WHY FLUOROPOLYMERS LIKE PTFE ARE DIFFERENT TO OTHER PFAS

[redacted]

W.L. Gore & Associates
*Executive Chairman,
SEC NEWGATE EU

[redacted] [redacted]

Together, improving life

Presentation Outline

- About Gore
- Gore Product Portfolio
- About Fluoropolymers
- Charles River Laboratories research
- Conclusions

About Gore

- Privately held US company based in Newark/Delaware
- Founded more than 60 years ago by Bill and Vieve Gore
- More than 12,000 Associates globally and $4.5 billion in annual revenues
- In Europe around 2,000 Associates

  - Manufacturing facilities and sales offices in Germany and Scotland

  -Sales offices in a number of European countries.

Gore‘s product portfolio based on ‚Fitness for use‘

Core Technology

Performance Solutions Division


Improving the processing and delivery of pharmaceutical products


Enabling the exploration of space for 50 years


Pioneering the use of ePTFE for industrial filtration to control emissions


Facilitating electrochemical conversion of a fuel cell to electrical energy with GORE-SELECT® Membrane
ices


Protecting portable electronics, automotive components and enclosures

Medical Products Division


Improving patient outcomes with stent graft technology


Advancing medicine with ePTFE cardiovascular and soft tissue repair patches


Reducing bleeding and time to hemostasis through GORE-TEX® Sutures


Treating more than 300,000 aortic aneurysm patients with GORE® EXCLUDER® Devices


Partnering with clinicians, more than 40 million medical devices implanted

Fabrics Division


Safeguarding firefighters from heat stress with GORE-TEX® Moisture Barrier


Protecting soldiers worldwide with GORE-TEX® Fabrics

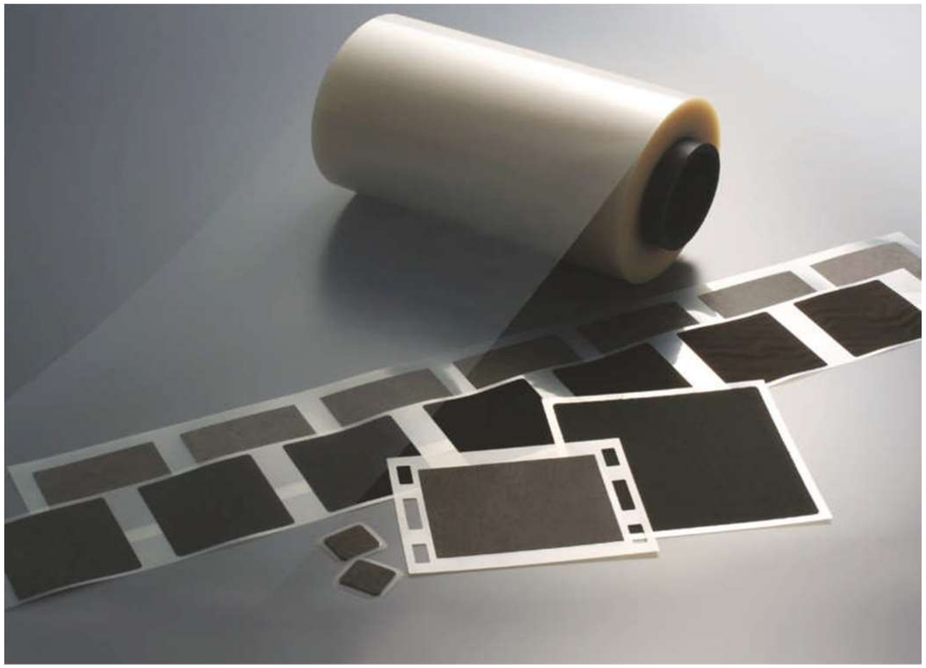

Combining durable waterproofness with optimal breathability in GORE-TEX® SURROUND® Footwear


Revolutionizing breathability with GORE-TEX® ACTIVE Products with SHAKEDRY™ Product Technology


Keeping workers safe with the lightest arc rated GORE-TEX® PYRAD® Products

GORE Fuel Cell Technologies

- Membrane electrode assemblies (MEAs) play a key role in the conversion of hydrogen to electrical energy. They consist of two electrodes (anode and cathode) on either side of a PTFE reinforced, ion-permeable polymer electrolyte membrane.
- Since 1994 Gore has developed:
- The GORE-SELECT® membrane for proton exchange between the anode and cathode
- The GORE® PRIMEA® membrane electrode assembly (MEA)
- In addition to automotive applications, Gore's products are also being used in stationary, emergency power and energy storage systems



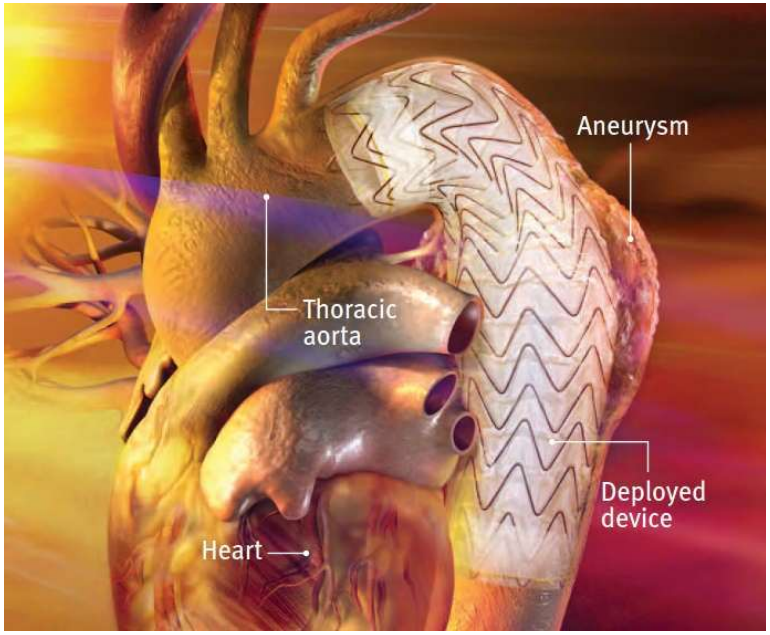
GORE Mercury and SO2 Control System (GMCS)

- A passive sorbent system for capturing elemental and oxidized gas phase mercury from industrial flue gas.
- A fluoropolymer-based Sorbent Polymer Catalyst (SPC) composite material.
- Discrete stackable modules with an open channel structure which provides low pressure drop, avoiding the need for an additional booster fan.
- Modules will continuously capture mercury for many years without requiring any adjustment, regeneration, or replacement. They also provide an SO2 removal as co-benefit
- Mercury emissions reduction up to 80% possible

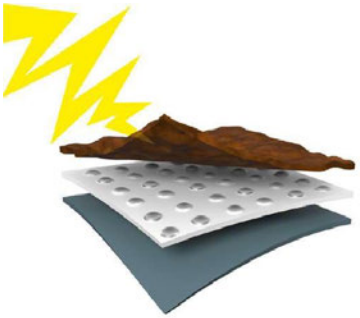
Installed in coal-fired power plants in the EU to match the EU updated regulation : Germany: Chemnitz, Schkopau, Czech Republic: Mělník and Prague; Poland: Belchatow and Patnow.

GORE® TAG® Conformable Thoracic Stent Graft

- Partially Uncovered Stent helps achieve 360° wall apposition in angulated anatomy
- Radiopaque Gold Bands aid in accurate device positioning and visualization at patient follow-up
- Compression-resistant design maintains radial strength and achieves wall apposition in angulated arch anatomy
- Distributes point load and contributes to long-term durability in maximum oversizing conditions
- Sutureless Construction eliminates risk of graft failure from sutures
- ePTFE graft technology on luminal and abluminal surface
- Sealing Cuffs engineered to provide increased security against endoleaks
- Leverages more than 36 years of experience with ePTFE and a reliable platform with proven clinical durability and strength
- Low permeability with abrasion-resistant properties



Weatherproof and flame-retardant GORE-TEX fabric arc rated



GORE® PYRAD® fabric technology blocks convective heat flow during arc exposure and stops flame propagation by forming a carbonaceous char with the textile. Hence, it reduces the heat transfer to skin. Arc rated GORE-TEX® PYRAD® Heat & Flame Garments are certified according to European Standard EN 61482-1-2 class 2.

After ignition of the electric arc - 400 Alternating Voltage (AC) and 7 Kiloampere kA – in the test case, a hot plasma and gas cloud hits the jacket.

Overview

Per- and Polyfluoroalkyl Substances (PFAS)

1 Group — PFAS Per- and Polyfluoroalkyl substances

2 Categories — Non-Polymers | Polymers

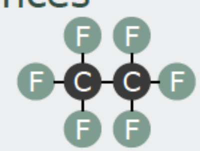
5 Classes

Perfluoroalkyl Acids (PFAAs) such as PFOA, PFOS, PFHxS, etc.

Non-Polymers

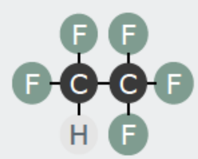
Perfluoroalkyl Substances

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



Polyfluoroalkyl Substances

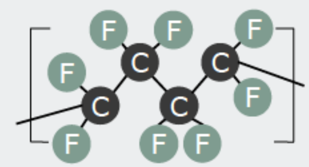
Compounds for which all hydrogens on at least one (but not all) carbon have been replaced by fluorines



Polymers

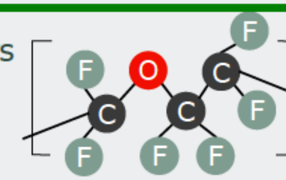
Fluoropolymers

Carbon-only polymer backbone with fluorines directly attached



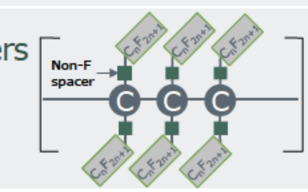
Polymeric Perfluoropolyethers

Carbon and oxygen polymer backbone with fluorines directly attached to carbon



Side-chain Fluorinated Polymers

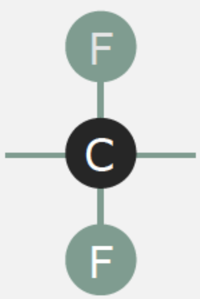
Variable composition non-fluorinated polymer backbone with fluorinated side chains



Overview

Per- and Polyfluoroalkyl Substances (PFAS)

Thousands of PFAS	with a wide variety of properties
Similarities	**Differences**



1 fully fluorinated carbon

- Gases
- Liquids
- Solids

PTFE on the spectrum

Stability: seconds ⟷ thousands of years

Toxicity: low ⟷ high

Mobility: insoluble / non-volatile ⟷ Highly mobile

Size: MW less than 1,000 Daltons ⟷ MW multi-million Daltons

Fluoropolymers – Key properties

Durability

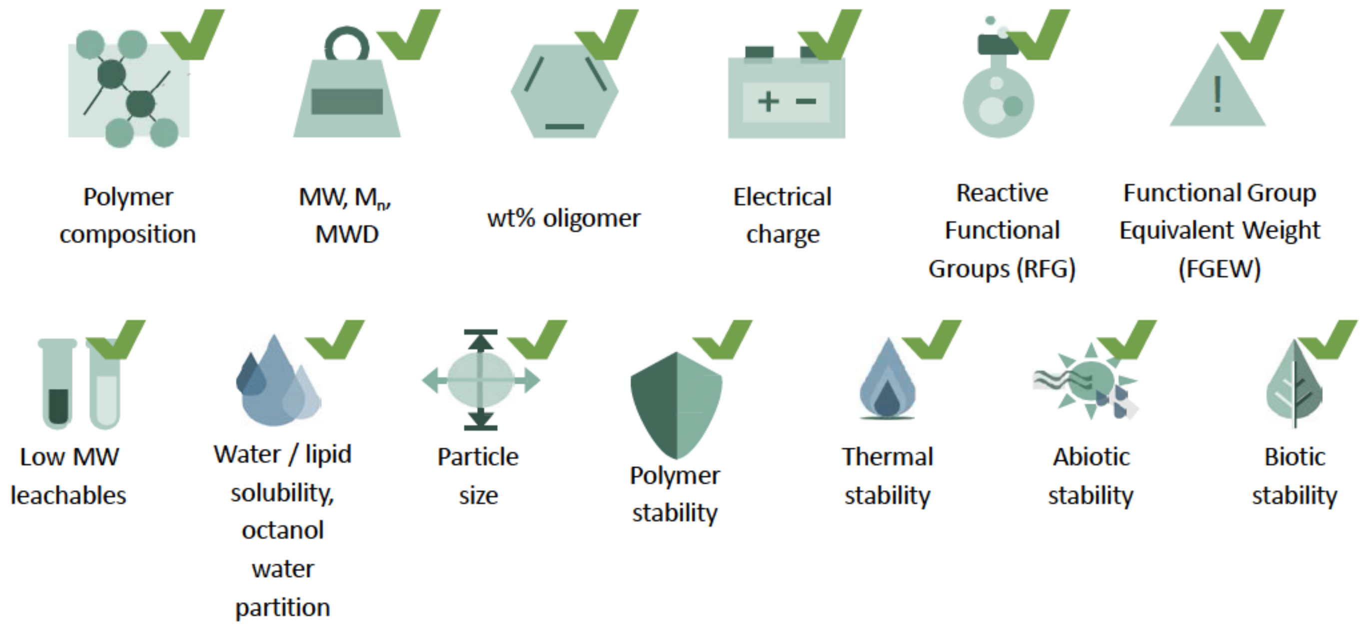
Inertness

Mechanical strength

Thermal stability

Resistance to degradation

Polymer Chemical/Physical Properties Predictive of Low Hazard



Fluoropolymers with these properties have demonstrated low health and environmental hazard.

Fluoropolymers with these low hazard properties are unique among the PFAS

- They are distinctly different from other polymeric and non-polymeric per- and poly-fluoroalkyl substances (PFAS)
- They should be separated from other PFAS for risk assessment or regulatory purposes
- Their Physical, Chemical and Biological properties are predictive of low health and environmental hazard
- PFAS are vastly different — one group for PFAS is not scientifically appropriate

PTFE used in Gore products has very low levels of low molecular weight leachables

- PTFE is impervious to microbial degradation.*
- Fine powder PTFE has low levels of low molecular weight leachables including residual monomer, low molecular weight oligomers, etc.**
- PTFE has a long history of performance in a variety of applications that require highly stable, clean and chemically inert materials.

  Examples: implantable medical devices,
  pharmaceutical processing equipment,
  semiconductor manufacturing

*King MW, Gupta BA, Guidoin R. 2013. Biotextiles as medical implants:15. Vascular prostheses for open surgery. Cambridge (UK): Woodhood. p 434–484; Charles River Labs studies.

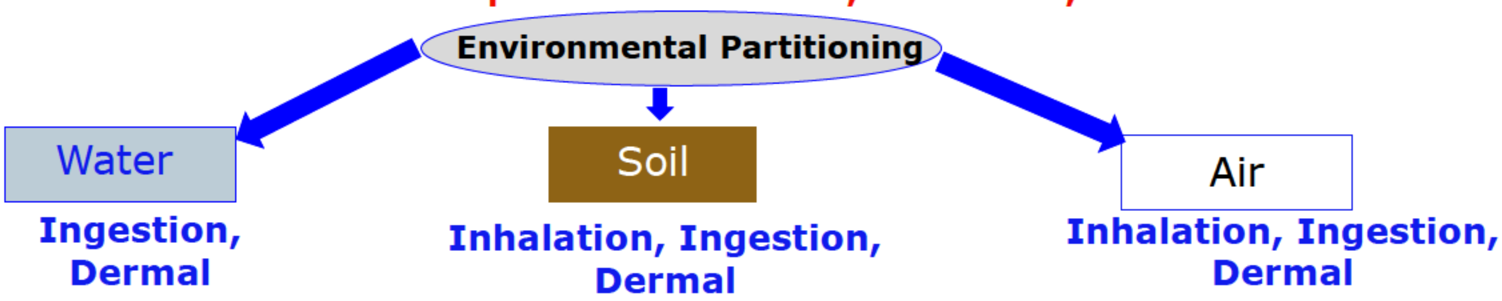
**See supplement to Henry et al., 2018, Integrated Environmental Assessment and Management, Vol. 17, No. 2, pp. 331-351.

Background – PTFE fine powder

Fine powder PTFE

- Polytetrafluoroethylene (PTFE; CAS no. 9002-84-0) is a polymer of the monomer tetrafluoroethylene, TFE
  - Granular
  - Aqueous Dispersion
  - Fine Powder (ASTM D4895)
- This presentation focuses on the PTFE fine powder, a polymer.
- Many textbooks and peer-reviewed publications exist on the properties of PTFE and how to manufacture and process PTFE, including
  - Introduction to Fluoropolymers: *Materials, Technology and Applications,* edited by Sina Ebnesjjad, William Andrews Applied Science Publishers. https://doi.org/10.1016/C2012-0-06184-4
  - Rudy Dams and Klaus Hintzer, Chapter 1:Industrial Aspects of Fluorinated Oligomers and Polymers , in *Fluorinated Polymers: Volume 2: Applications*, 2016, pp. 1-31 DOI: 10.1039/9781782629368-00001
  - *Technology of Fluoropolymers, 2nd Edition*, Jiri George Drobny, CRC Press, 2008.
  - *Fascinating Fluoropolymers and Their Applications, 1st Edition*, Editors Bruno Ameduri and Sergey Formin, Elsevier, 2020.
  - *The Promising Future of Fluoropolymers*, Bruno Améduri, Macromolecular Chemistry and Physics, 2020. **https://doi.org/10.1002/macp.201900573**

Potential Routes of Exposure: Air, Water, Soil



Studies Performed at Independent 3rd Party Laboratory (Charles River Labs in Den Bosch, the Netherlands)

- Standard protocols used (OECD Efate)
- Performed under Good Laboratory Practices
- Studies were performed to provide consistent evidence that persistence of PTFE does *not* imply
  - toxicity or bioaccumulation,
  - future degradation,
  - release or transformation into a continuous source of substances of concern.
- Data routinely shared at scientific meetings as studies are finalized
  - SETAC, FLUOROS 2021, Emerging Contaminants

OECD Test Title	Status/Results
Melting Point/Melting Range (OECD 102)	The melting temperature of the test item was determined using differential scanning calorimetry (DSC). Melt transition observed at ~350°C (662°F); no further melting /decomposition below 400°C. Supports thermal stability at environmentally relevant temperatures.
Determination of the Number-Average Molecular Weight and the Molecular Weight Distribution of Polymers using Gel Permeation Chromatography (OECD 118)	PTFE was not sufficiently soluble to be evaluated by guideline using GPC even after sonication and stirring (*19 hours*) in representative solvents tetrahydrofuran, dichloromethane, dimethylformamide, and dimethylacetamide. Standard Specific Gravity (SSG) and Melt Flow Rate (MFR) are used to determine fluoropolymers MW rather than rheological and dynamic light scattering methods. By alternative methods, PTFE MW is >500,000 Da.
Vapor Pressure (OECD 104)	$<1 \times 10^{-10}$ mm Hg @ 20°C by the isothermal thermogravimetric effusion method.
Henry's Law Constant	Expert Statement; Henry's law constant (HLC) is a measure of the concentration of a chemical in air over its concentration in water. HLC reflects volatility and likelihood to partition to air from water. High HLC means likely to volatize and have long range transport. Low HLC substances tend to persist in water and may be adsorbed onto soil or sediment.
Water Solubility (OECD 105)	PTFE was not soluble in water.
Behavior in water system	PTFE was not soluble in water.
Adsorption - Desorption Using a Batch Equilibrium Method (OECD 106)	Expert Statement
Partition Coefficient (n-octanol/water): Shake Flask Method (OECD 107)	Expert Statement; PTFE is not soluble in octanol or water. Therefore, no Partition Coefficient determination was possible.
Partition Coefficient (n-Octanol/Water), High Performance Liquid Chromatography (HPLC) Method (OECD 117)	Expert Statement; PTFE is not soluble in octanol or water. Therefore, no Partition Coefficient determination was possible.
Octanol-air partition coefficient (log K_{oa})	Expert Statement: PTFE is not soluble in octanol. Therefore, no Partition Coefficient determination was possible.

OECD Test Title	Status/Results
Hydrolysis as a Function of pH (OECD 111)	Study completed; awaiting report
Phototransformation of Chemicals in Water - Direct Photolysis (OECD 316)	Fine Powder PTFE should be considered completely photolytically stable.
Phototransformation of Chemicals on Soil Surfaces (OECD draft document)	Analytical method development in design
Screening Test for Thermal Stability and Stability in Air (OECD 113)	Stable at continuous processing temperature 260°C and only 5% loss in weight at 549°C (1020°F). PTFE is considered stable at room temperature when no decomposition or chemical reaction is observed < 150°C (302°F).
Ready Biodegradability (OECD 301B)	Not readily biodegradable.
Inherent Biodegradability OECD 302 C (METI)	No inherent biodegradability
Biodegradation of organic chemicals in Aerobic Sewage Treatment (OECD 303A)	Analytical method development in progress
Biodegradability in Seawater (OECD 306)	PTFE was not sufficiently soluble for evaluation by guideline even after sonication (*15mins*) and stirring (*83mins*). PTFE does not degrade in seawater.
Aerobic and Anaerobic Transformation in Soil (OECD 307)	Analytical method development in progress
Aerobic and Anaerobic Transformation in Aquatic Sediment Systems (OECD 308)	Analytical method development in progress

CONCLUSIONS OF PTFE OECD CHEMICAL/PHYSICAL/STABILITY TESTING

- **Air:** Vapor pressure, thermal stability in air and thermal gravimetric analysis show low volatility or partitioning to air at <150° C. Stable at continuous use processing temperature of 260° C. The melting point results show stability at environmentally relevant temperatures. **This data shows PTFE does not partition to air and is not subject to long-range transport via air.**

- **Water**: PTFE is not dissolvable in water (OECD 105, 120). The lack of solubility in octanol or water (OECD 107, 117), prevented determination of octanol/air or octanol/water partition coefficients. **This data shows the lack of mobility of PTFE, long-range transport in water, and impact via water solubility of PTFE on drinking water, plants and crops.**

- **Soil**: Upon completion of analytical method development, OECD 307, 308, 106 and phototransformation on soil surfaces will be performed and results shared publicly. **PTFE's extremely high molecular weight supports a lack of partitioning to soil.**

- **Biodegradation**: PTFE was not readily (OECD 301B) or inherently (OECD 302C) biodegradable. Upon completion of analytical method development, OECD 303A and 307 will be performed and results shared publicly. **PTFE is not biodegraded and not an ongoing source of substances of concern.**

- **Mobility** is considered by ECHA to be a contributing factor for potential for long-range transport via air, water, drinking water contamination, uptake in plants and crops, and, degrading or otherwise producing additional undesirable persistent substances available for increased internal concentrations in biota as environmental exposures increase. **The data presented here demonstrates the lack of PTFE mobility.**

Fluoropolymers Toxicity and Clinical Data

PTFE, FEP, and a TFE/PAVE copolymer passed these GLP tests		
Cytotoxicity (MEM)	(ISO 10993-5)	Not Cytotoxic
Skin Sensitization	(ISO 10993-10; OECD 406)	Non-Sensitizing
Irritation	(ISO 10993-10; OECD 406)	Not Irritating
Acute Systemic Toxicity	(ISO 10993-11; OECD 408)	Not Toxic
90-Day Subchronic Systemic Toxicity	(ISO 10993-11; OECD 408)	Not Toxic
Two *In Vitro* + One *In Vivo* Genotoxicity	(ISO 10993-3; OECD 471, OECD 474, OECD 476)	Not Mutagenic
2- or 4-Week Implantation	(ISO 10993-6)	No Significant Response
Hemocompatibility	(ISO 10993-4; ASTM F756. ASTMF2382)	Hemocompatible

Note: 90-Day Subchronic Toxicity Studies included hematology, urinalysis, clinical chemistry, gross pathology, microscopic histopathology, organ weights, clinical observations. Histopathology performed on: ovaries, testes, brain, heart, liver, kidneys, spleen, thymus, adrenal glands, lymph nodes

45 years of patients receiving permanently implanted PTFE, FEP or TFE/PAVE copolymer cardiovascular medical devices demonstrate no chronic toxicity, carcinogenicity, reproductive, developmental or endocrine toxicity.

Conclusions

The OECD guideline data presented here on PTFE under environmentally relevant conditions supports:

- PTFE does not partition to air, water or soil, nor lead to inhalation, oral or dermal exposures for biota, nor is it subject to long-range transport via air, water or soil
- PTFE is not mobile and does not impact drinking water, plants or crops
- PTFE is biotically/abiotically stable and not transformed to perfluoroalkyl acids (PFAAs)

Published data, such as that in Henry et al., 2018 (which has been accepted by US, AP and EU medical device regulators) demonstrate that PTFE (fine powder meeting ASTM D4895) has a lack of:

- low molecular weight oligomers, residual monomer and leachables
- toxicity and bioaccumulation

The stability, durability or persistence of fine powder PTFE enables "durable by design" products of high societal value (e.g., medical devices, wiring and cabling for satellites and aircraft, protective gear for hospital workers, spacesuits, cell phones, etc.).

THANK YOU

Questions:

Contact [redacted]

These slides provide a summary of the Chemical, Physical and Biological Properties of PTFE and identify some of the available technical support.

Acknowledgement: [redacted] Ph.D., W. L. Gore & Associates; [redacted] Ph.D., ERT, of Charles River Laboratories, Den Bosch, The Netherlands

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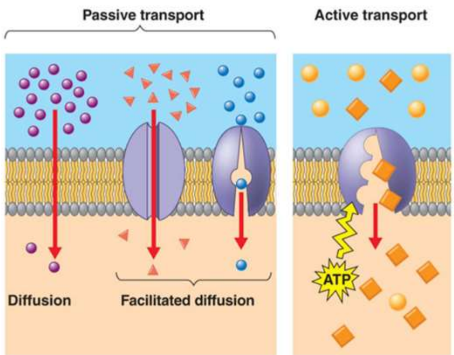
Annex

Description	Non-Polymer PFAS		Polymer PFAS		
	Perfluoroalkyl Substances	Polyfluoroalkyl Substances	Side Chain Fluorinated Polymers	Fluoropolymer	Perfluoropolyether
Substance	PFOA	6:2 FTOH	6:2 Fluorotelomer Methacrylate*	Polytetrafluoroethylene (PTFE)	1,1,1,2,2,3,3-heptafluoro-3-(1,1,2,2,2-pentafluoroethoxy) propane
CAS Number	335-67-1	647-42-7	2144-53-8	9002-84-0	60164-51-4
Chain Length	Long	Short	short	N/A	N/A
Molecular Weight	414.069 Da	364.1	432.18	389,000 - 45,000,000	NDA
Physical state/Description	White to off-white powder	clear, colorless to pale yellow liquid	yellow liquid	solid	colorless, viscous liquid
Boiling Point	192 °C	171 °C	210 °C	not applicable	NDA
Melting Point	54.3 °C	78 °C	not applicable for liquids	326 °C	NDA
Vapor Pressure	4.21 Pa at 25 °C	26.6645 Pa 25 °C	8.6 Pa at 25 °C	NDA	NDA
Stability (hydrolysis, photolysis,	stable	NDA	unstable	stable	stable
Water Solubility**	9.50×10^3 mg/L at 25 °C	"insoluble" 18.8 mg/mL	0.042 mg/L at 20 °C	practically insoluble or insoluble (1×10^{-5} mg/L)	insoluble
log Kow	4.81 (est)	4.54	5.2 at 23 °C	NDA	NDA
Particle Size µm	NDA	NDA	not applicable for liquids	100-500 µm (powders)	not applicable for liquids
Acute Dermal LD50	Low (>2000 mg/kg)	Low (5,000 mg/kg)	Low (>5000 mg/kg)	NDA	Low (>17,000 mg/kg)
Skin Irritant, Y/N	Y	Y	N	N	N
Eye Irritant, Y/N	Y	Y	N	N	N
Skin Sensitizer,	N	N	N	N	N
90-Day Animal Feeding Study (No Effect Dose)	0.06 mg/kg/day	5 mg/kg/day	5 mg/kg/d	NDA	NDA
Mutagen, Y/N	N	N	N	N	N
Caused Tumors in Lab Rats, Y/N	Y	NDA	NDA	N	NDA
Half Life in	3.3 - 3.8 years	NDA	NDA	NDA	NDA
References	Haynes 2014; Yalkowsky et al. 2010; Kennedy et al. 2004; Butenhoff et al. 2004; USEPA 2012; Bhhatarai and Gramatica 2011	Daikin 2007; Daikin 2009a; Daikin 2009b	ECHA 2019a; ECHA 2020b; Sigma Aldrich 2020; Anand et al. 2012.	Henry et al. 2018	DuPont SDS 11/2014
	**[USP] US Pharmacopeial Convention. 2011. US Pharmacopeia National Formulary 2011: USP 34 NF 29. Rockville (MD). General Notices, Section 5.3.0, p 6.				
Note	NDA = No data available				
	*Note these data are for the fluorinated side chains. Note also NDA means the no data available.				

Bioavailability and Bioaccumulation

- PTFE is not bioavailable due to very high molecular weight and is not subject to passive transport into the cell because:
  - Of size, the lack of lipid solubility to penetrate the cell membrane, the lack of oxygen and nitrogen atoms estimating groups accepting hydrogen atoms
  - They are highly hydrophobic and have little or no hydrogen bond donating potential because they have few or no hydrogen bonds
  - They are not structurally similar to steroids, peptides, natural compounds, etc.
- PTFE is not subject to Active Transport and Cell Surface Binding/Signaling
  - They depend on shape, volume/size, rotational bonds, etc. and requires interaction with cell surface
  - PTFE does not “fit” into cell surface receptors to signal events within the cell.
  - The types of high molecular weight compounds that can be bioavailable through active transport or cell surface binding/signaling are “natural compounds” like cyclosporine A, rapamycin, steroids, flavones, peptides, etc.

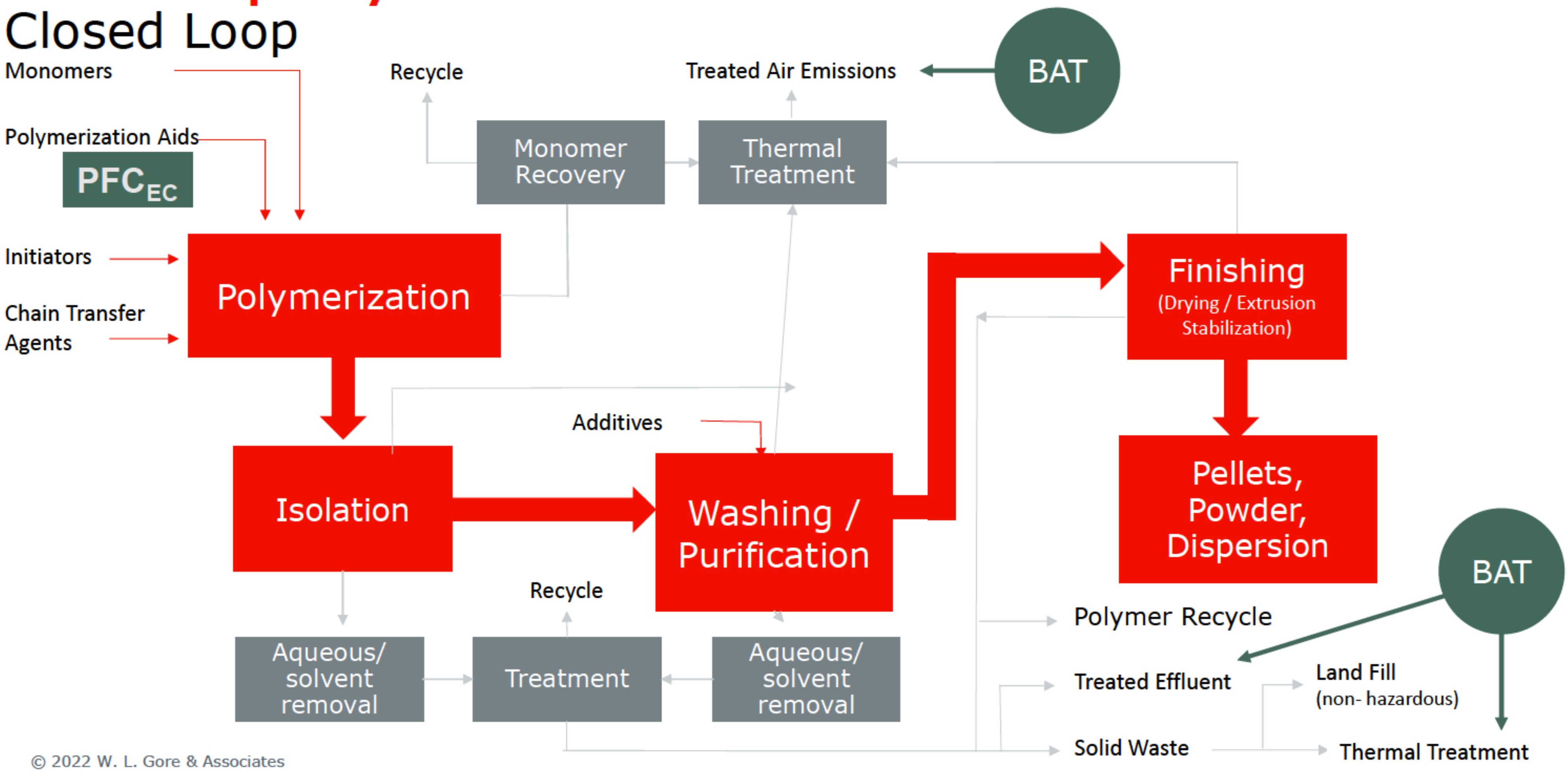


PTFE is not capable of being bioavailable or bioaccumulative.

Fluoropolymers with Low Hazard Properties – Beginning of Life

- Gore uses best available techniques (BATs) in its manufacturing processes, thus ensuring emission reductions and a closed-loop system.
- We support the implementation of a strong – independently verified - Industry Voluntary Stewardship Program, especially for PFOA replacements.
- We stand ready to collaborate with regulators, academia and industry e.g. ECETOC Task Force to ensure water protection and further eliminate risk of emissions.

Fluoropolymer Manufacture General Diagram: Closed Loop



Fluoropolymers with Low Hazard Properties – In Use

- Attributes of Fluoropolymers enable products of High Societal Value
- These fluoropolymers have thermal, chemical, photochemical, hydrolytic, oxidative, and biological stability. They have negligible residual monomer and oligomer content.
- These fluoropolymers are practically insoluble in water and not subject to long-range transport.
- With a molecular weight well over 100 000 Da, PLC fluoropolymers cannot cross the cell membrane.
- These 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, haemolysis, complement activation, and thrombogenicity.
- *We propose that stringent threshold levels are adopted for residuals in these low hazard fluoropolymers.*

Fluoropolymers with Low Hazard Properties – End of Life

- To reduce environmental impact of global solid waste, control measures (reuse, recycling, upcycling, take back/buy back, compliant incineration, etc.) should be implemented for all persistent materials, not just fluoropolymers, as much as possible in accordance with the transition to a Circular Economy.
- Municipal incineration of Fluoropolymers is safe, KIT paper.
- Further studies to:
  - Demonstrate contribution of low hazard fluoropolymers to circular economy (getting more from a product, durability longevity …)
  - Support industry efforts to eliminate open burning (partnerships with downstream users)
  - Promote recyclability – Dyneon upcycling pilot, Invertec Pilot project: Recycling of fluoropolymers (PTFE), Closing the recycling loop: Up-Cycling of End-of-Life Fluoroplastics

Fluoropolymers End of Life

Institute of Technical Chemistry at KIT, Germany

Incineration study of PTFE products for potential releases of a broad range of PFC_{EC} in municipal waste incinerator, published

Aleksandrov et al., Waste incineration of Polytetrafluoroethylene (PTFE) to evaluate potential formation of per- and Poly-Fluorinated Alkyl Substances (PFAS) in flue gas. Chemosphere, Volume 226, July 2019, Pages 898-906.

https://doi.org/10.1016/j.chemosphere.2019.03.191