrictions, or amending current restrictions in Annex XVII, for the manufacture, use or placing on the market of substances on their own, in mixtures or in articles, pursuant to the procedure set out in Articles 69 to 73. Any such decision shall take into account the socio-economic impact of the restriction, including the availability of alternatives."

(26) The Proposal, however, deviates from these requirements by broadly referring to the OECD definition of PFAS, including Fluoropolymers, without providing sufficient scientific evidence that there is an unacceptable risk to human health or the environment resulting from the manufacturing or use of Fluoropolymers.

# 1. Failure to meet the prerequisites established in Article 68 REACH: hazard to human health / environment

(27) The proposal fails to meet the requirements arising from the wording of Article 68(1) REACH with respect to Fluoropolymers. The wording requires that there is an unacceptable risk to human health or the environment, arising from the manufacture, use or placing on the market of substances, which needs to be addressed on a community-wide basis. The basic requirement is therefore that there is a hazard to human health or a hazard to the environment. Only in a subsequent step it has to be examined whether, due to exposure, a risk arises as a result of this. However, the dossier is not able to prove that Fluoropolymers pose a hazard to health or environment at all.

# a) Failure to conduct proper hazard assessment

(28) The Proposal is flawed from the very beginning since there is no hazard assessment conducted as required by REACH. As a mandatory prerequisite to adopt a restriction under REACH, Article 68(1) REACH requires that there is an unacceptable risk to human

health or the environment, arising from the manufacture, use or placing on the market of a substance, which needs to be addressed on a community-wide basis. The basic requirement is therefore that the substance under scrutiny has been identified to pose unacceptable risk to human health or the environment. Following the fundamental principles enshrined in the REACH Regulation, any corresponding risk assessment needs to be based on an assessment of the hazard properties of the substances involved.

(29) If a corresponding risk assessment would have been initiated in accordance with applicable requirements, it would have been already obvious from the relevant results that Fluoropolymers should not be included in the scope of the Proposal.

# aa) Hazard assessment as a mandatory starting point for restriction proposals

- (30) It follows already from the legal prerequisites that a profound hazard assessment is a mandatory starting point for any restriction proposal under REACH. This fundamental principle already follows from Article 69(4) of REACH, as any dossier submitter needs to refer to any corresponding dossier, chemical safety report or risk assessment established under REACH for the substance at issue in the restriction proposal. Any such dossier, however, mandatorily contains details on the hazard properties of the substances under scrutiny.
- (31) We submit in this context, that the term dossier refers to any dossier prepared under REACH as Article 69(4) REACH does not limit its scope to certain types of dossiers. Therefore, the Dossier Submitters were required to take into consideration corresponding registration dossiers or any available dossiers already established in accordance with Annex XV for substances within the scope of the proposed restriction. It should be noted, however, that for both types of dossiers, the identification and assessment of hazard properties is essential and, moreover, a mandatory requirement.
- (32) First, this holds true for registration dossiers as hazard properties according to Regulation (EC) No. 1272/2008 ("**CLP**") need to be indicated for any substance subject to registration requirements. This follows directly from Annex V Section 4 to REACH, but also hazard properties as defined in Annex XIII to REACH have to be assessed in connection with standard information requirements applicable to the registration of substances under REACH according to Annex VII.
- (33) Second, also any dossier established in accordance with Annex XV to REACH needs to comprise an assessment of hazard properties.
- (34) This holds true for dossiers established to identify potential substances of very high concern. The details for such dossiers are outlined in Annex XV Section 2 to REACH. Corresponding dossiers need to demonstrate that the prerequisites as set out in Article 57 REACH read in conjunction with Article 59 REACH are met. Insofar, such dossiers only relate to hazard properties of substances from the outset. In addition, Article 58(1)(b)

REACH emphasizes that properties as referred to in Article 57 REACH are to be considered as "intrinsic properties". Insofar, Article 58(1)(b) REACH follows the general principle as set forth in the CLP Regulation that hazard classification is to be determined on basis of the intrinsic properties of a substance (cf. Judgment of the General Court of 23 November 2022, Cases T-279/20 and T-288/20). The explicit reference to intrinsic properties underpins the fact that the identification of substances of very high concern is based on an assessment of the hazard properties of a substance.

- (35) We further submit, that the same holds true for dossiers according to Annex XV aiming at a proposal to establish a restriction under REACH as referred to in Annex XV Section 3 to REACH. This specific section states that the corresponding dossier needs to contain information on hazard and risk, whereby the risks to be addressed with the restriction shall be described based on an assessment of the hazard and risks according to the relevant parts of Annex I to REACH and shall be documented in the format set out in Part B of that Annex for the Chemical Safety Report. Therefore, also restriction proposals, as in the case at hand on PFAS, need to contain a sufficient assessment of related risks.
- (36) As far as Annex XV Section 3 to REACH refers to chemical safety reports according to Annex I to REACH, it should be taken into account, that these require, as a starting point, the consideration of information related to the hazards of a substance. The sub-paragraph following Section 0.5 explicitly states that "the information to be considered includes information related to the hazards of the substance". In addition, Section 0.6.1. of Annex I to REACH stipulates that the hazard assessment is the first step to perform a chemical safety assessment.
- (37) Moreover, Section 0.6.3 in Annex I to REACH clarifies that any risk characterization shall be based on an exposure assessment which need to relate to the identified hazard properties of the substance under scrutiny.
- (38) A hazard assessment is, therefore, a mandatory starting point for each and every proposal of a restriction under REACH. Only on that basis and in a subsequent step, it needs to be assessed if and to what extent a risk to human health or the environment arises from the corresponding hazards and relevant exposures. And only if the identified risk turns out to be unacceptable, a restriction according to Article 68(1) REACH is warranted (cf. Guidance for the preparation of an Annex XV dossier for restrictions, figure 4, p. 32).

#### bb) No alternative approach available

(39) We further submit, that a hazard assessment as an initial mandatory step cannot be replaced or circumvented by any other approach. Article 68(1) REACH read in conjunction with Annex XV to REACH and the corresponding guidance does not provide for any deviating option. This even holds true with respect to more generic options for potential restrictions as provided for in Article 68(2) REACH as such an approach mandatorily requires the identification of applicable hazard properties of the respective substances.

- (40) It should also be noted that Article 68 REACH does not contain any provision similar to Article 57(f) REACH, so that a restriction proposal can be justified on basis of some sort of an "equivalent level of concern". While already Article 57(f) REACH would require a hazard assessment as set out in Section 2 of Annex XV to REACH, it goes without saying that Article 68 REACH does not contain any language that could support the view that a hazard assessment could be negligible.
- (41) Only if risks derived from hazard properties of a substance and related exposure can be established and proven to meet the further criteria laid down in Article 68(1) REACH, a restriction proposal on basis of a dossier according to Annex XV to REACH would meet applicable legal requirements. Contrary to the underlying assumption referred to in the Proposal, it is not sufficient to bring forward merely general assumptions about a substance being hazardous or giving rise to a specific or general concerns.

# cc) No hazard property beyond persistence identified for Fluoropolymers

- According to the Proposal, persistence is the key property common to the thousands of (42) substances defined as "PFAS" under the Proposal (cf. Proposal, p. 22). Apart from persistence, the Proposal identifies additional concerns that differ depending on the type of PFAS, including, among others, Long-Range Transport Potential ("LRTP"), Mobility, Accumulation in plants, Bioaccumulation, Ecotoxicty, Endocrine Activity / Endocrine Disruption and effects on human health (p. 22). However, data do not exist for each and every of the thousands of substances that fall within the scope of the Proposal as established on basis of the respective "PFAS" definition, including Fluoropolymers. Without corresponding data, the Proposal lacks sufficient evidence to substantiate that one or more of additional concerns, i.e. hazard properties, apply to the substances within the scope of the contemplated restriction. Also other scientific methods to extrapolate such hazard properties are not provided in the Proposal. Instead, the Dossier Submitters seem to take the position that a sufficient risk within the meaning of Article 68(1) REACH can legally and scientifically be based on the (presumed) persistence of all PFAS that remain within the scope, and the additional assumption that any PFAS is likely to have also other hazard properties, although these are only substantiated for a limited number of the thousands of substances defined as "PFAS".
- (43) This approach, however, does not meet the prerequisites of Article 68(1) REACH and it cannot be based on any other provision of the REACH Regulation. Consequently, the Proposal fails to provide evidence for a sufficient hazard assessment as required by the REACH Regulation. This specifically holds true with respect to Fluoropolymers, as no hazard properties can be identified beyond the persistence.

#### b) Hazard to human health

(44) The proposal itself already states on a general level (cf. Proposal, p. 29) that while there is a vast amount of literature published on the health effects of PFAS, most of the liter-

ature relates to the PFAA arrowheads PFCAs and PFSAs, especially PFOA and PFOS. Furthermore, according to the proposal, other PFAS (like Fluoropolymers) have been less well-studied. Accordingly, the human health hazard assessment in Annex B of the dossier states in its first two sentences, that the majority of available data on human health effects address the toxicity of PFAAs (mainly PFCAs and PFSAs; in particular PFOA and PFOS), while less or no data are available for other PFAS groups and that for the vast majority of PFAS (estimated >99%), no data on repeated-dose toxicity, carcinogenicity, or reproductive toxicity is available (Annex B, p. 141).

- (45) The proposal admits (cf. Proposal, p. 29) that some precursors to PFAAs may be of less direct concern with regard to human health effects and only indirectly add to the concern (due to degradation). In addition, the proposal states with regard to PFAAs that data available for less well-studied PFAA arrowheads and some PFAA precursors indicate that these PFAS can have similar effects as the well-studied ones mentioned above (cf. Proposal, p. 30).
- (46) In this respect, the proposal already shows on the summary level that there is no scientific evidence for the existence of a risk to human health for all substances covered by the restriction proposal. In particular, there is no such evidence regarding Fluoropolymers, which, according to the Proposal, have been less researched.
- (47) In particular, the dossier explicitly states with regard to polymeric PFAS, and accordingly for Fluoropolymers, that properties of the substances can vary considerably and that a clear assignment of the substance to health effects is complicated, because unique identifiers are often not available (cf. Proposal, p. 31). Additionally, the proposal states that the end-of-life fate of the polymers is uncertain (cf. Proposal, p. 31). According to the dossier, only a few studies with toxicological information are available for this diverse group of oligomeric and polymeric PFAS. Most available toxicological studies of oligomeric/polymeric PFAS investigated oligomeric PCTFE oils and pure PCTFE oligomers (cf. Proposal, p. 31).
- (48) Hence, there is no significant proof or evidence that polymers and in particular Fluoropolymers pose a risk to human health equal or similar to other PFAS within the scope of the proposed restriction or any risk at all. To the contrary, scientific articles on Fluoropolymers demonstrate that fluoropolymers satisfy widely accepted assessment criteria to be considered as "polymers of low concern" ("PLC"; e.g. *Henry* et al., Integrated Environmental Assessment and Management, 2018, p. 316 et seqq., DOI: 10.1002/ieam.4035, available at <u>https://setac.onlinelibrary.wiley.com/doi/full/10.1002/ieam.4035;</u> Korzeniowski et al., Integrated Environmental Assessment, 2022, p. 326 et seqq., DOI:10.1002/ieam.4646, available at <u>setac.onlinelibrary.wiley.com/doi/ 10.1002/ieam.4646</u>). Accordingly, the dossier sees no clarity on effects after repeated exposure of polymeric PFAS based on available data (cf. Proposal, p. 31). In the end, the proposal concludes that polymeric PFAS contribute to the overall risks of non-polymeric

PFAS because, according to the Proposal, they "may generate and/or release non-polymeric PFAS", in particular at the end-of-life. In itself, this is not sufficient to substantiate a hazard to human health, since the proposal indicates no certainty that non-polymeric PFAS are generated or released at any point. Moreover, the proposal itself states that the end-of-life fate of the polymers is uncertain (see above), therefore it is contradictory when it is stated a few sentences later that there "may" be a release of non-polymeric PFAS in particular at the end-of-life.

- (49) In this respect, we reiterate that available data demonstrates that Fluoropolymers meet the criteria for PLC (*Henry* et al., loc. cit.; *Korzeniowski* et al, loc. cit.). Although the Proposal takes note of the corresponding publication (*Henry* et al., loc. cit; cf. Proposal, p. 46), the respective findings are only discussed in connection with bioavailability of Fluoropolymers. The Dossier Submitters, however, should have taken note of the fact that available fluoropolymer toxicity data (including available human clinical data) demonstrate that Fluoropolymers do not pose a risk to human health equal or similar to other PFAS within the scope. Moreover, an analysis of Annex B to the Proposal also shows that the scientific data with regard to the hazard of Fluoropolymers to human health is very weak and does not establish sufficient scientific evidence to justify the inclusion of Fluoropolymers in the scope of the Proposal. As shown below, the evidence with regard to the main category of polymers is not given:
  - Regarding toxicokinetics/ADME, the proposal states that no studies are available on toxicokinetics of polymeric PFAS (Annex B.5.1.2, p. 154)
  - With regard to liver effects in experimental animals, the proposal sums up that there are only indications that oligomeric PFAS (not Fluoropolymers) can cause adverse liver effects and that clarity on liver effects of oligomeric/polymeric PFAS cannot be given on the basis of available data (Annex B B.5.2.1.1, p. 159).
  - As for kidney effects in experimental animals, the proposal sums up that there are only indications that low molecular weight oligomeric/polymeric PFAS can cause kidney effects but clarity on kidney effects of oligomeric/polymeric PFAS cannot be given on the basis of available data (Annex B.5.2.1.3, p. 163) Moreover, it is not considered that Fluoropolymers have negligible residual oligomer content.
  - For oligomeric/polymeric PFAS, no studies observing thyroid parameters are known (Annex B.5.2.1.4, p. 164).
  - Regarding immune effects in experimental animals, the proposal concludes that for oligomeric/polymeric PFAS immunotoxic effects were shown, but only states evidence concerning oligomeric PFAS. (Annex B.5.2.1.5, p. 165).
  - As for developmental effects and fertility effects in experimental animals, no studies observing developmental toxicity are known for oligomeric/polymeric PFAS (Annex B.5.2.2.1., Annex B 5.2.2.2, p. 168).

- With regard to carcinogenicity, the proposal on the one hand quotes studies that found carcinogenic effects regarding polymeric PTFE. On the other, however, there is no evidence for such effects for other Fluoropolymers and for PFAS in general the proposal states, that human relevance of carcinogenicity of most PFAS is unclear (Annex B.5.2.3, p. 169).
- Regarding immune outcomes, the proposal sees evidence between PFAS and common infectious diseases, even though it states, "that more studies with objective measures of infections (not self-reports) are needed" and that "there are inconsistent findings" (Annex B, p. 171) regarding upper respiratory tract infections. In fact, this seems to be contradictory.
- (50) Moreover, the Proposal is not even able to justify a hazard to human health with regard to non-polymers, for which studies are available more commonly. It remains vague in various places and does not describe any clear scientific statements. For example, it is taken as evidence that absorption through the skin cannot be excluded, because small insignificant increases of plasma fluoride concentrations after dermal absorption of PCTFE oligomers were shown in rodent urine and plasma (Annex B.5.1.2, p. 155).
- (51) Against this background it needs to be concluded that the Proposal fails to demonstrate hazard properties of Fluoropolymers with respect to human health effects. Insofar, the prerequisites according to Article 68(1) REACH are not met.

# c) Hazard to environment

(52) Also, there is no conclusive scientific evidence that Fluoropolymers have hazard properties with respect to effects to the environment.

# aa) General considerations

- (53) Regarding ecotoxicity, the main part of the Proposal only states that there is evidence for (just) a subset of PFAS and because of the large number of different substances with heterogenous properties (e.g. due to different functional groups) in the group of PFAS the assessment of their ecotoxicity is very complex (cf. Proposal, p. 28). On a more detailed level, Annex B of the Proposal concludes that the available data on adverse effects of PFAS in the environment is limited to a small number of substances (B.7.1.11, p. 202). According to the Proposal, conventional ecotoxicological tests may not be suitable to detect long term effects from exposure to PFAS and the small subset of PFAS, for which such information is available, contains PFOA and PFOS (B.7.1.11, p. 202). Accordingly, there is no evidence or proof that Fluoropolymers pose any risk to the environment at all.
- (54) In this respect, it is not sufficient or convincing that the proposal states, that due to certain properties of PFAS it is not possible to demonstrate safe use of PFAS (B.7.1.11, p. 202). Contrary to the dossier, it cannot be concluded that this warrants for a restriction.

To the contrary, Article 68(1) REACH clearly states that there has to be a risk to the environment and, as stated above, any such risk needs to be identified on basis of a sufficient hazard assessment. If a risk to the environment cannot be concluded from available scientific data regarding hazard properties of the substance(s) within the scope of a proposed restriction, the provisions of Article 68(1) REACH are not fulfilled. A restriction under REACH is not a legitimate legal consequence if based on mere assumptions. To the extent that the Proposal (B.7.1.11, p. 202 et seq.) also points to the fact that future contamination is irreversible, it evidently fails to recognize that mere irreversibility in itself does not represent an environmental hazard and is only relevant in connection with other hazards, which, however, are not identified on basis of relevant scientific evidence for Fluoropolymers.

- (55) With respect to the effects on wildlife, the proposal concludes that the available studies provide evidence, that PFAS can cause adverse effects on wildlife species at currently relevant concentrations (Annex B.7.2.8., p. 207). This is wrongful, since according to the proposal, due to the limitations of the studies, a clear link between PFAS measurements in the environment, or PFAS-body-burdens in the animals and the observed effects can rarely be established (ibid.). Furthermore, it is stated that laboratory studies that can plausibly link effects in these species to PFAS exposure would be needed but are in most cases not available (ibid.). This contradiction is justified by the Proposal with a precautionary approach. However, this consideration is not convincing, because the precautionary principle requires reliable scientific data and logical reasoning, leading to a conclusion which expresses the possibility of occurrence and the severity of a hazard's impact. Such an assessment has not been conducted in the present case, in particular not with respect to Fluoropolymers.
- (56) As to the atmospheric compartment, only fluorinated gases are considered to be problematic, i.e. no specific hazard property has been identified with respect to Fluoropolymers in this regard.
- (57) With respect to endocrine activity and endocrine disruption, the proposal summarizes, that "indications" of interactions of "some" PFAS with the endocrine system of environmental species, adverse effects (some occurring cross-generational), and "first observations of possible influences" of PFAS body-burden on hormone levels in wildlife raise concerns about the presence of PFAS in the environment (Annex B.7.5.3.4., p. 218) and that adverse effects "cannot be excluded" (cf. Proposal, p. 28). Again, the wording clearly shows, that there is no conclusive evidence for any hazard and especially no conclusive evidence for a hazard with regard to every substance within the scope of the proposal, e.g. Fluoropolymers. As before, the proposal argues for a hazard with the persistence of the substances. Insofar, the above stated considerations again apply *mutatis mutandis*.
- (58) With regard to LRTP, the dossier concludes that many PFAS have potential for longrange transport mainly due to their high persistence (p. 25; Annex B.4.2.8., p. 112). However, according to the dossier, for the majority of PFAS no data on transport pathways

or point sources are available and thus substantial uncertainties on the concern of the long-range transport potential remain (Annex B.4.2.8., p. 112). As for accumulation in plants, it is stated that studies on accumulation of PFAS in plants are lacking for the majority of PFAS and that, while it is indicated that PFAS have the property to enrich plants, it remains unclear if all substances/subgroups may have this property (Annex B.4.4., p. 134, 135). Available data (as summarized in *Henry* et al., loc. cit.) Fluoropolymers are insoluble in water and LRTP is completely ruled out. Accumulation of fluoropolymers in plants is unthinkable due to their unique properties.

#### bb) Assessment of environmental hazard properties of Fluoropolymers

- (59) The proposal comments on the hazard characteristics of Fluoropolymers in a special section (B.7.6., p. 219 et seqq.) and states, that Fluoropolymers themselves can pose an environmental hazard. However, there is no sufficient evidence presented in this regard. For example, with regard to toxicity, conflicting studies are cited (see B.7.6.1., p. 220). Furthermore, the dossier admits, that the bioaccumulation potential for polymers in general is poorly understood so far and cell membrane penetration "cannot be excluded" (ibid.), while no further evidence is provided.
- (60) Apart from that, the dossier mainly refers to the hazard properties of microplastics, which is insufficient for several reasons. First, the dossier does not state any relevant intersections of Fluoropolymers and microplastics. This is guite astonishing because it is the only section in the entire dossier where reference is not made to specific PFAS or PFAS in general, but to a distinct category. Obviously, evidence presented for microplastics is not relevant in the current context, since there is no evident connection established between the category "Fluoropolymers" and the category "microplastics". Second, there has been a restriction process for microplastics in the past. Therefore, any evidence regarding microplastics seems to be brought forward either in the wrong restriction procedure or the Proposal at hand would result in an illicit double-regulation of the same matter. Third, and foremost, the current Proposal quotes the former RAC opinion regarding microplastics saying that, although there are uncertainties in the understanding of the hazard and risk of microplastics, there is sufficient evidence to conclude that they constitute an intrinsic hazard because of their persistence in combination with their potential to cause adverse effects. This consideration fails to meet the criteria and procedure set out in Article 68(1) REACH. Fourth, according to the dossier, several studies have investigated adverse effects of microplastics in general and no negative effects on population level have been demonstrated so far. Moreover, Microplastics are generated due to surface friction or abrasion whereas fluoropolymers like PTFE have the lowest coefficient of friction. Also, the concerns related to microplastics are connected to commodity uses of 100s of millions of tons of general plastics whereas fluoropolymers are mostly used in industrial applications and their global consumption is estimated at less than 350,000 tons. Comparison between microplastics and fluoropolymers is untenable, first due to the property of required friction and second due to the difference in consumption volumes particularly for commodity applications.

(61) In conclusion, the dossier fails to establish any relevant evidence that Fluoropolymers pose a risk to the environment. The mere persistence is not sufficient and moreover, the proposal states that persistence is only well known for some Fluoropolymers (B.7.6.3., p. 221 et seq.). Therefore, even according to the logic of the submitters, there is no evidence for hazard properties for the entire group of Fluoropolymers.

### cc) Failure to establish persistence as such as (environmental) hazard

- (62) Additionally, it needs to be noted that the Proposal is also unlawful insofar as it aims to establish risks to the environment by mainly referring to the persistence of the substances within the scope of the intended restriction. With respect to environmental hazards, the Proposal itself states that there is evidence for only a subset of PFAS and that, because of the large number of different substances with heterogenous properties in the group of PFAS, the assessment of their ecotoxicity is very complex (cf. Proposal, p. 28). Consequently, for the vast majority of PFAS, the only environmental property presented by the Proposal is "persistence" as defined in a broad and general manner. This approach, however, is unlawful for a variety of reasons.
- (63) Persistence as such does not qualify as a hazard property but is merely a physical and chemical property of a substance based on the identification of the degradation potential due to the half-life of a substance under various conditions. As a physical and chemical property, persistence alone does not qualify as an environmental hazard because persistence alone cannot cause or result in environmental effects. The mere persistence of a substance, therefore, simply means that a substance with this property exists for a long time. This finding also follows from the Proposal itself, i.e. is in line with the view of the Dossier Submitters.
- (64) With reference to the environmental aspects of any hazard assessment, testing will be used to determine the physical and chemical properties of a substance to identify and indicate the fate of the substance in the environment. This holds true for criteria like persistence, degradation or mobility. Only as a separate step, and with a set of different studies, potential environmental effects of a substance can be identified, like e.g. aquatic toxicity, mammalian toxicity, etc. The headings in Annex B to the Proposal only refer to defined environmental hazards such as ecotoxicity and effects on wildlife (cf. Annex B.7.), while persistence is discussed in the context of the "environmental fate properties" (cf. Annex B.4). Therefore, already systematically persistence is not considered as a hazard property relevant to the mandatory environmental hazard assessment. If mere persistence would already be considered as an environmental hazard, many other substances would also gualify for further regulatory measures. Such approach on a "P-only" basis is not supported by REACH or any other regulatory framework on EU level. Not even the most recent amendments under CLP support hazard classification on basis of the persistence of a substance, but only if further properties can be identified.

- (65) As far as the Proposal attempts to justify the existence of e.g. potential ecotoxicity or effects on wildlife in the context of the environmental assessment (cf. e.g. Proposal, Annex B.7.5.3.4., p. 218), it does so on basis of the assumption that there is a need for action because all PFAS within the scope are considered to be persistent and, therefore, any consequences would be irreversible, while the Dossiers Submitters nonetheless acknowledge that there is insufficient evidence for relevant environmental hazards which can be attributed to any and all PFAS within the scope of the Proposal, including Fluor-opolymers.
- (66) We therefore submit that the justification provided with the Proposal is invalid from a systematic point of view and does not support the inclusion of Fluoropolymers. The REACH Regulation does not contain any provision which states that the reversibility of a condition is important in connection with an environmental hazard assessment. Rather, it is the genuine task of the environmental hazard assessment to determine whether a given substance has intrinsic hazard properties. If this determination cannot be made, it is contradictory to presume environmental hazards simply because, in theory, a substance may be persistent and it may, in some respects, difficult to take countermeasures (referred to in the proposal as "threat of irreversible damage", cf. for example Annex B.7.5.3.4., p. 218). With this approach, the Proposal fails to demonstrate a sufficient hazard assessment as required for the preparation of a dossier in accordance with Annex XV to REACH and, consequently, no environmental hazards are demonstrated in an appropriate manner if the Dossier Submitters base their conclusion merely on the purported persistence of all PFAS alone.
- (67) Such an approach can also not be justified with a mere reference to the precautionary principle. It follows already from Commission Communication COM(2000) 1 of 2 February 2000 that the precautionary principle should be considered within a structured approach to the analysis of risk which comprises three elements: risk assessment, risk management and risk communication. It is commonly acknowledged that the precautionary principle comes into play subsequent to a risk assessment and, thus, where scientific information is insufficient, inconclusive, or uncertain and where there are indications that the possible effects on, inter alia, the environment may be potentially dangerous and inconsistent with the chosen level of protection. The precautionary principle, however, does not excuse the need for scientific information as a basis for a risk assessment in the first instance in favour of simply presuming that persistence equates to unacceptable risk.
- (68) As far as the Proposal (B.7.6.1., p. 219 et seq.) indicates that an intrinsic property results in a relevant hazard property due to mere persistency and additional further properties as already supported in the restriction of microplastic such argumentation has to be rejected as incorrect.
- (69) This argumentation fails because it deliberately circumvents the criteria of Article 68(1) REACH. It fails to recognize that there must be an unacceptable risk to the environment

for a restriction to be imposed in the first instance. If one were to dispense with this requirement, the result would be that a broad variety of substances could be restricted, because many substances are present in the environment in ever greater quantities due to continuous use and associated release, and for many of these substances there is also no possibility of removing them from the environment. In other words: If only the potential irreversibility of the condition and not the actual harmful effects on the environment are taken into account, Article 68(1) REACH would be interpreted in way which exceeds its actual wording.

(70) We further submit in this context, that such an approach results in a deviation from the prerequisites set out in Article 68(1) REACH. Insofar, the Proposal also infringes the principle of good administrative behaviour as well as legitimate expectations of market actors as it would not be possible to reasonably foresee whether a substance could and potentially would be restricted.

# d) Need to provide evidence for a hazard to human health or the environment for every subgroup

(71) It has, therefore, been shown that Fluoropolymers do not pose a risk to human health or the environment. As a precaution, it must be pointed out that the lack of corresponding scientific evidence for the identification of respective hazard properties and, as a consequence, the existence of a relevant risk within the meaning of Article 68(1) REACH, cannot be justified by the grouping approach. It is true that a restriction may regulate several substances at the same time, provided that the relevant requirements on grouping are met. However, this does not justify a deviation from the requirement to demonstrate compliance with the legal requirements for a restriction at least for each subgroup. The guidance document on groupings does not state at any point that lower evidence requirements apply in this respect. This applies in particular against the background that Fluoropolymers are treated in the proposal, as can be seen in Annex B.7.6 or the proposed Annex XVII entry, as a special PFAS category with special properties and circumstances that characterize them. While it may be justifiable with regard to the groupbased approach for individual substances to dispense the requirement for individual, substance-based evidence, such an approach cannot be considered permissible for a whole, high-profile subgroup. It is contradictory to the teleological background of the group-based approach that a group of substances, which is distinct from the other substances covered, is considered as belonging to a broader group so that the need to established a concrete proof of hazard properties is waived.

# e) No "justified" uncertainties and incorrect handling of uncertainties

(72) As a precautionary note, it should also be noted that the absence of hazardous properties cannot be justified by the fact that uncertainties are concerned and that such uncertainties are quite legitimate in the context of restriction procedures. This is because, on the one hand, in this respect the Dossier Submitters do not comply with ECHA's requirements for dealing with such uncertainties.

- (73) In this respect, it needs to be noted that the respective uncertainties are not uncertainties concerning the scientific evaluation of a certain question, i.e. hazard properties, but self-inflicted uncertainties which are solely due to the selected approach to cover a huge, non-homogeneous group of substances with the scope of the restriction proposal. For this reason, the Dossier Submitters cannot refer to the position that specific uncertainties are a regular part of every restriction dossier.
- (74) This notwithstanding, the Proposal contains a remarkably high number of uncertainties regarding the analysis and assessment of claimed hazards of PFAS, which are ultimately caused by the lack of sufficient scientific studies. When presenting these uncertainties, in some cases the Dossier Submitters did not adhere to the formal principles established by the document "Description of uncertainties in the evaluation of restriction proposals" by the Restriction Task Force (endorsed at the CARACAL-35 meeting on 31 March 2020, hereinafter referred to as "Guidance on uncertainties").
- (75) Compliance with these formal requirements already by the Dossier Submitters is by no means a mere formality, since according to the guidance document, RAC and SEAC have to indicate in their opinions regarding the dossier whether and to what extent the existing scientific data do not allow for a complete hazard assessment. This, in turn, should enable the Commission in the further course of the procedure to apply the precautionary principle in an appropriate manner when deciding whether restriction measures should be taken. The dossier fails to comply with the respective document in some important respects, as shown as follows.
- (76) According to the Guidance on uncertainties, the Dossier Submitters should have clarified which elements are uncertain. This requirement relates to, inter alia, hazards, uses, emissions, availability of alternatives and technologies, and the assessment of the socio-economic impacts of the restriction (cf. Guidance on uncertainties, p. 2). In the present case, deficits are particularly evident in the case of Fluoropolymers. For example, the Dossier Submitters on the one hand admit that no studies are known on the persistence of Fluoropolymers under environmental conditions (Annex B, p. 219) but, on the other, proceed to regard persistence as already proven (for example Annex B, p. 218). This contradiction would have required a precise presentation of the uncertainties. The lack of such a precise presentation will consequently also have an impact on the quality of the opinions to be established by RAC and SEAC.
- (77) Furthermore, the Dossier should indicate the extent to which remaining uncertainties affect the conclusions drawn (cf. Guidance on uncertainties, p. 2). For example, regarding the mobility of PFAS, the dossier states that there is insufficient data, but it is not clear how this insufficient data is reflected in the subsequent conclusion (see Annex B, p. 79).

Insofar, the Dossier does not comply with the rules set out in the respective guidance document.

- (78) Another requirement for a dossier is to indicate the timeframe and costs to be expected in order to fill the identified gap through additional scientific studies (cf. Guidance on uncertainties, page 2). This is related to the consideration that, within the framework of the precautionary principle, the Commission could order further studies instead of deciding for a restriction. Again, the dossier fails to comply with this requirement. For example, within the conclusions for environmental monitoring in Annex B.4.2.7.10. (p. 104) it is made clear that "significant fractions of organofluorine in environmental samples are unknown and are therefore not captured by monitoring using only targeted PFAS analysis". Contrary to the requirements, however, it is not stated whether more precise findings on this are to be expected from further studies and, if so, what duration and costs are to be expected in this respect. There are also uncertainties regarding the toxicity of polymeric PFAS in animal experiments, which are due to insufficient data. However, the Dossier Submitters do not give an outlook on future data collection or its costs and duration (Dossier, Annex B p. 154). Furthermore, it is conceded that further studies are required, without specifying their predicted time span (Annex B, page 116).
- (79) Overall, the requirements laid down in the Guidance on uncertainties are not met for various reasons. This complicates the further proceedings, in particular because it is unclear which uncertainties are relevant and have to be solved, e.g. by commissioning further studies, and which uncertainties can remain as regular part of any science-based evaluation. However, the mere identification of uncertainties without further description or information can by no means suffice.

# f) Insufficient hazard assessment regarding new hazard classes

- (80) The aforementioned inconsistencies regarding the hazard assessment of PFAS within the scope of the Proposal, in particular with respect to Fluoropolymers, also hold true against the background that the proposal refers to the mobility of PFAS. The assumed mobility of PFAS is clearly not derived from the intrinsic properties of the substances within the defined scope, i.e. properties which the substances may have individually to varying degrees in and of itself. It is rather the exposure of the substances and their potential availability especially in water compartments that supports the criterion against the background of the outline provided with the Proposal. The mere fact that PFAS might emerge in the aquatic environment, however, is not linked to any intrinsic property of the substances but qualifies as a result of their (presumed) persistence and an assumed availability in the water cycle. The Proposal, however, fails to sufficiently consider the fact that Fluoropolymers do not dissolve in water and therefore are not mobile.
- (81) This also holds true with respect to the further considerations outlined in Recital (8) of Commission Delegated Regulation (EU) 2023/707. Nothing in this Delegated Regulation

can additionally support the Proposal. The aforementioned Delegated Regulation introduced, inter alia, new hazard classes for substances being identified as PMT (persistent, mobile, toxic) and vPvM (very persistent, very mobile). But according to the Recital (8) of the Delegated Regulation, PMT and vPvM criteria mainly focus on persistence and mobility, whereby the overall basis for the introduction of the corresponding hazard classes is the mere fact that such substances

"can enter the water cycle, including drinking water, and spread over long distances. Many PMT and vPvM substances are only partly removed by wastewater treatment processes and can even break through the most advanced purification processes at drinking water treatment facilities. Such incomplete removal coupled with new emissions mean that the concentration of those PMT and vPvM substances in the environment increase over time. Once released into the environment, exposure to PMT and vPvM substances is difficult to reverse, which leads to cumulative exposure of both animals and humans via the environment. Any effects from this exposure are unpredictable in the long-term."

- (82) Insofar, the underlying justification for the introduction of the hazard classes PMT and vPvM is similar to the justification provided for in the Proposal. We submit, however, that this Delegated Act has been adopted by the Commission in misuse of powers conferred to the Commission according to the CLP Regulation and, therefore, the newly introduced hazard classes cannot justify the proposed restriction or support the risk assessment outlined therein.
- (83) The Commission is only empowered under the CLP Regulation to adopt delegated acts in accordance with Article 53a of CLP to amend Articles 6(5), 11(3), 12 and 14, 18(3)(b), 23, 25 to 29, 35(2) subparagraphs 2 and 3 and Annexes I to VIII of CLP for adaptation to technical and scientific progress, taking due account of the further development of the Globally Harmonised System ("GHS"), in particular any amendments at level of the United Nations relating to the use of information on similar mixtures, and taking into account developments in internationally recognized chemical programs and data from accident databases. The amendment of the CLP Regulation to introduce new hazard classes does not fall under these powers.
- (84) Although the Proposal does not specifically refer to the contemplated new hazard classes due to the fact that the respective delegated act was published in the Official Journal of the EU only on 31 March 2023 (OJ of 31 March 2023, L 93, p. 7) the corresponding prerequisites and criteria are nonetheless applied. Due to the misuse of powers, however, the Delegated Act cannot be used to justify or support the Proposal. This moreover as the Proposal was established even prior to the entry into force of Commission Delegated Regulation (EU) 2023/707.
  - 2. Failure to meet the prerequisites established in Article 68 REACH regarding risk assessment

(85) As stated above, an unacceptable risk within the meaning of Article 68(1) REACH is formed of a hazard to human health or the environment and a relevant exposure. The dossier not only fails to proof such hazard and, therefore, any further risk assessment already lacks a sufficient basis.

# a) Insufficient evidence regarding exposure to Fluoropolymers.

- (86) Any risk assessment needs to be based on identified hazard properties and relevant exposure to the substance at hand. With respect to Fluoropolymers, the Proposal is already lacking a sufficient assessment of respective hazard properties. But also the identification of related exposures is not convincing. For example, according to the proposal, very little is known about the levels of polymeric PFAS in the environment (cf. Proposal, p. 45). As for human exposure assessment, the proposal states, that the bioavailability and thus the potential for human exposure to Fluoropolymers has been an issue for discussion (cf. Proposal, p. 46). Thus, according to the Proposal, it has been proposed that absorption of Fluoropolymers in humans is obstructed due to their large sizes (Henry et al., 2018).
- (87) Despite these findings, it has been argued that the production, processing, use, and endof-life treatment of Fluoropolymers lead to emissions of bioavailable compounds (ibid.). In sum, there seems to be no clarity regarding the exposure to Fluoropolymers.
- (88) And even if one would consider it appropriate to consider corresponding risks with respect to the use of fluorinated polymerisation aids used for the manufacture of Fluoropolymers, although the underlying hazard assessment is lacking sufficient evidence, it would have been possible and sufficient to propose a restriction for the use of fluorinated polymerisation aids qualifying as PFAS in connection with the manufacture of Fluoropolymers. The manufacture and use of Fluoropolymers as such, however, should not be included in the scope of the Proposal, i.e. an exemption or non-time-limited derogation would be justified. Also because more than 50% of commercially produced fluoropolymers do not require the use of any polymerization aids let alone fluorinated polymerization aids (cf. *Sales* et al., ICRL 2022, p. 13, 19 with further references).

# b) Deviation from principles for risk assessment

(89) With respect to risk assessment requirements as set out in Article 68(1) REACH, the Proposal itself demonstrates a deviation from applicable principles. The Proposal states that the procedures in Sections 1 to 6 in Annex I to REACH are impracticable to describe the particular effects of PFAS within the scope of the restriction proposal, as the PFAS in scope are very persistent in combination with identified and possible other concerns. Therefore, the Proposal states that the respective risk is described on a case-by-case basis as reflected in Section 0.10 of Annex I to REACH.

- (90) The Proposal, however, ignores the fact that already the wording of Section 0.10 of Annex I to REACH states that (only) in "relation to particular effects, such as ozone depletion, photochemical ozone creation potential, strong odour and tainting, for which the procedures set out in Sections 1 to 6 are impracticable, the risks associated with such effects shall be assessed on a case-by-case basis". Against this background, it is against the law that the entire risk assessment for all hazard properties and all corresponding exposures is carried out on a case-by-case basis. Moreover, a "case-by-case" approach according to Section 0.10 of Annex I to REACH is established as a more specific and tailored approach for certain effects. The corresponding section does not support the view that a deviation from Sections 1 to 6 of Annex I to REACH is also possible to establish a broad and generic restriction proposal and to circumvent a possible, although complex and potentially difficult assessment according to Sections 1 to 6 of Annex I to REACH. Rather, the wording of Annex I suggests that a case-by-case approach is only intended in justified individual cases and only for certain effects. These requirements are not met with respect to PFAS, not even in the view of the Dossier Submitters.
- (91) As is demonstrated with the further evidence provided as part of the broader submission of GFL, a risk assessment according to Sections 1 to 6 of Annex I to REACH would have resulted in the conclusion that manufacturing and use of Fluoropolymers do not entail a risk in accordance with Article 68(1) REACH.
- (92) But even if a case-by-case approach according to Section 0.10 of Annex I to REACH would be considered appropriate with respect to PFAS, including Fluoropolymers, it needs to be noted that "a full description and justification of such assessments" still would be required. Deviating from the general approach for a risk assessment in line with Section 1 to 6 of Annex I to REACH and applying a restriction-specific assessment cannot circumvent the requirement to establish sufficient scientific evidence and justification that environmental hazards actually are present. Mere presumptions and referenced possibilities do not qualify as a sufficient basis. Therefore, the Proposal erroneously follows a route for the hazard assessment, which is not supported by the REACH Regulation and, thus, cannot justify the proposed restriction.
- (93) Therefore, it must be concluded that the Proposal is lacking sufficient evidence and justification as to why all PFAS have intrinsic properties which result in environmental hazards. The Proposal does not comply with Article 68(1) REACH and erroneously deviates from applicable statutory requirements and established guidance. By doing so, the Proposal breaches the principle of good administration and legitimate expectations.
- (94) The Proposal and the underlying justification deviates from statutory prerequisites and established guidance. Due to this deviation, it is not only difficult to identify the specific scientific basis for the conclusion as to why any and all substances within the scope of the Proposal do have relevant hazard properties that result in a relevant risk as required by Article 68(1) REACH. Insofar, the Proposal infringes the principle of good administration due to inconsistency of the underlying administrative behaviour and a breach of

legitimate expectations of stakeholders and other market actors regarding the proceeding, the underlying assessment, and the intended decision-making process.

# 3. Unlawful grouping

(95) Although various inconsistencies of the grouping as referred to in the Proposal are already demonstrated with respect to the hazard and risk assessment, as outlined above, we further submit that the grouping of all known and unknown PFAS as proposed by the Dossier Submitters is unlawful.

# a) Deviation from available guidance

(96) In the respective guidance document, it is stated, that grouping could be considered

"when the key property in combination with the exposure that causes the risk leading to the proposal of a restriction is shared by several related substances"

(cf. Guidance for the preparation of an Annex XV dossier for restrictions, p. 23). As is apparent from the wording, the substances do not only need to share the same property or properties but also, in effect, the same risk. In the present case, the PFAS within the scope of the Proposal share, according to the Proposal itself, one single property, i.e. persistence, which as such does not even qualify as a hazard property.

- (97) While the Dossier Submitters emphasize that this is the relevant key property, we submit that persistence as such does not qualify as a hazard property nor as a risk. Therefore, persistence as such is not a sufficient basis for a grouping approach. According to the Proposal (cf. p. 22), the additional properties of PFAS differ and vary among the PFAS, while it is not even demonstrated that any and all PFAS within the scope of the Proposal have additional hazard properties beyond their persistence at all. A common hazard property and profile and, thus, any substantially similar risk shared by all substances within the scope of the Proposal cannot be established and the Proposal does not even claim to achieve the applicable prerequisites for grouping. Consequently, the requirement for grouping is not met, and the Proposal is further legally deficient on this basis.
- (98) Besides not meeting the criteria as laid down in the respective guidance document, the group-based approach is erroneously established for another reason. The background of this approach is that different substances can and should be examined together on the basis of similarities, in particular to improve the effectiveness of the restriction and the procedure (cf. Grouping of substances to be covered in a single restriction dossier (Restriction Task Force), p. 1). It is true that the PFAS within the scope of the proposal arguably all show some persistence. However, the numerous scientific uncertainties do not arise with regard to the question of persistence, but rather with regard to any potential additional hazardous properties. In this respect, the Proposal itself states that there are major differences between the PFAS covered (Proposal, p. 22). However, this undermines the conceptual origin of the group-based approach. Indeed, if no reciprocal

links can be established with respect to the issues at stake, there are no efficiency gains from the process. Moreover, the group-based approach in the present case leads to the conclusion that the properties of certain PFAS are related to the properties of other PFAS, without this being scientifically substantiated (cf., representative of many examples, for example Proposal, Annex B, page 181). Logically, such cross-references should take place precisely for the common property and precisely not with regard to such properties, which differ greatly. In this respect, the group-based approach is not persuasive. This specifically holds true with respect to the distinct sub-group of Fluoropolymers.

- (99) Against this background, the grouping can also not be justified by the fact that a regrettable substitution should be prevented. For example, with regard to Fluoropolymers, the extent to which such substitution behaviour would be possible at all has not been established. Furthermore, the consideration is not proportionate, especially with regard to substances that are still completely unresearched, because it does not make any gradation between more dangerous and less dangerous substances. It is evident that there are more dangerous and less dangerous PFAS. In this respect, in order to maintain proportionality, certain groups of PFAS could have been included in the restriction proposal with the aim of displacing the market and certain other PFAS, whose effects on humans and nature have been proven to be low, could have been excluded from the scope. This is especially true in light of the fact that certain persistent substances will continue to be needed in industry in the future. For these uses, a persistent alternative must inevitably be available, so that in terms of proportionality it should have just been enshrined to allow certain substitutions instead of restricting all PFAS with the argument of preventing any "regrettable substitution".
- (100) Moreover, specifically with respect to Fluoropolymers, it is impractical and ultimately erroneous to have them regulated together with other PFAS. This is because the dossier shows in several sections that it considers Fluoropolymers to be a special, distinct category of PFAS. An example of this is the specific environmental hazard assessment for Fluoropolymers in Annex B.7.6 (p. 219 et seqq.), in which it is significantly stated that the main problem of Fluoropolymers lies in the release of other PFAS. The dossier thus admits that Fluoropolymers as such do not have the same intrinsic hazard properties as other PFAS. In this respect, it is legally incorrect that Fluoropolymers are treated the same way as other PFAS and, thus, are subject to conclusions derived from hazardous properties of other PFAS due to the group-based approach.
- (101) This applies in particular against the background that Fluoropolymers compared to all other PFAS - are partially treated as microplastics in the dossier. Furthermore, the proposal of the restriction text also shows the autonomy of the category of Fluoropolymers, because special derogations apply to them (cf. proposed restriction, Column 2, Nos. 6 and 8). In particular, according to Column 2, No. 8 of the proposed restriction, only Fluoropolymers are subject to certain further information requirements in the event that a derogation is used. This is contradictory in itself, because an exemption actually presupposes sufficient information.
(102) Above all, however, this distinct approach shows that there are obviously major knowledge gaps for Fluoropolymers. Against this background, too, it seems absurd to regulate Fluoropolymers together with other PFAS such as PFCAs, PFOA, for which corresponding information on the hazardousness is actually available. Due to the already acknowledged difference between Fluoropolymers and other PFAS, the principle of the rule of law requires that Fluoropolymers are regulated separately if a corresponding regulatory measure is justified at all.

# b) Grouping not justified with respect to PFAS definition established by OECD

(103) The grouping approach as applied in the Proposal can also not be justified with the definition of PFAS as established with OECD guidance "Reconciling Terminology of the Universe of Per- and Polyfluoroalkyl Substances: Recommendations and Practical Guidance" ("**OECD (2021)**").

# aa) PFAS definition according to OECD

- (104) Prior to the assessment of the justification of the grouping approach it needs to be noted that the perception and definition of PFAS as established by the OECD were subject to some major changes in recent years.
- (105) In Buck et al. (2011), PFAS were defined as "the highly fluorinated aliphatic substances that contain 1 or more C atoms on which all the H substituents (present in the nonfluorinated analogues from which they are notionally derived) have been replaced by F atoms, in such a manner that they contain the perfluoroalkyl moiety CnF2n+1–" (i.e. must contain at least –CF3). The definition highlights the presence of at least one fully fluorinated saturated carbon atom in the PFAS molecules.
- (106) PFAS were re-defined by the OECD in 2021 as follows:

"PFAS are defined as fluorinated substances that contain at least one fully fluorinated methyl or methylene carbon atom (without any H/Cl/Br/I atom attached to it), i.e. with a few noted exceptions, any chemical with at least a perfluorinated methyl group (–CF3) or a perfluorinated methylene group (–CF2–) is a PFAS."

(OECD (2021), Reconciling Terminology of the Universe of Per- and Polyfluoroalkyl Substances: Recommendations and Practical Guidance, OECD Series on Risk Management, No. 61, OECD Publishing, Paris, p. 8)

(107) According to the OECD, the introduction of the new definition is triggered by two main reasons (cf. OECD (2021), p. 7, 18). First, the OECD/UNEP Global PFC Group prepared a new list of PFAS that may have been on the global market in 2018. In total, a set of substances with over 4.730 CAS numbers have been identified, including substances that contain fully fluorinated carbon moieties, but do not meet the PFAS definition in Buck et al. (2011) due to a lack of a –CF3 group in the molecular structures. Second, according to the OECD, recent advancement of non-target screening analytical techniques using high-resolution mass spectrometry has enabled identification of many unknown substances in different environmental and product samples. Thus, the development and broaden of the definition is motivated by the identification of overlooked PFAS (cf. OECD (2021) p. 18) and the closing of identified gaps in the previous PFAS definition (cf. OECD (2021) p. 21, 23).

- (108) Furthermore, according to the OECD, the rationale behind the revision is to have a general PFAS definition that is coherent and consistent across compounds from the chemical structure point of view and is easily implementable for distinguishing between PFAS and non-PFAS, also by non-experts (OECD (2021), p. 8). The OECD claims, that the decision to broaden the definition is not connected to decisions on how PFAS should be grouped in regulatory and voluntary actions (ibid.) and that the intention of the revision of the PFAS definition is not to expand the PFAS universe, but to comprehensively reflect it (OCED (2021), p. 23).
- (109) The OECD states, that the term "PFAS" is a broad, general, non-specific term, which does not inform whether a compound is harmful or not, but only communicates that the compounds under this term share the same trait for having a fully fluorinated methyl or methylene carbon moiety (OECD (2021), p. 8). Accordingly, the general definition of PFAS is based on molecular structure alone and serves as a starting and reference point to guide individual users to have a comprehensive understanding of the PFAS universe and to keep the big picture of the PFAS universe in mind (ibid.)
- (110) The broadening of the definition is to be taken critically, since, in particular, it is contradictory and seems artificial. The justifications quoted above are subject to an error of logic. Ultimately, the OECD justifies the broadening of the definition by saying that PFAS overlooked by the former definition have been identified and that this gap is now to be closed.
- (111) In this respect, it is already linguistically illogical that a definition is supposed to have "gaps" just because certain substances are not covered by it. According to this logic, every definition of a group of substances would logically have a gap, because some substances are of course not covered by the definition. Consequently, every definition would need to be broadened. This train of thought shows that the OECD's justification is not correct in this respect and, therefore, cannot justify a grouping approach for a restriction proposal under REACH.
- (112) Moreover, the argument that new PFAS (!) have been identified in the meantime (e.g. by new screening methods) is illogical. After all, according to the definition applicable at the time, the substances identified were not PFAS by definition.
- (113) Consequently, it is not a matter of closing gaps, but of expanding the definition. This is already clear from the fact that, as the OECD itself admits, the revised definition now

covers significantly more substances than before. Against this background, it is not comprehensible that the OECD states that the amendment of the definition was not intended to expand the universe of PFAS. After all, this is exactly what has happened by changing the definition in such a way that certain substances that were previously not covered by the definition, for example due to the absence of a –CF3 group, are now covered.

- (114) As far as the OECD states that the new definition is necessary for a coherent and consistent distinction of PFAS, it fails to provide any evidence to what extent the previous definition was not coherent and not consistent. As already stated, the mere fact that certain, possibly even similar, substances are not covered by a definition does not make the definition inconsistent. On the contrary, it must be stated that the exclusion of certain substances from the definition has precisely shown that it functions and is therefore consistent and coherent.
- (115) Thus, the impression arises that the OECD, contrary to its attempts at explanation, has changed the definition precisely because it wanted to classify the newly discovered substances as PFAS. As shown, the attempts to explain otherwise are not convincing. In particular, the reference to the fact that classification is based solely on molecular structure is also not sufficient. After all, it has not been shown whether and to what extent the previous definition was deficient in this respect. Overall, therefore, the conclusion remains that the OECD has significantly expanded the definition of PFAS for reasons other than those listed in the paper.

# bb) OECD definition not based on hazard or risk assessment

- (116) Furthermore, it has to be noted, that the broadening of the PFAS definition is not at all connected to any scientific findings of hazards or risks of certain substances but only based on chemical considerations (cf. OECD (2021), p. 31: does not include [...] any other considerations beyond chemistry). This is remarkably, since the PFAS restriction proposal adopts (more or less) the definition and states that all substances within the scope of this definition are hazardous and thus must be restricted (Proposal, p. 22).
- (117) It already follows from this misinterpretation of the revised OECD definition that the Proposal is flawed from a scientific and legal perspective. While the Proposal, on the one hand, acknowledges that the "OECD definition of PFASs is based on chemical structure" and hazardous properties or risks are not part of it" (cf. Proposal, p. 19) and, thus, some substances are excluded from the scope due to the fact that "they will ultimately mineralize in the environment" (ibid.), it needs to be noted, on the other, that the Proposal only presumes that all PFAS that remain within the scope of the restriction proposal "share a common hazard and risk", while a lack of scientific data on hazards for PFAS within the scope is broadly acknowledged. In other words, the Proposal is essentially based on the PFAS definition as established by the OECD which does not consider any hazard properties or risks, and the Proposal does not substantiate or justify for all sub-stances within its scope if and which specific hazard properties apply. Therefore, the

Proposal is based on a non-hazard-/non-risk-based definition of the scope. Such approach is infringing the basis for a restriction proposal as established in Article 68(1) REACH and cannot be used to justify a grouping approach.

# cc) Deviating scope of the restriction proposal does not justify grouping approach

(118) For the purpose of the restriction proposal, the Dossier Submitters define PFAS -compared to the OECD - slightly different as substances that contain at least one fully fluorinated methyl (CF3-) or methylene (-CF2-) carbon atom, without any H/Cl/Br/l attached to it. For the purpose of the Proposal, the Dossier Submitters propose the following scope (cf. Proposal, p. 14):

"Any substance that contains at least one fully fluorinated methyl (CF3-) or methylene (-CF2-) carbon atom (without any H/Cl/Br/I attached to it).

A substance that only contains the following structural elements is excluded from the scope of the restriction: CF3-X or X-CF2-X',

where X = -OR or -NRR' and

X' = methyl (-CH3), methylene (-CH2-), an aromatic group, a carbonyl group (-C(O)-), -OR'', -SR'' or -NR''R''';

and where R/R'/R''/R''' is a hydrogen (-H), methyl (-CH3), methylene (-CH2-), an aromatic group or a carbonyl group (-C(O)-)."

- (119) Thus, the Proposal introduces an exception which concerns certain fully degradable PFAS subgroups that contain some specific structural elements. PTFE is a fluoropolymer and it uses TFE (Tetra Fluoro Ethylene) and HFP (Hexa Fluoro Propylene) as raw materials. While TFE is not a PFAS as per the definition, HFP is. Such anomalies exist for other fluorinated monomers used in the production of fluoropolymers.
- (120) Thus, the proposed scope of the restriction is a rather crude combination of the broad OECD definition and slight exemptions for subgroups which are considered to be not persistent by the Dossier Submitters. The derivation of the scope and its justification is, however, flawed for various reasons.
- (121) As can be seen from the Proposal, the starting point for the development of the scope for the proposed restriction remains the OECD definition of PFAS. According to the proposal, the substance scope is "additionally" considered to be a concern-based one, which wants to cover all PFAS that are persistent (cf. Proposal, p. 19). For this reason, the Dossier Submitters exclude identified non-persistent subgroups from the scope, while it is not demonstrated that any relevant hazard or risk profile can be established for the remainder of the substances considered to be within the scope.

- (122) It follows already from these considerations that the PFAS definition cannot justify a grouping approach. If it would be correct to assume that all PFAS within the scope, i.e. within the scope of the definition as established by the OECD, qualify as being persistent, it should not be possible to exclude certain PFAS as they cannot be considered persistent.
- (123) But this notwithstanding, the Proposal only assumes that all PFAS, except for the few subgroups excluded from the scope, are persistent while this assertion is not substantiated in the justification of the scope of the Proposal or in any other section of the Proposal. To the contrary, the Dossier Submitters concede that they have no positive knowledge about the persistence of most substances, because they request stakeholders to prove that specific substances used by them are not persistent and can therefore be excluded from the scope (cf. Proposal, Annex B, p. 3).
- (124) However, this approach does not meet the requirements of a diligent elaboration on the scope of a restriction proposal. This applies in particular against the background that the OECD has stated in the context of the justification of its extremely broad definition that, on the one hand, the broad definition cannot be connected to the scope of possible regulatory measures (p. 8), and, on the other hand, the definition is only a "starting point" due to its broadness (p. 31). It is true that the narrowing down of the definition to persistent substances, basically, can be considered a plausible refinement of the OECD definition. However, it would have been necessary to prove to what extent the many thousands of substances still covered within the scope are persistent, as far as this is considered the "main concern" (cf. Proposal, p. 24). By merely making an unsubstantiated claim, the scope (with the small exception of substances known to be non-persistent) corresponds nearly to the extremely broad OECD definition, which is clearly not based on a hazard or risk assessment.
- (125) The aforementioned concerns especially hold true against the background that the OECD highly recommends that users clearly provide the context and rationale for selecting their PFAS working scope in order to provide transparency and avoid confusion by others (OECD (2021), p. 8). In the case at hand, such a rationale is not given except for the short statement that the aim is to address the concerns associated with the persistent nature of the substances (cf. Proposal p. 19).
- (126) As a matter of fact, the Dossier Submitters, when justifying the scope of the restriction proposal, did not even bother to change the wording of the OECD paper which introduced the new definition. As an example, we would like to emphasize that the sentence

"(...)attracted much public attention since the late 1990s and early 2000s, when the hazards and ubiquitous occurrence in the environment of two PFAS, perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS), started to be reported and recognized",

is taken from pages 7 and 17 of the OECD paper and is repeated on page 18 of the Proposal without indicating that it is a citation from the OECD paper and without source citation.

- (127) Furthermore, it should be noted that the proposal only refers to persistence and not to hazards for humans or the environment. This is already questionable on the level of the elaboration of the scope, because persistence as such does not qualify as a hazard property as referred to in the REACH Regulation by reference to the CLP Regulation, and therefore not a suitable reference point for the mandatory risk assessment in accordance with Article 68(1) REACH.
- (128) The mere fact that the OECD paper assumes that a limitation for potential regulatory measures is possible, *inter alia*, on basis of the criterion of persistency (OECD (2021), p. 26). However, against the background of the clear wording of Art. 68 REACH, this cannot apply to a restriction under REACH.

# dd) Violation of OECD guidance on PFAS

- (129) Furthermore, the Proposal violates the underlying OECD guidance because its wording does not meet the requirements laid down in chapter 3 of OECD (2021). In chapter 3.2, OECD (2021) gives a practical guidance on how to identify and use suitable PFAS terms. As stated in the guidance, it is strongly recommended that the PFAS terminology be used in a clear, specific and descriptive manner which is due to the fact that the term "PFAS" does not inform whether a compound is harmful or not, but only communicates that the compounds under this term share the same trait for having a fully fluorinated methyl or methylene carbon moiety (cf. OECD (2021), p. 32). A clear and specific wording is necessary to prevent ambiguity or factual errors. Thus, the OECD asks regulators to use terms that most clearly describe the substance(s) referred to in their statement and provides for concrete examples (cf. ibid.).
- (130) The proposal violates these requirements in numerous points, of which only a few are listed below as examples.
- (131) For example, it is linguistically extremely unfortunate that the Proposal, when developing the scope, does indeed clarify that certain (non-persistent) substances are excluded from the scope of the Proposal. This results in the scope containing only a subset of the substances that are to be considered as PFAS according to the current OECD definition. Nevertheless, the proposal refers in some places to "all PFAS" (e.g. Proposal, p. 22: "All PFAS are considered to be very persistent (...)") and thus leaves great linguistic ambiguity as to which substances are meant. Moreover, the above quoted passage is also fundamentally wrong as the proposal itself states that some PFAS are not persistent.
- (132) A further linguistic inaccuracy is that in many places the term "some PFAS" is used (see e.g. Proposal p. 26, 35, 36, 48, 50; Annex B p. 133, 165, 208 and many more); in addition, sometimes a "subset of PFAS" is referred to (e.g. Proposal p. 28, 48). Both is entirely

insufficient against the background of the OECD's requirement to designate the respective substance or group of substances as accurately as possible.

- (133) In addition, there are passages in the proposal in which the properties of specific substances or groups are first discussed (in accordance with the OECD specifications) and then generalized in the course of consideration. For example, the mobility is first explained on the basis of concrete substances and 5 paragraphs later the generalizing statement is made that "Mobility of PFAS in water contributes to their long-range transport potential (...)" (cf. Proposal p. 25).
- (134) As a result, it must be stated that the Dossier Submitters did not comply with the requirements that emanates from the broad OECD definition. In many places they did not differentiate between PFAS in the sense of the definition and PFAS in the sense of the scope and, moreover, often made unnecessary generalizations. Insofar, the definition of PFAS as established with OECD (2021) and modified with the Proposal cannot justify the grouping approach due to the broad variety of inconsistencies.

# 4. Breach of principle of proportionality

(135) Furthermore, the proposal infringes the principle of proportionality for various reasons.

# a) Availability of less onerous measures

- (136) The proposal is disproportionate as there would have been less onerous measures to achieve the intended aim and purpose. According to settled case-law, the principle of proportionality, which is part of the general principles of EU law, requires that EU measures do not exceed the limits of what is appropriate and necessary in order to attain the objectives legitimately pursued by the legislation in question; when there is a choice between several appropriate measures recourse must be had to the least onerous, and the disadvantages caused must not be disproportionate to the aims pursued (judgments of 8 July 2010, Afton Chemical, C 343/09, EU:C:2010:419, paragraph 45; of 21 July 2011, Etimine, C 15/10, EU:C:2011:504, paragraph 124; and of 1 February 2013, Polyelectrolyte Producers Group and Others v Commission, T 368/11, not published, EU:T:2013:53, paragraph 75). The clearly communicated objective of the restriction proposal is to eliminate PFAS from the market as far as possible. Regardless of the question to what extent this is a legitimate goal, there would have been less onerous measures in several respects that would have served the goal with equal effectiveness.
- (137) First, an authorization under Art. 55 REACH would have had to be considered. The ultimate aim of an authorization is that the use of substances of very high concern are replaced by suitable alternative substances or technologies where these are economically and technically viable (see judgment of 7 March 2013, Rütgers Germany and Others v ECHA, T 94/10, EU:T:2013:107, paragraph 134 and the case-law cited).

- (138) Irrespective of the fact that the approach supported by the Dossier Submitters with the Proposal are in any case more similar to those of an authorization, an authorization obligation would have had the relevant advantage for stakeholders that they would have been provided with an orderly procedure for obtaining an authorization for their use. With the Proposal and the subsequent restriction procedure, stakeholders are now limited to requesting an exemption or derogation in connection with the consultation procedure. In this context it needs to be noted that the approach chosen by the Dossier Submitters leaves stakeholders in a less secured legal position.
- (139) Other than in a regular authorisation procedure, there is no specific decision which is directly addressed to the applicant and which can be subject to further legal action if considered necessary in case of deviations from the underlying application. In the case at hand, however, a rejection of a request for an exemption or derogation does not even result in a decision addressed to the respective stakeholder and, even worse, the REACH Regulation does not even establish any legal prerequisite that a further justification for such rejection is provided. As no decision is adopted to that effect, not even the general principle to justify decisions would apply although this is enshrined e.g. in Article 18 of the Code of Good Administrative Behaviour for the Staff of the European Chemicals Agency (adopted by Decision of the Management Board MB/11/2008 of 14 February 2008, as amended by Decision of the Management Board MB/21/2013 of 20 June 2013) and the European Code of Good Administrative Behaviour (cf. C(2000) 3614, OJ L 308, 8 December 2000, p. 26).
- (140) Even irrespective of the specific case at hand, which has the peculiarity that there must be different exceptions for many different uses, a restriction is generally the milder measure compared to the obligation to obtain authorization. It is true, however, that case law does not assume a special priority relationship between authorization and restriction in this respect. However, there is case law stating that a restriction is not (!) a less onerous measure compared to the identification of a substance for the candidate list (cf. Judgment of 25 September 2015, PPG and others vs. ECHA, Case T-268/10).
- (141) This implies that the route via an authorization must in principle be considered as less onerous. Since the objective of the authorization and the objective of the restriction are otherwise identical, namely, with the exception of substances that are exempt from the restriction or have to be authorized, market elimination is to be achieved, the path via an authorization would have been a more proportionate measure in the present case.
- (142) We understand that the Dossier Submitters identified various obstacles and regulatory shortcomings in connection with a potential authorisation approach for PFAS (cf. Proposal, Section 2.2.2.3, p. 69). We submit, however, that the aspects referred to in the Proposal in this context only address benefits for authorities as regards potential efforts which cannot justify deviations from the principle of proportionality.

- (143) The Proposal already acknowledges that according to Article 58(3) REACH, priority for inclusion of SVHC in Annex XIV shall normally be given to substances with (a) PBT or vPvB properties, or (b) wide dispersive use, or (c) high volumes. While the Proposal also correctly states that only substances that were previously added to the Candidate List can be subject to authorisation requirements, the Proposal states that SVHC identification of all PFAS meeting the chemical definition would be very difficult (cf. Proposal, Section 2.2.2.3, p. 69). The Proposal, however, ignores the fact that already today a significant number of PFAS is included in the Candidate List (including but not limited to PFBS, PFHxS, PFHpA, PFOA, PFNA, PFDA, PFUnDA, PFDoDA, PFTrDA, PFTeDA). In addition, the Proposal conceals the fact that it would be possible to include all PFAS in the candidate list on basis of Article 57(f) REACH. If a corresponding grouping approach is considered feasible for the proposed restriction (regardless further concerns in this regard as already outlined above), the same approach could be used for SVHC identification. To that end, the template for corresponding Annex XV reports explicitly refers to the option to propose SVHC identification on basis of grouping.
- (144) The same holds true for the prioritisation of SVHC for inclusion in Annex XIV as explicitly stated in ECHA's outline "General prioritisation approach: practical implementation examples" (Section 3, p. 4). Although no PFAS are listed in Annex XIV to REACH so far, nothing in the underlying procedural provisions would exclude this approach. The argument raised by the Dossier Submitters, that SVHC identification and subsequent inclusion in Annex XIV of all PFAS "fitting the chemical definition would be very difficult", is not convincing.
- (145) Moreover, we submit that a decisive aspect has not been considered by the Dossier Submitters. With respect to enforcement, authorisation requirements seem to provide relevant advantages as all market actors using a substance would need to either apply for an authorisation or submit a notification according to Article 66 REACH, i.e. need to identify themselves and their respective uses vis-à-vis authorities. Enforcement of restrictions and corresponding exemptions or derogations do not require proactive identification of market actors and uses, which creates a significant likelihood of non-compliance on side of market actors and insufficient enforcement and control measures on the side of authorities.
- (146) This notwithstanding, we further submit that with respect to Fluoropolymers any appropriate hazard assessment against the background of Article 57 REACH would have demonstrated that beyond the persistence no specific hazard properties can be identified for all Fluoropolymers in a way that would justify an identification as substances of very high concern or subsequent inclusion in Annex XIV. Therefore, an authorisation approach would have resulted in a regulatory approach excluding Fluoropolymers and, thus, would have been a less onerous approach for this subgroup of PFAS.
- (147) And even if the Dossier Submitters would have considered less onerous options only within the framework of a restriction under REACH, it would have been appropriate to

provide for an initially unlimited exemption for Fluoropolymers because there are at least uncertainties regarding the hazard and risk profile and, if considered necessary by the Dossier Submitters, to link this to a mechanism a review period for the Commission to assess whether and to what extent specific properties have been identified. Although there is no sufficient basis for such further review according to the information presented in the Proposal, such approach would qualify as a less onerous measure and a wellestablished approach in connection with multiple other restrictions.

- (148) In addition, such approach would also have supported any further assessment of specific uses and related alternatives. As far as an assessment of certain uses is not possible in connection with the decision on the Proposal, it would be possible to establish a review period for the Commission to assess whether suitable alternatives are available. In this respect, stakeholders would also have sufficient pressure to develop alternatives. However, it would not come to the scenario that the development of alternatives actually fails and thus, under certain circumstances, entire supply chains or industrial sectors are massively and possibly permanently disrupted by a certain deadline.
- (149) It is true that the Commission could subsequently amend the text of the restriction and thus react to this situation. However, experience shows that the Commission has not made use of this possibility even in justified cases. Therefore, such approach cannot be considered as suitable alternative.

# b) Inappropriate assessment of the alternatives available

- (150) The dossier breaches the principle of proportionality for another reason, as it makes an inappropriate assessment of the alternatives available.
- (151) The wording of Article 68(1) REACH already requires that a decision on a restriction has to take the availability of alternatives into account. Accordingly, Section 3 of Annex XV to REACH states that available information on alternative substances and techniques shall be provided, including information on the risks to human health and the environment related to the manufacture or use of the alternatives, availability (including the time scale) and technical and economic feasibility. The Guidance for the preparation of an Annex XV dossier for restrictions specifies these requirements and states that the respective aim is to provide information for the analysis of whether the equivalent function provided by the substance can be obtained by other substances or techniques (cf. Guidance, p. 68).
- (152) Furthermore, according to the guidance document, an alternative shall mean alternative chemical substances or alternative techniques (processes and technologies) or combinations thereof that can be used to replace (partially or totally) the substance of concern in a given use or a number of uses by providing the equivalent function that the substance delivers in those uses or by making the function redundant (cf. Guidance, p. 69).

- (153) Moreover, the information on alternatives should be used to "defining a proportionate restriction that is targeted to the identified risk" (cf. Guidance, p. 68) and in developing the justification that the proposed restriction is the most appropriate measure (cf. Guidance, p. 69). Thus, the guidance document clearly states, that the evaluation of alternatives is a necessary and mandatory part of a proportionate restriction proposal.
- (154) In the present case, the assessment of available and, above all, future alternatives suffers from a decisive logical error. As can be seen in many passages, the assessment focuses on other substances that can have an equivalent function to PFAS. In this respect, the dossier adheres to the requirements of the guidance document, which specifies this as the definition of an alternative. However, the dossier fails to recognize that the decisive function of Fluoropolymers is precisely their persistence or their ability to persist in challenging environments like extremely high temperatures, inertness to highly reactive chemicals. Persistency in adverse environment is also the function of reliability or durability which is a requirement of many applications in particular aerospace, semiconductor, chemical process industry etc. In this respect, the dossier states in some passages that the common property of Fluoropolymers is their persistence and the dossier justifies the proposed restriction mainly with the fact that the substances are persistent. Other properties therefore play an additional role at best (cf., for example, Proposal, p. 22).
- (155) Against this background, it contradicts any logic of thought that alternatives are sought which possess the same decisive property, because according to the logic of the dossier, the alternatives would not be allowed at all and would consequently have to be restricted. In this respect, the analysis of existing and future alternatives should necessarily revolve around alternatives of use and not around alternatives of substance.
- (156) To that end, however, it needs to be submitted that, in general, no alternatives for Fluoropolymers are available. In addition, it is evident that for many applications there are no non-persistent alternatives available because Fluoropolymers are used precisely because of their unique properties, including persistence. This is especially true against the background that the Dossier Submitters want to prevent a "regrettable substitution". This consideration, however, is led ad absurdum if there is inevitably nothing that can be used as a suitable alternative. Consequently, persistent alternatives are not to be considered in the present case. Thus, on the one hand, there is a major error in the information about the alternatives, which makes the dossier disproportionate. On the other hand, the dossier is already disproportionate in general because it contains alternatives which are under scrutiny according to the logic of the dossier due to their persistence.

# 5. Infringement of the principle of good administration

(157) The Dossier also infringes the principle of good administration due to further inconsistencies. The principle is codified in Article 41 of the Charter of Fundamental Rights of the European Union, the Rules of Procedure of the Commission and the European Code of Good Administrative Behaviour. The principle comprises the general principle that authorities need to be consistent in their administrative behaviour and shall follow their normal practice, with the effect that legitimate expectations of the public are met.

- (158) A deficiency of the procedure results from the fact that, according to the dossier, the stakeholders are supposed to prove that specific PFAS are not hazardous or persistent (cf. Proposal, Annex B, page 3). This is the consequence of the group-based approach, by which a large number of individual substances are to be covered by the restriction, although for the vast majority of the substances no studies or evidence with regard to their hazard properties are available.
- (159) However, such a procedure violates the procedural rules for a restriction procedure under REACH with regard to the burden of proof. Articles 68 et seqq. REACH do not state at any point that the stakeholders, i.e. affected market actors, must provide evidence of the non-hazardousness of a particular substance. The hazard assessment described in the corresponding guidance document also explicitly provides only for such an assessment by the Dossier Submitters and not by the stakeholders (cf. Guidance, p. 34 et seqq.). Thus, in the context of the PFAS restriction, the German competent authority (BAuA) also stated that in the case of restriction, the burden of proof lies with the authority and, in contrast, in the case of authorization, the burden of proof lies with the industry (cf. BAuA webinar of 3 April 2023, presentation by Dr. Herkert, slide 5). By leaving concrete evidence with regard to the non-hazardousness of a concrete substance to industry, the present restriction procedure acts contrary to the applicable burden of proof rules.
- (160) This is particularly unacceptable in view of the fact that the individual stakeholders contrary to the Dossier Submitters cannot opt for a group-based approach because they only use one or a few of the substances and thus have information on them. It is almost audacious that the Dossier Submitters admit that for many substances there is a lack of concrete scientific evidence for a hazardous property, but at the same time demand evidence for non-hazardousness from the stakeholders in connection with requests for exemptions or derogations.
- (161) Incidentally, it should be noted that the consultation process does not affect these considerations. It is true that the stakeholders have the opportunity to make a submission on the hazardousness or non-hazardousness of certain substances. However, they are not obliged to do so, so that the de facto reversal of the burden of proof is fully at their expense if they do not participate in the consultation procedure.
- (162) We further submit that the approach also infringes procedural rights of affected market actors. If the authorities would have chosen an authorisation process, affected market actors would have been in the position to prepare an application for authorisation typically within a time period of 18 to 24 months after inclusion of substances in Annex XIV to REACH. In connection with the determination of the respective last application date

(cf. Article 58(1)(c)(ii) REACH) a broad variety of factors need to be considered as established with the corresponding ECHA Practical Implementation document on Setting Latest Application Dates (cf. https://echa.europa.eu/documents/10162/17232/recom\_gen\_approach\_draft\_axiv\_entries\_impl\_doc\_2020\_en.pdf). It follows already from the details set out in this document that a complex ban as supported with the Proposal would have resulted in a time period of 24 months after inclusion of substances in Annex XIV to REACH to set the last application date.

- (163) By illicitly initiating a restriction proceeding under Titel VIII of REACH, the time period for affected market actors to create convincing submissions to request and justify exemptions or derogations, including supporting data on alternatives, environmental fate and socio-economic considerations as requested in connection with the public consultation, is significantly shortened to roughly six months, i.e. the duration of the public consultation according to Article 69(6) REACH.
- (164) The burdens associated with this are also not compensated by the fact that the restriction proposal was already under discussion beforehand and affected actors could thus have prepared themselves at an early stage. It needs to be noted that the actual restriction proposal was initially published only on 7 February 2023 and the version currently subject of the public consultation was in fact only published on 22 March 2023, i.e. the date on which the public consultation was initiated.

# 6. Breach of precautionary principle

- (165) The Proposal does not align with the precautionary principle but has an arbitrary nature.
- (166) According to Article 191(2) TFEU, every REACH measure aiming at a Union policy on the environment has to take into account the precautionary principle. In contrary, such measures shall not be of an arbitrary nature. There is no definition for the precautionary principle in the EU treaties, but the Commission and case law have specified the content.
- (167) As already stated (cf. paragraph (67) above) the Commission has laid down its interpretation of the principle in a separate communication on the precautionary principle (cf. COM(2000) 1 final, dated 2 February 2000). According to this, the determination of appropriate action including measures based on the precautionary principle should start with a scientific evaluation to perform an as objective and complete as possible scientific evaluation to cast light on the existing objective evidence, the gaps in knowledge and the scientific uncertainties (cf. ibid, p. 16). In particular, the precautionary principle can under no circumstances be used to justify the adoption of arbitrary decisions (cf. ibid, p. 13). This requires reliable scientific data and logical reasoning, leading to a conclusion which expresses the possibility of occurrence and the severity of a hazard's impact (cf. ibid, p. 13). The limits of scientific knowledge may ultimately affect the foundation for protective or preventive action (ibid, p. 13). Particularly, this applies for the scenario, that scientific data are not sufficient and therefore cause-effect relationships are suspected

but have not been demonstrated (cf. ibid, p. 14). Furthermore, according to the Commission, the measures based on the precautionary principle must not be disproportionate to the desired level of protection and must not aim at zero risk (cf. ibid, p. 17). Accordingly, in some cases a total ban may not be a proportional response to a potential risk (cf. ibid, p. 17).

- (168) According to the ECJ, the precautionary principle entails that, where there is uncertainty as to the existence or extent of risks to human health, protective measures may be taken without having to wait until the reality and seriousness of those risks become fully apparent. Where it proves to be impossible to determine with certainty the existence or extent of the alleged risk because the results of studies conducted are inconclusive, but the likelihood of real harm to public health persists should the risk materialise, the precautionary principle justifies the adoption of restrictive measures (Judgement of 1 October 2019, Case C-616/17, ECLI:EU: C:2019:800, para. 43.). However, a correct application of that principle presupposes, first, identification of the potentially negative consequences for health of the proposed use of the substance at issue, and, secondly, a comprehensive assessment of the risk to health based on the most reliable scientific data available and the most recent results of international research (Judgement of 4 April 2019, Case T-108/17, ECLI:EU:T:2019:215, para. 281).
- (169) Measured against these criteria, the implementation of a general ban on (almost) all known and even currently unknown PFAS after the expiry of certain transitional periods, as proposed by the Dossier Submitters, would violate the precautionary principle, since it would be based to a large extent on a mere risk hypothesis and not on scientifically substantiated risk assessment. If the Commission were to follow the proposal, it would violate its self-imposed principles, according to which a restrictive measure may not be taken on the basis of the principle of general precaution alone, in order to limit a potential risk to zero, without any comprehensible, scientific evidence for this in detail.
- (170) There are numerous examples of such violations in the dossier. The group-based approach applied by the Dossier Submitters already raises fundamental concerns with regard to the precautionary principle (cf. Proposal, p. 21). Such an approach does not allow the exact determination of the possible risks of a certain substance, but is only able to draw conclusions, which cannot be scientifically justified in detail, from possible risks of certain substances belonging to a group to other substances of this group which have not been investigated.
- (171) By seeking to prevent substitutions with other PFAS, the Dossier Submitters are abandoning the principle of precaution and are pursuing a risk minimization to zero, which in fact is neither needed with regard to the precautionary principle, nor can it be justified by a mere reference to this principle.
- (172) Furthermore, the Dossier Submitters are not able to present logically comprehensible, scientifically based prediction tools for possible negative effects of Fluoropolymers in the

environment (cf. Proposal, p. 37). A substantiated risk assessment is not possible in this way; rather, the approach contradicts the requirements linked to the application of the precautionary principle as established by both, the Commission and the ECJ, according to which restrictions may only be made on the basis of a risk assessment based on the most reliable scientific data available and the latest results of international research, and not merely on a purely hypothetical risk assessment based on mere conjecture that has not yet been scientifically verified.

- (173) Although, as shown, for many PFAS except Fluoropolymers, there are no or only few scientific studies available with regard to their possible hazardousness, the dossier does not provide for the possibility of extending the maximum possible 13,5-year derogation if no alternative substances have been found within this period of time. Nor does the dossier take into account the fact that future studies could disprove or at least relativize the hazards of Fluoropolymers assumed by the dossier authors. The correct application of the precautionary principle, however, requires a consideration of such possibilities. Moreover, for Fluoropolymers available data already supports a non-time-limited derogation which is also not sufficiently reflected in the Proposal.
- (174) Further examples of violations of the precautionary principle can be found in Annex B. With regard to risk assessment, for example, it is described that a decreasing trend can be seen in humans, but in creatures the trends were inconsistent and (only) in some cases increasing (Annex B p. 97). However, the studies refer to PFSA and PFCA and precisely not to all PFAS and especially not to Fluoropolymers. The same applies, for example, to the immunological analysis, in which conclusions are drawn for all PFAS on the basis of studies on only specific PFAS without further justification (Annex B, p. 181). In this respect, the principle of caution is applied and not the precautionary principle as established by the Commission and the ECJ. In particular, there is an approach to achieve zero risk, which, as explained above, does not correspond to the precautionary principle.

# 7. Infringement of right to be heard / right to comment

- (175) The dossier infringes the stakeholders` right to be heard and right to comment. This follows from the fact that the proposed measure is, in effect, an authorization in the guise of a restriction.
- (176) In fact, the initial situation and the circumstances of the PFAS case strongly imply that the Dossier Submitters should rather have sought an authorization procedure. By failing to do so, they curtailed the participation rights and procedural rights enshrined in Article 59 REACH. In addition, if stakeholders were required to seek authorization, they would have a regulated process (namely, the authorization process) open to them in which they could argue socio-economically for certain uses in a regulated process. In contrast, the restriction process does not provide for mandatory participation; moreover, in contrast to the necessarily individual authorization decision, there is also no obligation

on the part of the authorities to deal with the specific use and to make an individual, judicially reviewable decision in the specific case.

- (177) The objective circumstances correspond to those of a potential authorization procedure. This is evident in particular from the fact that the Dossier Submitters obviously largely lack information on the concrete uses of the substances. After all, they themselves state that there are further uses not addressed in the dossier (cf. Information note on restriction report, Consultation on a proposed restriction on the manufacture, placing on the market and use of per- and polyfluoroalkyl substances (PFAS), p. 5).
- (178) Moreover, there is obviously only a rather low level of knowledge regarding the socioeconomic consideration. In particular, information on existing and future alternatives is largely lacking, which is now to be provided by stakeholders within the framework of the consultation procedure, as is already evident from the structure and content of the corresponding ECHA webform (cf. Information note on restriction report, Consultation on a proposed restriction on the manufacture, placing on the market and use of per- and polyfluoroalkyl substances (PFAS), p. 5).
- (179) This applies above all to Fluoropolymers. For this subgroup the level of knowledge is apparently so low that for them in contrast to the other PFAS it is even included in the proposed entry text of the restriction proposal (cf. Proposal No. 8) that (for the use of derogations already provided for) a management plan must be drawn up, from which, among other things, information on the substance and the product and a justification for the use must be provided.
- (180) However, it is precisely this initial situation that requires the issuance of an authorization procedure. After all, authorization and restriction must be differentiated on the basis of the fact that the burden of proof, especially for exemptions, lies with the authority for the restriction and precisely not for the authorization. If the authorities have so little information, particularly in the socio-economic dimension, as in the present case, this system dictates to consider an authorization and that the stakeholders should therefore have the opportunity to obtain exemptions in an orderly procedure. They were deprived of these rights due to the choice of the wrong measure, so that the participation and procedural rights were and are violated.

# III. Reference to other parts of the submission

(181) As shown in detail above, the proposal is entirely insufficient from a legal point of view with regard to Fluoropolymers. As demonstrated above, the requirements of Article 68 REACH have not been met, in particular because, contrary to all known systematics and dogmatics, persistence was considered to be the key hazardous property. In addition, various superior legal principles were violated, in particular the principle of proportionality and the precautionary principle.

- (182) Following on from this conclusion, it should be noted, that the Proposal cannot provide a detailed socio-economic consideration and an assessment of the exposure and hazard of the PFAS in question for all uses of PFAS. This can already be seen from the fact that the Dossier Submitters as ECHA admits, cf. e.g. No. 6 of the Specific Information Requests do not have knowledge of all use cases of PFAS and therefore could not include them in the Proposal.
- (183) Especially, regarding the socio-economic analysis, the Dossier Submitters seem to lack in particular an estimation of the expected costs of a possible replacement of products, including the immediate phase-out of products. Only with the help of such data, however, is it possible to conclude how this relates to, for example, the expected environmental impact costs.
- (184) Moreover, the Dossier Submitters did not conduct a hazard and risk assessment for each PFAS and not even for each PFAS group. This unlawful grouping results in the consequence that it is up to the stakeholders to contribute various information for their respective product or use and for the corresponding PFAS. In this respect, ECHA's webform on the consultation process and the corresponding guidance reveal that information is missing and what data should be provided by stakeholders for both known uses and as yet unknown uses.
- (185) Against this background, GFL submits further information as part of its broader submission. From a legal perspective, these additional studies, reports and papers precisely support the legal assessment at hand. In particular, the breach of the principle of proportionality, the breach of the precautionary principle and the conclusion, that the proposal fails to provide a sufficient socio-economic analysis for each substance concerned arise already from these papers.

# IV. Conclusion

(186) Against the background of the aforementioned arguments, a general exemption or derogation without any time limit for Fluoropolymers is warranted. Without a corresponding exemption or derogation, a restriction, if adopted, would constitute infringements of the prerequisites as set out in the REACH Regulation as well as fundamental principles enshrined in the European Union Charter of Fundamental Rights. We therefore suggest incorporating a corresponding section in the potential REACH Annex XVII entry regarding PFAS:

> "Paragraph 1 and 2 shall not apply to Fluoropolymers. This derogation does not apply to PFAS used as polymerisation aids for the production of Fluoropolymers."

- (187) In addition, the Proposal should be amended accordingly to ensure that no additional provisions as proposed with Nos. 5 a), 6, 7 and 8 of the contemplated entry to Annex XVII to REACH contradict the aforementioned derogation.
- (188) Therefore, we respectfully request ECHA, RAC, SEAC and the Dossier Submitters to consider the concerns raised with this submission and the further arguments as brought forward and supported by the broader submission of GFL to avoid procedural shortcomings which might give rise to further legal concerns.

Augsburg, 21 June 2023

Produktkanzlei Ahlhays Handorn Niermeier Schucht Rechtsanwaltsgesellschaft mbH

Rechtsanwalt Dipl.-Verwaltungswirt (FH)

# ANNEX V

# Gujarat Fluorochemicals

Transition from Fluorinated polymerization aid to Non-Fluorinated polymerization aid in the manufacturing of PTFE fine powders

# **Gujarat Fluorochemicals Limited**



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11<sup>th</sup> August, 2023

# Transition from Fluorinated polymerization aid to Non-Fluorinated polymerization aid in the manufacturing of PTFE fine powders

Dear Valued Partner,

From the U.S. to Europe and beyond, authorities are developing legislative and regulatory approaches to limit exposure to, and adverse health and environmental effects from, per- and polyfluoroalkyl substances (PFAS). Currently, many of the proposals include fluoropolymers in their definition of PFAS, likely because some manufacturers use and emit fluorinated polymerization aids (FPAs) in the polymerization of their fluoropolymers. Regulators and scientists believe that the use of fluorinated polymerization aids in the manufacture of fluoropolymers is a considerable source of PFAS pollution in the environment. The EU REACH PFAS restriction proposes to restrict the use of FPAs in the manufacture of PTFE, PVDF and FKM without any derogation.

In this regard, GFL has decided to move away from the use of FPAs in the manufacturing of its fluoropolymers (please refer company announcement dated 30/11/2022). GFL has already made a complete switchover from FPA (Gen-X) to non-fluorinated polymerization aid (NFPA) in the manufacturing of PTFE aqueous dispersions, PVDF and FKM. Furthermore, GFL plans to stop the use of FPA in the manufacturing of PTFE Fine powders before the end of 2023. GFL is committed to completely stop the use of FPAs in the manufacture of its entire portfolio of fluoropolymers during 2024.

We recommend our esteemed clientele to complete qualification of PTFE fine powders produced using environmentally sustainable and regulatory compliant non-fluorinated polymerization aid technology.

GFL has decided to stop producing GN7040 and GN7045 products made using Gen-X from 1<sup>st</sup> October, 2023. These products will be replaced by FP7040EX produced using NFPA. Starting 1<sup>st</sup> January 2024, all PTFE fine powder products shall be manufactured using NFPA technology replacing Gen-X. Samples of all these products are available for your qualifications. We request you to kindly communicate your requirements to your respective Account Managers for planning purposes.

Being a responsible manufacturer, GFL's priority is to offer products manufactured using environmentally sustainable technologies and raw materials.

Please do not hesitate to contact your Account Manager/Technical Manager at GFL for any technical support which would help expedite a smoother and timely transition.

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# ANNEX VI

Teflon PTFE Properties Handbook

**Properties Handbook** 

# Teflon® PTFE fluoropolymer resin



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# Introduction

*Teflon*<sup>®</sup> is a registered trademark of the DuPont Company for its fluoropolymer resins. *Teflon*<sup>®</sup> PTFE fluoropolymer resins are part of the DuPont family of fluorine-based products that also includes *Teflon*<sup>®</sup> FEP and *Teflon*<sup>®</sup> PFA fluoropolymer resins and *Tefzel*<sup>®</sup> fluoropolymers. These materials can be used to make a variety of articles having a combination of mechanical, electrical, chemical, temperature, and friction-resisting properties unmatched by articles made of any other material. Commercial use of these and other valuable properties combined in one material has established *Teflon*<sup>®</sup> resins as outstanding engineering materials for use in many industrial and military applications. *Teflon*<sup>®</sup> resins may also be compounded with fillers or reinforcing agents to modify their performance in use.

The design and engineering data presented in this handbook are intended to assist the design engineer in determining where and how *Teflon*<sup>®</sup> resins may best be used. It is recommended that the design engineer work closely with an experienced fabricator because the method of fabrication may markedly affect not only production costs, but also the properties of the finished article.

# **Typical Properties**

**Table 1** lists physical property data relating to the *Teflon®* PTFE resins. All properties presented in this handbook should be considered as typical values and are not to be used for specification purposes. The age of this data varies greatly, ranging in origin from the 1950s to the 1990s.

# Patents

A large number of existing patents relate to various *Teflon*<sup>®</sup> resins, but no attempt has been made in this publication to refer to any of these patents by number, title, or ownership. The descriptions of a process, an apparatus, a composition, or any article may fall within a claim of an existing patent, but we do not intend that such a description should induce anyone to infringe any existing patent. It is the responsibility of the prospective user of fluoropolymer resins to determine whether his/her use constitutes infringement or noninfringement of any patent.

# **Effects of Processing**

*Teflon®* PTFE fluoropolymer resins are tetrafluoroethylene polymers, usually fabricated into parts by coldforming and sintering techniques. *Teflon®* PTFE resins have a continuous service temperature of 260°C (500°F). Much higher temperatures can be satisfactorily sustained for shorter exposures.

Various physical properties can be obtained with *Teflon®* PTFE resins by varying the processing technique. *Teflon®* PTFE resins are versatile and can, within limits, be "tailored" to provide fabricated parts with particular physical properties.

Processing can have more impact on the performance of parts made from *Teflon*<sup>®</sup> PTFE than for those made from other types of polymers. For example, preforming pressure, sintering time, cooling rate, void content, and crystallinity level can have a significant effect on certain end-use physical properties, such as tensile properties, permeability, and dielectric strength. **Table 2** lists features of *Teflon*<sup>®</sup> resins that are relatively independent of fabrication conditions.

#### Table 2 Properties Relatively Independent of Fabrication Conditions

#### **Chemical Properties**

Chemical resistance to corrosive reagents Nonsolubility Long-term weatherability Nonadhesiveness Nonflammability

#### **Electrical Properties**

Low dielectric constant Low dissipation factor High arc-resistance High surface resistivity High volume resistivity

#### **Mechanical Properties**

Flexibility at low temperatures Low coefficient of friction Stability at high temperatures

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	ASTM		Teflon® PTFE	
Property	Method	Unit	Granular Resin	Fine Powder
Tensile Strength, 23°C (73°F)	D4894/4895	MPa (psi)	31.0 (4,500)	20.7 min. (3,000 min.)
Elongation, 23°C (73°F)	D4894/4895	%	400	200 min.
MIT Flex, 2 kg load, 10 mil	D2176		Did not bre	eak at 10 <sup>6</sup> cycles
Flex Modulus, 23°C (73°F)	D790	MPa (psi)	345–620 (50,000–90,000)	275–620 (40,000–90,000)
Stretching Void Index	D4895		—	15–200+
Impact Strength, Izod -40°C (-40°F) 21°C (70°F) 24°C (75°F) 77°C (170°F) 204°C (400°F)	D256	J/m (ft·lb/in)	80 (1.5) 106 (2) 160 (3) >320 (>6) No break	133–267 (2.5–5) — — — No break
Hardness, Durometer	D2240	Shore D	55	50–65
Coefficient of Linear Thermal Expansion per °C (°F), 23–60°C (73–140°F)	E228	mm/mm·°C (in/in·°F)	10 x 10 <sup>-5</sup> (7 x 10 <sup>-5</sup> )	_
Thermal Conductivity, 4.6 mm (0.18 in)	D435ª	W/m·K (Btu∙in/h∙ft².°F)	0.25 (1.7)	_
Specific Heat 20°C (68°F) 40°C (104°F) 150°C (302°F) 260°C (500°F)	D4591	kJ/kg·K (Btu/lb·°F)	1.4 (0.33) 1.2 (0.29) 1.3 (0.31) 1.5 (0.37)	1.5 (0.35) 1.2 (0.29) 1.3 (0.31) 1.4 (0.33)
Thermal Instability Index	D4894/4895		50 max.	50 max.
Deformation Under Load, 23°C (73°F) 3.4 MPa (500 psi) 6.9 MPa (1000 psi) 14 MPa (2000 psi)	D621	%	<0.5 2 10	<0.5 2 5
Heat Deflection Temperature 450 kPa (66 psi) 1800 kPa (264 psi)	D648	°C (°F)	73 (160) 45 (115)	140 (280) 55 (130)
Dielectric Strength, Short Time, 2.03 mm (0.0	80 in) D149	kV/mm (V/mil)	24 (600)	24 (600)
Surface Arc-Resistance <sup>b</sup>	D495	sec	>300	>300
Volume Resistivity	D257	ohm∙cm	>10 <sup>18</sup>	>10 <sup>18</sup>
Surface Resistivity	D257	ohm∙sq	>10 <sup>18</sup>	_
Dielectric Constant, 60 to 2 x 109 Hz	D150		2.1	2.1
Dissipation Factor, 60 to 2 x 109 Hz	D150		<0.0001	_
Water Absorption, 24 hr	D570	%	<0.01	<0.01
UL 94 Flame Rating <sup>°</sup>			94 V-0	94 V-0
Resistance to Weathering			Excellent	Excellent
Static Coefficient of Friction Against Polished Steel <sup>d</sup>			0.05–0.08	_
Specific Gravity	D4894/4895		2.16	2.1–2.3

 Table 1

 Typical Properties of Teflon<sup>®</sup> PTFE Fluoropolymer Resins

<sup>a</sup>This standard is no longer in use.

<sup>b</sup>Does not track

<sup>c</sup>These numerical flame spread ratings are not intended to reflect hazards presented by this or any other material under actual fire conditions.

<sup>d</sup>Various methods used

*Teflon®* PTFE resins are fabricated to form parts by a number of techniques, including ram extrusion, screw extrusion, compression molding, and paste extrusion with an extrusion aid. Although different, these techniques have three basic steps in common: cold forming, sintering, and cooling. These fabricating steps refer to operations that involve, respectively: compacting molding powder to shape by pressing, bonding adjacent surfaces of particles by heating, and controlling crystal-linity content of the article by cooling.

Previous work has pointed out that about 15 mechanical properties plus several electrical and chemical properties of *Teflon®* PTFE resins are influenced by molding and sintering conditions. Most notably affected are flex life, permeability, stiffness, resiliency, and impact strength. The five basic factors that influence these end-product properties are:

- **Presence of Macroscopic Flaws**—Internal bubbles, tears, foreign impurities, shear planes, or poor charge-to-charge bonds.
- Extent of Microporosity—Number and size of microscopically visible voids created by imperfect particle fusion.
- **Percent Crystallinity**—A percentage based on the weight fraction of a sample consisting of polymer chains fitted in a close-packed, ordered arrangement.
- **Molecular Weight**—A measure of the average length of polymer chains.
- **Degree of Orientation**—A measure of the extent of alignment of polymer chains in a given direction.

While, ideally, a quality control system should be based on direct measurements of these basic factors, simple and direct measuring methods suitable for routine use are not usually available. Instead, a number of highly sensitive, indirect tests have been devised. They are based on measurement of *dielectric strength*, *tensile strength*, *ultimate elongation*, *specific gravity*, *and heat of fusion*. Simple, applicable to a variety of shapes, reproducible, and sensitive, the tests and their relation to the five basic quality factors are explained in the following text.

# **Dielectric Strength**

Dielectric strength is a function of the degree of microporosity. **Table 3** shows that it correlates well with size and number of microvoids visible with a microscope. On the other hand, dielectric strength is independent of molecular weight and crystallinity.

Table 3
<i>Teflon</i> <sup>®</sup> PTFE Granular Resin: Relation of
<b>Dielectric Strength to Degree of Microporosity</b>

Sample	Appearance of Cross Section in Microscope	Dielectric Strength, V/mil*
A	No visible voids at 100x magnification	760
В	Scattered 0.001-in voids between particles	575
С	Scattered 0.005-in voids	445
D	Numerous 0.005-in voids	250

\* 1/16-in sheets immersed in A-80 transformer oil per ASTM D149

#### Tensile Strength and Ultimate Elongation

Tensile strength and ultimate elongation depend to some degree on all five quality factors. **Table 4**, for example, points out the effect of microvoids on the samples described in **Table 3**. Limited data indicate that this reduction of tensile properties by microvoids is influenced to some extent by crystallinity. While definite evidence indicates that tensile strength falls with rise of percent crystallinity, ultimate elongation increases at first, and then drops. Microvoids have their greatest effect in lowcrystallinity products.

Table 4	
Teflon <sup>®</sup> PTFE Granular Resin:	
Effect of Microporosity on Tensile Strength	
and Elongation	

Sample*	Extent of Microporosity	Tensile Strength, MPa (psi)	Ultimate Elongation, %
A	Negligible	24.8 (3,600)	390
В	Slight	17.4 (2,520)	350
С	Moderate	13.9 (2,020)	300
D	Severe	12.4 (1,800)	170

\*Free-cooled 1/16-in specimens with relative crystallinity of 65–68% tested by ASTM D4894/4895

Degree of orientation also affects tensile properties. In general, tensile strength is greater in the direction of orientation, but ultimate elongation is lower.

While all flaws can reduce tensile strength to some degree, imperfect fusion between successive charges during extrusion of rod and heavy-wall tubing are probably the defects of most common concern.

# Specific Gravity

Specific gravity can be readily measured by waterdisplacement and gradient-tube techniques, such as those described in ASTM D792 or D1505. These tests do not necessarily give the inherent or precise specific gravity, however, because microvoids introduce a disparity between the measured and the inherent specific gravity. In effect, the displaced water, from which the measured value is derived, accounts for both the resin sample and its contained voids. The void content, as described later on, although not easy to determine, should be known or accounted for in the following manner:

> Measured S.G. = Inherent S.G. – (Inherent S.G. × 0.01 × [% Void Content])

Without this correction, such as shown in the lower portion of the equation, the precise conversion of the inherent specific gravity to percent crystallinity as shown in **Figure 1** will be in error by the amount shown in the two lines representing, by way of example, two arbitrarily chosen void levels, namely 0.5 and 1%.

**Table 5** indicates the relative effect of three of the basicfactors on a number of properties, many of which

depend upon the level of crystallinity. Relatively few properties depend directly upon molecular weight. However, crystallization rates, and therefore final levels of crystallinity, do depend upon molecular weight. Molecular weight thus exerts its greatest influence on properties through crystallinity.

To supplement standard quality control methods, a number of laboratory techniques have been developed to check directly the presence of macroflaws, extent of microporosity, percent crystallinity, and molecular weight. Because of their complexity, these methods are not ordinarily suited to routine product testing. As research tools, however, they do aid interpretation of reasons for quality variations.

#### **Macroscopic Flaws**

For detection of macroscopic flaws, X-ray radiographic examinations may be employed. Sufficient views are taken to give complete coverage of the piece. In parts more than 2 in thick, at least two views, 90° apart, are required. ASTM method E94 is a useful guide in establishing testing procedures.

	•	, ,	
Physical Property	Increasing Molecular Weight	Increasing Crystallinity	Increasing Void Content
Flex Fatigue Life	+100 fold	-100 fold	–1,000 fold
Compressive Stress at 1% Deformation	0	+50%	0
Compressibility	0	-50%	_
Recovery	0	-70%	_
Permeability to Carbon Dioxide	0	-30%	+1,000 fold
Flexural Modulus	0	+5 fold	-30%
Hardness: Durometer Rockwell Scleroscope	0 0 0	+20% -20% -70%	-30% -10%
Tensile Impact Strength	0	–15 fold	-80%
Dielectric Strength	0	0	-70%
Proportional Limit	0	+80%	-20%
Yield Stress	0	+15%	-20%
Yield Strain	0	–15 fold	0
Tensile Strength	+25%	-50%	-50%
Ultimate Strength	+50%	-70%	-50%
Ultimate Elongation	-20%	+100%*	-30%

 Table 5

 Effect on Teflon® PTFE Resin Properties Caused by Change in Basic Factor

\*Reaches a maximum at 85% crystallinity

#### **Microscopic Voids**

While X-ray radiographic methods are satisfactory for detecting macroscopic flaws, they are not sensitive enough for detection of microscopic voids. There are, however, a number of methods developed specifically for this purpose, as discussed below.

#### **Visual Inspection**

Visual inspection by a trained observer without a microscope can be of real value in detecting excessive microporosity and other gross quality defects. While it is difficult to convey in words the experience that enables one to judge varying degrees of microporosity, some worthwhile hints are:

- Prepare a comparison series of samples having varying degrees of microporosity. It is best to collect samples that have been processed by the same sintering and cooling conditions. These will have the same inherent specific gravity.
- It is easier to inspect for porosity by transmitted, rather than reflected, light.
- Use a powerful light source directly behind the sample. A large illuminated panel with a ground-glass surface is best for inspecting sheet stock.
- Small cracks are often more readily seen by viewing at an angle of 45°.
- If permissible, cut off a thin section with a sharp knife and inspect it.

#### **Dye Penetrants**

Vividly colored penetrants are valuable as an aid in detecting microporosity or gross defects when:

- The part to be tested is less than 1/2-in thick.
- Comparison standards of both acceptable and nonacceptable quality are available.

Both end user and fabricator should agree on the significance of occasional structural flaws, such as edge cracks and adhered flakes of resin, or saw marks.

# Specific Gravity Comparisons

As has been previously discussed, void content provides a measure of degree of microporosity. It follows, then, that void content\* can be defined by rearrangement of the specific gravity equation, as follows:

% Void Content =  $\frac{(\text{Inherent S.G.} - \text{Measured S.G.})}{\text{Inherent S.G.}} \times 100$ 

A number of techniques have been investigated for determining data for this equation. These methods include: torsional damping<sup>3</sup> (torsion pendulum), infrared spectroscopy,<sup>4</sup> ultrasonics,<sup>7</sup> rebound resiliency,<sup>7</sup> and X-ray diffraction.<sup>5</sup> Infrared and torsional damping techniques appear to be the most sensitive methods.

While it is beyond the scope of this article to cover the details and theory behind these two methods, their comparative precision and limitations can be pointed out. Inherent specific gravity based on an average of two infrared determinations is usually precise within  $\pm 0.003$  specific gravity units (95% confidence limits). Inherent specific gravity for an average of two torsion pendulum determinations is usually precise to within  $\pm 0.002$  specific gravity units.

While the torsion pendulum gives slightly better reproducibility than the infrared method, it is considerably less versatile, because it requires a fixed-size specimen. However, its cost is considerably less than that of a suitable spectrometer.

With both methods, degree of orientation introduces errors. Because means of correcting these errors are currently unknown, inherent specific gravity of paste-extruded wire coatings, tubing, film, and coined sheeting cannot yet be accurately measured. With paste-extruded products, however, apparent specific gravity measurements may be used to estimate degree of crystallinity, because void contents are normally low.

#### **Crystallinity and Molecular Weight**

Degree of crystallinity is controlled by molecular weight and by the length of time during fabrication that a part is maintained within the temperature range for rapid crystallization (307–327°C [585–620°F]). By reheating fabricated parts according to a standard thermal cycle (ASTM D4894/4895), relative molecular weights may be estimated through crystallinity or inherent specific gravity measurements. In parts with low void contents, relative molecular weights may be approximated from apparent specific gravity measurements.

#### **Practical Crystallinity Limits**

Technical papers<sup>8,10</sup> have discussed at length the influence of degree of crystallinity and voids on properties of parts fabricated from *Teflon*<sup>®</sup> PTFE fluoropolymer resins. A number of questions have arisen, however, pointing to the need for further clarification of normal limits for these basic variables. While, theoretically, fabricators can control percent crystallinity or inherent specific gravity over wide ranges, there are certain practical limits.

<sup>\*</sup> Because of combined errors in inherent and measured specific gravity determinations, it is difficult to distinguish between samples having less than 0.5% voids. Precision of measurement is as good as  $\pm 0.2\%$  in homogeneous samples, but may be no better than  $\pm 0.5\%$  in nonuniform samples.

For instance, in parts thicker than 1/4 in, it is not practical for fabricators to cool the interior fast enough to reduce crystallinity below about 55%. Even in thin films rapidly cooled in water, it is difficult to reduce crystallinity below about 46% (inherent specific gravity 2.135). An important point to keep in mind, then, is that measured specific gravities below 2.135 generally reflect some voids in any specimen.

Often, it is also impractical for fabricators to obtain high crystallinity levels, because certain parts must be cooled against cold metal surfaces to obtain close tolerances.

# How to Specify Typical Fabricated Parts

When setting property and tolerance specifications, the needs of the application must be balanced against the capabilities of both resin and method of fabrication. If needs are considered and designs frozen before any suppliers of fabricated parts are consulted, confusion, inefficiency, and often unnecessary costs may result.

As an aid in tailoring specifications to wed design needs with capabilities of fabricated parts of *Teflon*<sup>®</sup> resins, the following suggestions are offered:

- At the inception of a design program, engineers should acquaint themselves with the properties of *Teflon*<sup>®</sup> resins as given in texts such as the *Modern Plastics Encyclopedia*.
- As soon as the preliminary design is on paper, mechanical properties and dimensions for the application should be reviewed. A number of articles on designing have appeared in the literature and may be consulted.<sup>10</sup>

Also at this point, competent suppliers of fabricated parts should be consulted. Usually, there are several quality grades of a given fabricated form. By having a supplier point out what is available at an early stage, it is often possible to adjust design to accommodate most economic usage of materials.

Once design is frozen, there are several routes toward setting specifications. In many cases, suitable specifications are already available from such sources as ASTM, SAE, SPI, NIST, and MIL specifications.

In special situations, the previously cited specification sources may not be satisfactory. In such instances, the following guides on test methods may be useful.

# Suggested Test Methods for Various Shapes

**Table 6** summarizes specific tests for quality checks on extruded rod, molded sheet, molded parts, and tapes or films made from  $Teflon^{\text{(B)}}$  PTFE resins. The significance of most of these tests has already been discussed.

In the case of extruded rod, tensile strength and ultimate elongation are standard methods for quantitatively determining the strength of charge-to-charge bonds. There are also three qualitative methods sometimes used for the purpose: X-ray radiographic inspection (previously discussed), mandrel bend tests for rods smaller than 1 in, and resintering.

In the latter, an unconfined section of rod is resintered at 371–382°C (700–720°F) for a period of 1 to 4 hr, depending on rod diameter. Extruded rods with poor charge-to-charge bonds develop distinctly visible cracks as a result of this heat-aging cycle.

With extruded rods, determination of dielectric strength and measured specific gravity may be used to check for excessive microporosity.

For testing sheet, dielectric strength and dye penetrant methods give an indication of microporosity. Measured specific gravities also relate to microporosity. The usual purpose of measured specific gravity determinations, however, is to provide an approximate indication of the sheet's percent crystallinity. Tensile strength and elongation are indicative of overall quality.

With molded parts, X-ray and dye penetrant methods are suggested for detection of surface and internal flaws. Measured specific gravities detect variations in degree of microporosity and percent crystallinity, although again, these effects are not separated in this test. Dimensional stability at elevated temperatures is usually checked by measurements after annealing a part at 288°C (550°F).

For films and tapes, pinhole counts and dielectric strength indicate degree of microporosity and the incidence of localized flaws. Measured specific gravity is used as an index of percent crystallinity. Tensile measurements, as in the case of sheeting, are used as an all-around index of quality.

			••		
Property	Extruded Rod	Molded Sheet	Molded Parts	Films and Tapes	Extruded Tubing
Tensile Strength	D1710	D3293	D3294	D3308 D3369	D3295
Ultimate Elongation	D1710	D3293	D3294	D3308 D3369	D3295
Measured Specific Gravity	D1710	D3293	D3294	D3308	D3295
Dielectric Strength	D1710	D3293	D3294	D3308 D3369	D3295
X-Ray	D1710	_	D3294	_	_
Melting Point	D4894	D3293 D4895	D3294	D3308 D3369	D3295
Dye Penetrant	_	D3293	D3294	_	_
Dimensional Stability	D1710	D3293	D3294	_	D3295
Pinhole Count	—	—	—	D3308 D3369	_

 Table 6

 *Teflon*<sup>®</sup> PTFE Resins: ASTM Tests Applicable to Fabricated Parts

\*Central section of test specimens machined to 60% of nominal diameter. Tested at 2 in/min crosshead speed

Figure 1. Relation of Percent Crystallinity to Specific Gravity



# Strength and Stiffness General Characteristics

Fabricated shapes of *Teflon*<sup>®</sup> PTFE fluoropolymer resins are tough, flexible in thin sections, and fairly rigid in thick sections. Useful but varying mechanical properties are maintained from -268 to 260°C (-450 to 500°F) for *Teflon*<sup>®</sup> PTFE. Surfaces of fabricated parts have an extremely low coefficient of friction. Almost nothing sticks to them. However, specially treated surfaces will accept conventional industrial adhesives. *Teflon*<sup>®</sup> PTFE resins are almost completely inert to chemical attack, but, under special conditions, are affected by such substances as alkali metals and halogens. Low-loss electrical characteristics remain essentially constant, regardless of frequency, over a wide temperature range.

*Teflon*<sup>®</sup> PTFE resins tend to be opaque, crystalline, and malleable.

*Teflon*<sup>®</sup> PTFE resins can be aggregated into dense, coherent shapes at normal temperatures by various "preforming techniques," which apply uniform pressure to the unheated *Teflon*<sup>®</sup> PTFE resin. Preformed products are strengthened by heating above  $327^{\circ}C$  ( $620^{\circ}F$ ), generally  $371-382^{\circ}C$  ( $700-720^{\circ}F$ ), until the resin particles coalesce, and then cooling below  $327^{\circ}C$  ( $620^{\circ}F$ ). Products sintered in this manner may be further shaped by various postforming techniques that are preformed most readily at temperatures approaching but below the  $327^{\circ}C$  ( $620^{\circ}F$ ) transition temperature. Because *Teflon*<sup>®</sup> PTFE resins enter into a gel state at  $327^{\circ}C$  ( $621^{\circ}F$ ), which is not conducive to melt flow, preforming, sintering, and postforming are the processing techniques most commonly used.

# **Design Considerations**

Parts to be made of *Teflon*<sup>®</sup> may be designed in exactly the same manner as parts made of other materials, such as steel, brass, lead, concrete, etc. Even the same formulas may be used if careful attention is paid to special characteristics of the resin. A *Teflon*<sup>®</sup> resin may be chosen in preference to other materials because of its better chemical resistance, heat resistance, friction coefficient, dielectric strength, toughness, weather resistance, or combination of such properties. Most materials are affected to some extent by temperature, moisture, and environment. Because *Teflon*<sup>®</sup> resins exhibit zero moisture absorption and are unaffected by almost all environmental conditions, designers will be interested mainly in property changes resulting from temperature variation.

When load is applied over a period of time, creep and cold flow must be considered. Consequently, data are presented for long-term loading as well as short-term loading. Information for the tables and charts was obtained from samples described in **Table 7**. These samples are representative of commercially available moldings.

# Strength and Stiffness

*Teflon*<sup>®</sup> resins are engineering materials whose performance in any particular application may be predicted by calculation in the same manner as for other engineering materials. However, just as properties of woods are different from those of metals, the properties of *Teflon*<sup>®</sup> resins are different from those of other engineering materials. From the following data, strength and stiffness values can be selected which, with appropriate safety factors, will allow standard engineering formulas to be used in designing parts.

Teflon <sup>®</sup> PTFE Granular Resin: Description of Samples Used in Tests				
Fabricated Form	Average Specific Gravity	Void Content	Crystallinity	Preform Pressure, MPa (psi)
Rod, 6 in long x 0.6 in diameter (molded)	2.17	<0.3%	60% ± 2%	17.2 (2,500)
Sheet, 14 in x 14 in, 1/8 in and 1/16 in thick	2.17	<0.3%	60% ± 2%	17.2 (2,500)

Table 7 Teflon<sup>®</sup> PTFE Granular Resin: Description of Samples Used in Tests

# **Tensile Stress**

Stress-strain curves for temperatures in the usual design range (see **Figure 2a**) show that yield occurs at high deformations. Elastic response begins to deviate from linearity at strains of only a few percent, as with most plastics. Therefore, in designing with *Teflon*<sup>®</sup>, it is often best to work with acceptable strain and determine the corresponding stress. Curves that show ultimate tensile strength, the point at which fracture occurs, are given in **Figure 2b**.

Figure 3 shows strain at corresponding stresses for various temperatures. The percent strain selected for design calculations should take into account the highest temperature at which the part will operate. Because it is not always possible to work with an acceptable strain, **Table 8** gives the yield strength in psi as a function of temperature.

Table 0

Yield Strength at Various Temperatures			
Temperature, °C (°F)	<i>Teflon</i> <sup>∞</sup> PTFE Yield Strength, MPa (psi)		
-251 (-420)	131 (19,000)		
–196 (–320)	110 (16,000)		
–129 (–200)	79.3 (11,500)		
-73 (-100)	53.1 (7,700)		
–56 (–68)	26.2 (3,800)		
0 (32)	12.4 (1,800)		
23 (73)	9.0 (1,300)		
70 (158)	5.5 (800)		
121 (250)	3.4 (500)		

# **Compressive Stress**

Compression and strain are indicated at three temperatures for *Teflon*<sup>®</sup> PTFE resins (see **Figure 4**). Stressstrain curves for compression are similar to those for tension at low values of strain (see **Figure 5**). However, as strain increases, the curves become less similar. Yield points for compression and tension occur at about the same stress values. For compression, the lower strains at higher stress may be a result of analyzing test data on the basis of original cross sections.

#### **Shear Stress**

**Figure 6** is a plot of shear stress against shear strain. In a part subject to shear, a specified strain should be selected and the corresponding stress used for design calculations as mentioned previously.

# **Poisson's Ratio**

Poisson's ratio is 0.46 at 23°C (73°F) and approaches a limiting value of 0.50 with increasing temperature.

# **Modulus of Elasticity**

No attempt has been made to include data on modulus of elasticity. Because modulus of elasticity E is

$$E = \frac{\text{Stress (psi)}}{\text{Strain (in/in)}}$$

the preceding stress-strain curves permit substitution, when working at a specified strain, of the corresponding stress so that modulus of elasticity can be determined.

Figure 2a. Tensile Stress, Based on Original Cross Section



Figure 2b. Stress vs. Strain in Tension



Figure 3. Tensile Stress vs. Temperature at Constant Strain


Figure 4. Stress vs. Strain in Compression (ASTM D695)





Figure 5. Stress vs. Strain in Tension and Compression (ASTM D695)

Figure 6. Stress vs. Strain in Shear to 20%



## **Creep and Cold Flow**

A plastic material subjected to continuous load experiences a continued deformation with time that is called creep or cold flow. A similar phenomenon occurs with metals at elevated temperatures. With most plastics, however, deformation can be significant even at room temperature or below; thus, the name "cold flow."

Creep is the total deformation under stress after a specified time in a given environment beyond that instantaneous strain that occurs immediately upon loading. Independent variables that affect creep are time under load, temperature, and load or stress level.

Initial strain or deformation occurs instantaneously as a load is applied to *Teflon*<sup>®</sup> resins. Following this initial strain is a period during which the part continues to deform but at a decreasing rate. Creep data over a wide range of temperatures are plotted for tensile loading in **Figures 7a** through **7d**, for compressive loading in **Figures 8a** and **8b**, and for torsional loading in **Figures 9a** and **9b**.

### **Apparent Modulus of Elasticity**

The concept of "apparent modulus" is a convenient method for expressing creep because it takes into account initial strain for an applied stress plus the amount of deformation or strain that occurs with time. Thus, apparent modulus EA is

$$E_{A} = -\frac{Stress (psi)}{Initial Strain + Creep}$$

Because parts tend to deform in time at a decreasing rate, the acceptable strain based on service life of the part must be determined—the shorter the duration of load, the higher the apparent modulus and the higher the allowable stress. Apparent modulus is most easily explained with an example.

As long as the stress level is below the elastic limit of the material, modulus of elasticity E is obtained from the above equation. For a compressive stress of 1,000 psi, **Figure 4** gives a strain of 0.015 in/in for *Teflon*<sup>®</sup> PTFE resin at 23°C (73°F). Then,

$$E = \frac{1,000}{0.015} = 66,700 \text{ psi}$$

If the same stress level prevails for 200 hr, total strain will be the sum of initial strain plus strain due to time. This total strain is obtained from **Figure 8a** where total deformation under compressive load for 200 hr is 0.02 in/in for *Teflon*<sup>®</sup> PTFE resin. Therefore,

$$E_{A} = \frac{1,000}{0.02} = 50,000 \text{ psi}$$

Similarly,  $E_A$  can be determined for 1 yr. Extrapolation of the curve in **Figure 8a** gives a deformation of 0.025 in/in, and

$$E_{A} = \frac{1,000}{0.025} = 40,000 \text{ psi}$$

When plotted against time, these calculated values for "apparent" modulus provide an excellent means for predicting creep at various stress levels. For all practical purposes, curves of deformation versus time eventually tend to level off. Beyond a certain point, creep is small and may be neglected for many applications.

### Stress Relaxation

When materials that creep or cold flow are used as gaskets in flanged joints, the phenomenon of stress relaxation is generally encountered. In flanged, bolted connections, parts of *Teflon*<sup>®</sup> will cold flow between the flange faces with a resultant decrease in bolt pressure. Such relaxation in gasket stock may result in a leaky joint. Tightening the flange bolts during the first day after installation will usually maintain bolting pressure and prevent leakage; thereafter, stress relaxation will be negligible.

Typical curves for tensile stress relaxation illustrate the rates at which tensile stress decays when the specimen is maintained at constant strain (see **Figures 10a** and **10b**).

### **Compressive Recovery**

Specimens that were successively compressed and allowed to recover from various percentages of strain indicate that they experience no work hardening. Recovery of the specimen is nearly complete, provided the original strain does not exceed the yield strain.

### **Recommendation for Gasket Design**

To minimize creep and stress relaxation in gaskets, the following rules are recommended:

- Use bolting loads less than 6.9 MPa (1,000 psi) for unconfined gaskets.
- Specify the thinnest possible gasket that will accommodate flange roughness. Gaskets thicker than approximately 1.6 mm (1/16 in) increase the amount and rate of stress relaxation.
- Use reinforced compositions made with *Teflon*<sup>®</sup> resin, such as 60% *Teflon*<sup>®</sup> resin and 40% fiber, for temperatures higher than 149°C (300°F).
- Design a "self-contained" joint with captive gasket when such construction is desirable.

It is advisable to check the torque on a gasket made from *Teflon*<sup>®</sup> PTFE and to retighten once, if needed, following the first 24 hr in service.

The three forces that act on a gasket that is bolted securely in position are: bolt load, hydrostatic end force, and internal pressure. The procedure in the 1959 ASME Boiler and Pressure Vessel Code, Section VIII, Appendix II, may be used to calculate required bolt loadings for solid gaskets of *Teflon*<sup>®</sup> PTFE resins. The method requires knowledge of the "yield stress" and the "gasket factor." Yield stress is the stress required to seal the gasket or the minimum stress that will effect a seal against even slight fluid pressure. As internal pressure is applied to the vessel, the flanges tend to separate, thus lowering the effective stress on the gasket. Obviously, to maintain the seal requires that resultant stress on the gasket exceed the internal pressure. The minimum required ratio of these pressures is called the gasket factor.

Proved values for yield stress and gasket factor are listed in **Table 9** for solid *Teflon®* PTFE resins. With these values, the necessary gasket load can be calculated from Formula UA-47-2 given in the above ASME reference. Required gasket load can then be converted to bolt load by standard mechanical engineering calculations (see Mechanical Engineers' Handbook, Marks, Sixth Edition, Section 3, page 48).

Table 9
Values for Calculations of Required Gasket Loads

	-	
<i>Teflon</i> ® PTFE Thickness, mm (in)	Yield Stress, MPa (psi)	Gasket Factor
3.1 (1/8)	8.3 (1,200)	2.00
2.4 (3/32)	9.3 (1,350)	2.50
1.6 (1/16)	11.0 (1,600)	2.75
0.8 (1/32)	22.1 (3,200)	3.50

Gaskets made by enveloping fillers or rubber in molded *Teflon®* PTFE resin are widely used for flanged connections to glass-lined reaction vessels and to glass-lined pipe. Spiral-wound gaskets of stainless steel and sheet stock of *Teflon®* resin have been used successfully in both large and small flanged joints requiring high bolting pressures. Molded *Teflon®* PTFE resins, either alone or in combination with other gasket materials, also give excellent service under the most corrosive conditions encountered in the chemical industry.

The performance of *Teflon*<sup>®</sup> PTFE resins is improved considerably by use of fillers. Such modification affects certain mechanical properties and permits resin filler compositions to be tailored to the requirements of a wide variety of mechanical, electrical, and chemical applications.

In general, *Teflon*<sup>®</sup> PTFE resins can be compounded to increase:

- Resistance to initial deformation under load by approximately 25%
- Resistance to rotating shaft wear by as much as 500×
- Stiffness by a factor of two or three
- Thermal conductivity by a factor of five
- · Resistance to creep approximately twofold
- Thermal dimensional stability by a factor of two
- Hardness by approximately 10%

Further, modified compositions retain the desirable properties of uncompounded *Teflon*<sup>®</sup>.



Figure 7a. Total Deformation vs. Time Under Load at -54°C (-65°F)

Figure 7b. Total Deformation vs. Time Under Load at 23°C (73°F)





Figure 7c. Total Deformation vs. Time Under Tensile Load at 100°C (212°F)

Figure 7d. Total Deformation vs. Time Under Tensile Load at 200°C (392°F)





Figure 8a. Total Deformation vs. Time Under Compressive Load at 23°C (73°F)

Figure 8b. Total Deformation vs. Time Under Compressive Load at 100°C (212°F)







Figure 9b. Total Deformation vs. Time Under Torsional Load at 100°C (212°F)







Figure 10b. Tensile Strength Relaxation at 100°C (212°F)



# **Effect of Temperature, Fatigue, and Impact**

### **Thermal Expansion**

Linear expansion of *Teflon*<sup>®</sup> PTFE fluoropolymer resins is shown in **Figure 11** and **Table 10**. A marked change in volume of 1.0 to 1.8% is evident for *Teflon*<sup>®</sup> PTFE resins in the transition zone from 18–25°C (65–77°F). A part that has been machined on either side of this zone will obviously change dimensions if permitted to go through the zone. Thus, final operating temperature of a precision part must be accurately determined. Measurement on a production basis must allow for this volume change if the transition zone is traversed in either manufacture or operation of the part. **Table 11** gives the coefficient of cubical expansion for various temperature ranges.

Table 10*Teflon*® PTFE ResinsLinear Coefficients of Expansion

Temperature Range, °C (°F)	Linear Co of Expa 10⁻⁵ mm/mm·°C	efficient nsion, : (10⁻⁵ in/in·°F)
25 to –190 (77 to –310)	8.6	4.8
25 to –150 (77 to –238)	9.6	5.3
25 to –100 (77 to –148)	11.2	6.2
25 to –50 (77 to –58)	13.5	7.5
25 to 0 (77 to 32)	20	11.1
10 to 20 (50 to 68)	16	8.9
20 to 25 (68 to 77)	79	43.9
25 to 30 (77 to 86)	16	8.9
25 to 50 (77 to 122)	12.4	6.9
25 to 100 (77 to 212)	12.4	6.9
25 to 150 (77 to 302)	13.5	7.5
25 to 200 (77 to 392)	15.1	8.4
25 to 250 (77 to 482)	17.5	9.7
25 to 300 (77 to 572)	22	12.1

#### Table 11 *Teflon*® PTFE Resins Cubical Coefficients of Expansion

Temperature Range, °C (°F)	cm³/cm³.°C	in³/in³.°F
-40 to 15(-40 to 59)	2.6 x 10 <sup>-4</sup>	1.5 x 10 <sup>-4</sup>
15 to 35 (59* to 95)	1.7	7%
35 to 140 (95 to 284)	3.1 x 10 <sup>-4</sup>	1.7 x 10 <sup>-4</sup>
140 to 200 (284 to 392)	6.3 x 10 <sup>-4</sup>	3.5 x 10⁻⁴
200 to 250 (392 to 482)	8.0 x 10 <sup>-4</sup>	4.4 x 10 <sup>-4</sup>
250 to 300 (482 to 572)	1.0 x 10⁻³	5.7 x 10 <sup>-4</sup>

\*Quinn et al., J. Applied Phys. 22, 1085 (1951)

### Low Temperature Properties

Parts fabricated of *Teflon*<sup>®</sup> PTFE resins exhibit high strength, toughness, and self-lubrication at low temperatures. *Teflon*<sup>®</sup> PTFE resins are useful from  $-268^{\circ}C$  ( $-450^{\circ}F$ ) and are highly flexible from  $-79^{\circ}C$  ( $-110^{\circ}F$ ).

### Thermal Conductivity and Specific Heat

The average thermal conductivity of *Teflon*<sup>®</sup> PTFE is  $1.7 \pm 0.3$  Btu·in/h·ft<sup>2.</sup>°F. The average heat capacity is 0.3 Btu/lb·°F for *Teflon*<sup>®</sup> PTFE. These data were obtained at temperatures ranging from 20–260°C (68–500°F).

### **Heat Distortion**

Temperatures obtained for heat distortion of *Teflon*<sup>®</sup> PTFE are (ASTM D648) 122°C (252°F) for a stress of 66 psi and 56°C (132°F) for a stress of 264 psi.

### **Elastic Memory**

Parts made from *Teflon*<sup>®</sup> PTFE resins tend to return to their original dimensions after a deformation, but the process of recovery may require a long time. A fabricated part that creeps or deforms over a period of time under stress will recover its original shape when stress is removed and the part is raised to sintering temperature. However, partial recovery will occur at lower temperatures. At any given temperature, recovery to be expected at that temperature is substantially complete in 15 min or less, but extent of recovery increases with increased temperature.

For example, a filament of *Teflon*<sup>®</sup> PTFE 4 in long, stretched to a length of 12 in and heated at 100°C (212°F), recovers to approximately 11 in within 15 min and then remains substantially unchanged. A similar piece heated to 200°C (392°F) recovers to 10 in. The first piece, after additional heating to 200°C (392°F), undergoes further recovery until it is 10 in long. When heated to 350°C (662°F), both pieces return to their original length of 4 in.

Figure 11. Linear Thermal Expansion vs. Temperature



	Rate of Decomposition, %/hr			
	Fine Powder	Granular Resin		
Temperature, °C (°F)	Initial	Initial	Steady State	
232 (450)	0.0001-0.0002	0.00001-0.00005	1 x 10 <sup>-11</sup>	
260 (500)	0.0006	0.0001-0.0002	100 x 10 <sup>-11</sup>	
316 (600)	0.005	0.0005	0.000002	
371 (700)	0.03	0.004	0.0009	

 Table 12

 Teflon® PTFE Resins: Decomposition Rates at Elevated Temperatures

### Decomposition at Elevated Temperatures

Rate of decomposition of a part of *Teflon*<sup>®</sup> PTFE depends on the particular resin, temperature, heat-exposure time, and, to a lesser extent, pressure and nature of the environment. In designs where the rate of outgassing is important, as in high-vacuum work or for safety considerations, initial rates of decomposition in **Table 12** may be used. For most applications these decomposition rates are small enough below the maximum service temperature (260°C [500°F] for *Teflon*<sup>®</sup> PTFE resins), and no special precautions are necessary. Where temperatures run above 343°C (650°F) during fabrication, proper ventilation is required.

Experience indicates that in many instances the rate of decomposition of an article fabricated from  $Teflon^{\text{(B)}}$  PTFE resin decreases after continual exposure. For example, when parts made of  $Teflon^{\text{(B)}}$  PTFE are used, a very low, fairly steady decomposition rate is established after less than 1% of the resins have decomposed.

### Impact

Ability to absorb impact energy, or impact toughness, is difficult to predict in a part because shape has a major effect on performance. Understanding how a part resists impact, however, helps in selecting a good design.

The energy of an impact has to be absorbed by a force developed within the part multiplied by the distance the part can deform. Designing flexibility into the part to lengthen the distance over which the energy is absorbed greatly reduces the internal force required to resist the impact. For example, a rigid base made from spring steel would not have as high a capacity for absorbing energy as a coil spring made from the same material. The same factors that affect metals also affect plastics. As more and more flexibility is designed into a part subject to impact load, the better the part will perform.

*Teflon®* PTFE resins have excellent impact strength over a wide range of temperatures. Average values for specimens subjected to the tensile and Izod impact tests are given in **Table 13**. There is no exact method for relating impact test data to actual design calculations or performance. Generally, in addition to incorporating flexibility, the most important method for obtaining toughness or impact resistance is to eliminate all sharp corners and other features subject to high stress concentration. For exact design, prototype models must be tested under actual loads.

Table 13	
Tensile and Izod Impact Strengt	h

		Impact Strength	
Resin	Temperature, °C (°F)	Tensile, ft•lb/in³	lzod,* ft•lb/in
Teflon <sup>®</sup> PTFE	23 (73)	320	2.9
	-54 (-65)	105	2.3

\*ASTM D256

## Hardness and Friction Hardness

**Table 14** lists the hardness of *Teflon*<sup>®</sup> PTFE resins as determined by various tests. Fillers elevate the hardness of *Teflon*<sup>®</sup> PTFE resins by 10 to 15% and much of the improvement is retained over a wide temperature range. In general, the greater the filler loading, the harder the compound. Spherical or flake fillers impart the best hardness.

Table 14 Hardness				
Resin	Rockwell R Scale* <sup>11</sup>	Durometer D Scale**	Durometer A Scale**	
Teflon <sup>®</sup> PTFE	58	52	98	

\*ASTM D785 or D2240

\*\*23°C (73°F)

### Friction (Granular)

*Teflon*<sup>®</sup> PTFE has a smooth surface with a slippery feel. Because of the low coefficient of friction of *Teflon*<sup>®</sup> PTFE (see **Table 15**), there have been many practical nonlubricated and minimally lubricated mechanical systems developed.

Table 15
<b>Coefficient of Friction</b>

Property	Teflon <sup>®</sup> PTFE
Static Load, 500 psi	0.05–0.08
Dynamic PV, 8,000 to 10,000, at 10 fpm at 100 fpm at 1,000 fpm at 1,000 fpm	0.10 0.13 Unstable Operation

*Teflon®* PTFE resins exhibit exceptionally low friction in nonlubricated applications, especially at low surface velocities and pressures higher than 5 psi. The coefficient of friction increases rapidly with sliding speeds up to about 100 ft/min, under all pressure conditions. This pattern of behavior (see **Figure 12**) prevents "stick-slip" tendencies. Moreover, no "squeaking" or noise occurs, even at the slowest speeds. Above 150 ft/min, sliding velocity has relatively little effect at combinations of pressure and velocity below the composition's PV limit. **Figure 13** indicates that static friction of *Teflon®* PTFE resins decreases with increases in pressure.

PV limits presented in **Table 16** define the maximum combinations of pressure and velocity at which these materials will operate continuously without lubrication. They are based on operation in air at ambient temperatures of  $21-27^{\circ}$ C (70–80°F). The PV limits of all *Teflon*<sup>®</sup> PTFE resin matrix compositions approach zero at 288–315°C (550–600°F) ambient temperature. In other words, the limiting surface temperature for operation of *Teflon*<sup>®</sup> PTFE compositions is 288–315°C (550–600°F), regardless of the cause of the temperature. Reduced ambient temperatures, below 21°C (70°F), and/or cooling will provide increased PV limits.

PV limit does not necessarily define useful combinations of pressure and velocity because wear is not considered in its determination. The useful PV limit of a material cannot exceed the PV limit and must take into account the composition's wear characteristics and the allowable wear for the application. Wear factor, K, is a proportionality factor relating to the wear of a nonlubricated surface (operating against a specific mating surface at combinations of pressure and velocity below the material's PV limit). The wear factors listed in **Table 16** can be used to predict wear against specific mating surfaces, using the following expression:

t	=	KPVT
where t	=	wear, in
K	=	wear factor, $\frac{in^3 \cdot min}{lb \cdot ft \cdot h}$
Р	=	pressure, psi
V	=	velocity, fpm
Т	=	time, h

Table 16 PV and Wear Performance

Property	Teflon <sup>®</sup> PTFE
PV Limit (lb/in² x fpm)*	
at 10 fpm	1,200
at 100 fpm	1,800
at 1,000 fpm	2,500
PV for 0.005 in radial wear in	
1,000 hr** (nonlubricated)	20
Wear Factor, K (x 10 <sup>-10</sup> )	
(in <sup>3</sup> ·min/ft·lb·hr)***	2,500

\* Ambient temperature 21–27°C (70–80°F)

\*\*Based on (1) unidirectional load on fixed bushing or (2) thrust washer

\*\*\*At PV values below the composition's PV limit when operating unlubricated against soft carbon steels (R<sub>c</sub>20 to 25) finished to 12–20 μin (AA). Factor is also applicable for operation against most stainless steels and cast irons.

### Abrasion and Wear (Granular)

Parts fabricated from *Teflon®* PTFE resins have good wear properties as previously shown in **Table 16**. **Tables 17, 18,** and **19** indicate the abrasion resistance of unfilled fluoropolymer resins for various types of tests. These three tests do not represent typical bearing wear because in each a new abrading surface is being continuously presented versus a repeating surface.

Figure 12. Coefficient of Friction vs. Sliding Speed



Figure 13. Coefficient of Friction vs. Load (at <2 ft/min and room temperature)



Table 1/ Weight Loss Caused by Sliding Tape*			
Resin	Average Weight Loss, g/in²		
Teflon <sup>®</sup> PTFE	0.337		

- - - --

\*Armstrong Abrasion Test (ASTM D1242): This test measures abrasion resistance of flat surfaces by drawing abrasive tape, under load, over test specimens at a slip rate of 100 g/in<sup>2</sup>. With No. 320 abrasive under a 15-lb load, weight loss was measured after 200 revolutions (1 hr, 40 min).

Table 18 Weight Lost from Revolving Disk\* (Cumulative weight loss in milligrams)

	Test Cycles					
Resin	10	50	100	500	1,000	2,000
Teflon <sup>®</sup> PTFE	0.35	1.65	2.2	5.7	8.9	13.4

\*Taber Abrasion Test: This test measures abrasion resistance of a flat surface by rotating a 4-in diameter specimen disk beneath an abrasive under load. A 1,000 g load was used on a Calibrase wheel No. CS-17F.

Table 19		
Tape Length Required to Abrade		
through Wire Coating*		
(Average tape length in inches)		

	Heat Aging					
Resin	None	96 hr at 150°C (302°F)	500 hr at 150°C (302°F)	96 hr at 200°C (392°F)		
Teflon <sup>®</sup> PTFE	76	78	98	84		

\*Tape Abrasion Test (MIL-T-5438): This test measures abrasion resistance of wire coatings by drawing, under load, a clean abrasive cloth tape of continuous length across the test wire until the coating is worn through. A 1-lb load on No. 400 grit tape was used on a coating thickness of 0.015 in.

## **Electrical Properties**

*Teflon*<sup>®</sup> PTFE fluoropolymer resins offer remarkable electrical stability over a wide range of frequency and environmental conditions. In this respect, they differ markedly from other insulating materials.

## **Dielectric Constant**

The dielectric constant of *Teflon*<sup>®</sup> PTFE resins shows less change over a wide range of temperatures and frequencies than any other solid material. This value remains essentially constant at 2.1 over the entire frequency spectrum.

*Teflon*<sup>®</sup> PTFE specimens have been heat-aged at 300°C (572°F) for six months, and then cooled to room temperature for measurement, with no change in dielectric constant. Nonfluoropolymer insulating materials do not show these properties.

## **Dissipation Factor**

The dissipation factor of *Teflon*<sup>®</sup> PTFE resins remains below 0.0004 over a frequency range up to 10<sup>8</sup> Hz.

The dissipation factor of *Teflon*<sup>®</sup> PTFE resins remains quite constant. For *Teflon*<sup>®</sup> PTFE at room temperature, it reaches a peak at about 10<sup>9</sup> Hz. This peak value is 0.0004 for *Teflon*<sup>®</sup> PTFE resins. Theoretical analysis of this phenomenon and spot checks indicate that as temperature increases, the peak will occur at higher frequencies.

## **Dielectric Strength**

The dielectric strength of *Teflon®* PTFE resins is high and does not vary with temperature and thermal aging. Initial dielectric strength is very high (600 V/mil for 1.5 mm [0.06 in] thickness) as measured by the ASTM short-time test. As with any material, the value drops as thickness of specimen increases.

Life at high dielectric stresses is dependent on corona discharge. The absence of corona, as in special wire constructions, permits very high voltage stress without damage to *Teflon*<sup>®</sup> PTFE resins. Changes in relative humidity or physical stress imposed upon the material do not diminish life at these voltage stresses.

## Surface Arc-Resistance

Surface arc-resistance of *Teflon*<sup>®</sup> PTFE resins is high and is not affected by heat-aging. When *Teflon*<sup>®</sup> PTFE resins are subjected to a surface arc in air, they do not track or form a carbonized conducting path. When tested by the procedure of ASTM D495, *Teflon*<sup>®</sup> PTFE resins pass the maximum time of 300 sec without failure.

The unique nonstick surface of these resins helps reduce surface arc phenomena in two ways:

- It helps prevent formation of surface contamination, thereby reducing the possibility of arcing.
- If an arc is produced, the discharge frequently cleans the surface of the resin, increasing the time before another arc.

### **Volume and Surface Resistivity**

Volume resistivity (>10<sup>18</sup> ohm·cm) and surface resistivity (>10<sup>16</sup> ohm·sq) for *Teflon*<sup>®</sup> PTFE resins are at the top of the measurable range. Neither resistivity is affected by heat-aging or temperatures up to recommended service limits.

# Other Properties

### Weathering

Parts fabricated of *Teflon*<sup>®</sup> PTFE fluoropolymer resins are virtually unaffected by weather. Conclusive tests on samples exposed for 15 yr to practically all climatic conditions confirm these weather-resistant properties. Thus, where applications demand the ultimate in dependability under these conditions, these resins are the answer. Resistance to extreme heat, cold, and ultraviolet light encountered in radar and other electronic components, such as antenna bushings, are excellent examples of the value of this material to the industrial designer.

### Miscellaneous

Molded *Teflon*<sup>®</sup> PTFE fluoropolymer resins have excellent vibration dampening properties both at sonic and ultrasonic frequencies. Installations for this purpose have been very successful. The thickness of material required must be sufficient to absorb the energy produced and is usually determined experimentally.

# Chemical Properties

## **Resistance to Chemical Attack**

*Teflon*<sup>®</sup> PTFE fluoropolymer resins are essentially chemically inert. Up to the upper use temperature (260°C [500°F]) for *Teflon*<sup>®</sup> PTFE, only very few chemicals are known to chemically react with these resins, i.e., molten alkali metals, turbulent liquid, or gaseous fluorine; and a few fluorochemicals, such as chlorine trifluoride,  $\text{CIF}_3$ , or oxygen difluoride,  $\text{OF}_2$ , which readily liberate free fluorine at elevated temperatures.

The unique degree of inertness of *Teflon*<sup>®</sup> PTFE resins reflects their chemical structure. Molecules of *Teflon*<sup>®</sup> PTFE resin are formed simply from strong carbon-carbon and super-strong carbon-fluorine inter-atomic bonds; moreover, the fluorine atoms form a protective sheath around the carbon core of each molecule. This structure also produces other special properties, such as insolubility and low-surface adherability and friction.

To a minor degree, halogenated organic chemicals may be absorbed by fluoropolymer resins. This will cause a very small weight change and in some cases slight swelling. If absorption is very high, it usually indicates a fabricated part of high porosity.

### Permeability

Fluoropolymer resins may be permeated to a limited extent by some substances. Permeation rates are generally comparable to those observed for other thermoplastics.

For more detailed data on exposure of *Teflon*<sup>®</sup> PTFE resins to chemical media, please contact your DuPont representative or call the appropriate sales office listed on the back cover.

## **Forming and Fabrication**

When extreme tolerance must be specified, or when product shapes are very complex, or when just one or two prototypes are required, the machining of *Teflon*<sup>®</sup> PTFE resins becomes a logical means of fabrication.

All standard operations—turning, facing, boring, drilling, threading, tapping, reaming, grinding, etc.—are applicable to *Teflon*<sup>®</sup> PTFE resins. Special machinery is not necessary.

When machining parts from *Teflon*<sup>®</sup> PTFE resins, either manually or automatically, the basic rule to remember is that these resins possess physical properties unlike those of any other commonly machined material. They are soft, yet springy. They are waxy, yet tough. They have the cutting "feel" of brass, yet the tool-wear effect of stainless steel. Nevertheless, any trained machinist can readily shape *Teflon*<sup>®</sup> PTFE to tolerances of ±0.001 in and, with special care, to ±0.0005 in.

### **Choose Correct Working Speeds**

One property of *Teflon*<sup>®</sup> PTFE resins strongly influencing machining techniques is their exceptionally low thermal conductivity. They do not rapidly absorb and dissipate heat generated at a cutting edge. If too much generated heat is retained in the cutting zone, it will tend to dull the tool and overheat the resin. Coolants, then, are desirable during machining operations, particularly above a surface speed of 150 m/min (500 fpm).

Coupled with low conductivity, the high thermal expansion of  $Teflon^{\mbox{\sc vert}}$  PTFE resins (nearly 10× that of metals) could pose supplemental problems. Any generation and localization of excess heat will cause expansion of the fluoropolymer material at that point. Depending on the thickness of the section and the operation being performed, localized expansion may result in overcuts or undercuts and in drilling a tapered hole.

Machining procedures then, especially working speeds, must take conductivity and expansion effects into account.

Surface speeds from 60–150 m/min (200–500 fpm) are most satisfactory for fine-finish turning operations; at these speeds, flood coolants are not needed. Higher speeds can be used with very low feeds or for rougher cuts, but coolants become a necessity for removal of excess generated heat. A good coolant consists of water plus water-soluble oil in a ratio of 10:1 to 20:1.

Feeds for the 60–150 m/min (200–500 fpm) speed range should run between 0.05–0.25 mm (0.002–0.010 in) per revolution. If a finishing cut is the object of a high-speed operation (e.g., an automatic screw-machine running at

240 m/min [800 fpm]), then feed must be dropped to a correspondingly lower value. Recommended depth of cut varies from 0.005–6.3 mm (0.0002–0.25 in).

In drilling operations, the forward travel of the tool should be held to 0.13–0.23 mm (0.005–0.009 in) per revolution. It may prove advantageous to drill with an in-out motion to allow dissipation of heat into the coolant.

## **Properly Shape and Use Tools**

Along with working speeds, choice of tools is quite important to control of heat buildup. While standard tools can be used, best results come from tools specifically shaped for use with *Teflon*<sup>®</sup> PTFE resins. The table below presents shape information important to proper single-point tool design:

Top rake	0–15° positive
Side rake and side angle	0–15°
Front or end rake	0.5–10°

Boring tools normally require the higher angles listed.

The quality of a tool's cutting edge not only influences the amount of heat generated, but it also controls tolerances in a different way. A tool that is not sharp may tend to pull the stock out of line during machining, thereby resulting in excessive resin removal. On the other hand, an improperly edged tool tends to compress the resin, resulting in shallow cuts.

An extremely sharp edge is, therefore, highly desirable, especially for machining work on filled compositions. "Stellite" and carbide-tipped tools will help to minimize required resharpening frequency.

To partially compensate for tool wear, it is helpful to grind tools with a slight nose radius. All drills, either twist or half-round, should have deep, highly polished flutes.

Adequate material support is also important, especially when machining long, thin rods of *Teflon®* PTFE. If support is not provided, stock flexibility may lead to poor results.

Another characteristic of *Teflon*<sup>®</sup> PTFE resins will be noted immediately after beginning any turning operation. Rather than chips and ribbons of removed stock, as encountered during the machining of most materials, a *Teflon*<sup>®</sup> PTFE resin turns off as a long, continuous curl. If this curl is not mechanically guided away from the work, it may wrap around it, hampering the flow of coolant, or worse, forcing the work away from the tool. On an automatic screw machine, a momentary withdrawal of the tool from the stock will suffice.

### **Rules for Dimensioning and Finishing**

Normally, *Teflon*<sup>®</sup> PTFE resins are machined to tolerances of about 0.13 mm (±0.005 in). While closer tolerances are occasionally required, they usually are not necessary. The natural resiliency of these resins allows machined parts to conform naturally to working dimensions. For example, a part with an interference can be press-fitted at much lower cost than that required for final machining to exact dimensions, and the press-fitted part will perform equally well.

### **Closer Tolerances**

When it is necessary to produce shapes with extremely close tolerances, it is usually essential to follow a stress-relieving procedure. By heating a fluoropolymer resin stock to slightly above its expected service temperature (but below 327°C [621°F]), initial stresses are relieved.

Holding this temperature for 1 hr per 2.5 cm (1 in) of thickness, followed by slow cooling, completes the initial annealing step. (Stress-relieved stock can also be purchased from processors.) A rough cut will then bring the stock to within 0.38–0.76 mm (0.015–0.030 in) of final dimensions. Reannealing prior to a final finishing-cut will remove stresses induced by the tool.

A transition occurs in *Teflon*<sup>®</sup> PTFE resin, resulting in a 1-1.5% increase in volume as temperature is increased through the neighborhood of 19°C (66°F). This must be considered when measuring a part for a critical application.

### **Measuring Tolerances**

Personnel should exercise caution when measuring tolerances on parts machined from *Teflon*<sup>®</sup> PTFE resins; in general, results will be better if the measuring instruments do not exert excessive pressure on the piece.

For example, a micrometer used by inexperienced personnel could easily read 0.13–0.25 mm (0.005–0.010 in) under the true dimension because of the compressibility of the *Teflon*<sup>®</sup> PTFE resin being used. Optical comparators are often useful in eliminating this type of error.

It is best to check dimensions at the expected service temperature, but temperature compensations will suffice if this is not practical. Parts machined to final size and measured at room temperatures or below will not meet specifications at higher temperatures. The reverse is also true.

### Surface Finishes

Surface finishes better than 0.4  $\mu$ m (16  $\mu$ in) are possible on parts made with *Teflon®* PTFE resins, but rarely are needed because of the resin's compressibility and low coefficient of friction. Precision-honed and lapped cutting tools will produce a 0.4- $\mu$ m (16- $\mu$ in) surface when required; standard equipment yields a finish of about 0.8  $\mu$ m (32  $\mu$ in).

Lapping compounds may be used, but these as well as grinding compounds may become embedded in the fluoropolymer and may prove to be very difficult to remove. Contaminants from machinery not used exclusively for *Teflon*<sup>®</sup> resins can also embed in the resin surface.

## Safe Handling

As with all organic polymers exposed to high temperatures, good safety practice requires the use of adequate ventilation when processing Teflon® PTFE fluoropolymer resins. The heated fluoropolymer should be kept enclosed, or exhaust ventilation should be used, to prevent inhalation of fumes and gases that may arise. Heating may produce fumes and gases that are irritating or toxic. Similarly, care should be taken to avoid contamination of smoking tobacco or cigarettes with fluorine-containing resins. Precautions are to be used in the handling, processing and use of *Teflon*<sup>®</sup> PTFE or other fluoropolymer resins. Before using Teflon®, read the Material Safety Data Sheet and the detailed information in the Society of the Plastics Industry publication, "Guide to the Safe Handling of Fluoropolymer Resins." Copies may be obtained from your DuPont representative.

# **Typical Applications**

## Flexible Pipe Joint



Chemical Transfer Hose



Heat Exchanger Tube Sheet



**Filled Seals** 



### Tubing



### **Electrical Insulators**



### Valve Body



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