SUPPLEMENTAL DATA

A Critical Review of the Application of Polymer of Low Concern Regulatory Criteria to Fluoropolymers II: Fluoroplastics and Fluoroelastomers

S. H. Korzeniowski*[1], R. C. Buck[2], R. M. Newkold[2], A. El kassmi[3], E. Laganis[3], Y. Matsuoka[4], B. Dinelli[5], S. Beauchet[5], F. Adamsky[6], K. Weilandt[7], V. K. Soni[8], D. Kapoor[9], P. Gunasekar[9], M. Malvasi[10], G. Brinati[10], S. Musio[10]

1 BeachEdge Consulting, LLC, Media, PA 19063, USA

2 The Chemours Company, 1007 Market Street, Wilmington, Delaware, 19899, USA

3 AGC Chemicals Americas, 55 E. Uwchlan Ave, Exton, PA 19341, USA

4 AGC Performance Chemicals General Division, Shin-Marunouchi Bldg., 1-5-1 Marunouchi, Chiyoda-ku, Tokyo, Japan 100-8405

5 Arkema, 420 rue d'Estienne d'Orves, 92700 Colombes, France

6 Daikin America, Inc., 905 State Docks Road, Decatur, Alabama, U.S.A. 35601

7 3M Company Advanced Materials Division 3M Center, Building 280-01-W-03, St. Paul, MN 55144, USA

8 Gujarat Fluorochemicals Limited, INOX Towers, Plot No. 17, Sector 16A, Noida, U.P., India

9 Gujarat Fluorochemicals GmbH, Regus Centre Watermark 14th Floor Überseeallee 10, 20457 Hamburg, Germany.

10 Solvay Specialty Polymers, V.le Lombardia, 20 - I-20021 Bollate (MI), Italy

* Corresponding Author – [redacted]@gmail.com

Contents

1. Glossary of Terms

ACC	American Chemistry Council
ABS	Acrylonitrile Butadiene Styrene terpolymer
Active Leachables by USP Class VI Testing	USP Class VI testing is aimed at certifying that there are no harmful reactions or long-term bodily effects caused by chemicals that leach out of plastic materials.
AEM	Anion Exchange Membrane
Amorphous Fluoropolymer	Perfluoro(alkenyl vinyl) ether polymer (See 4.13, 5.13)
Biocompatible	The ability of a material to perform with an appropriate host response in a specific application.
CDC	Centers for Disease Control
CF4Polymers	CEFIC Conceptual Framework for Polymer Risk Assessment
Clean Energy	clean energy as energy derived from renewable, zero-emissions sources ("renewables"), as well as energy saved through energy efficiency ("EE") measures
CPI	Chemical Process Industry
CPT	Terpolymer of chlorotrifluoroethylene, tetrafluoroethylene and perfluoroalkyl-vinyl-ether
CTFE	Chlorotrifluoroethylene
Da	Dalton (Measure of molecular weight or molecular mass)
DMA	Dimethylacetamide, a solvent
DMF	Dimethylformamide, a solvent
DMSO	Dimethyl sulfoxide, a solvent
ECETOC	European Centre for Ecotoxicology and Toxicology of Chemicals
ECHA	European Chemicals Agency
ECTFE	Ethylene-chlorotrifluoroethylene copolymer
EFEP	Terpolymer of ethylene, tetrafluoroethylene, and hexafluoropropylene
EOL	End of Life
EPDM	Ethylene Propylene Diene Monomer rubber
e-PTFE	Expanded polytetrafluoroethylene
ETFE	Ethylene-tetrafluoroethylene copolymer
EVOH	Ethylene Vinyl Alcohol
FEP	Fluorinated ethylene-propylene; a co-polymer of tetrafluoroethylene (TFE) and hexafluoropropylene (HFP)
FEPM	Tetrafluoroethylene (TFE) - propylene co-polymer
FEVE	Fluoroethylene-vinyl ether copolymer

FFKM	Perfluoroelastomer
FKM	Fluoroelastomer. 1-propene,1,1,2,3,3,3-hexafluoro-(HFP) polymer with1,1-difluoroethene (VF2)
Fluorinated Ionomer	Copolymer of tetrafluoroethylene and a perfluorinated vinyl ether containing an ionic group
Fluorinated Polymer	The broad generic term to encompass all polymers for which one or more of the monomer units contains the element F, in the backbone and/or in side chains.
Fluorochemical	General, nonspecific name that describes a universe of organic and inorganic substances that contain at least 1 F atom, with vastly different physical, chemical, and biological properties. Synonyms include “fluorinated substance” and “fluorinated chemicals.”
Fluoroelastomer	An elastic rubber-like polymer to which fluorine is bound. Fluoroelastomers are highly durable and resistant to heat, oils, solvents, fuels, and ozone.
Fluoroplastic	A distinct subset of polymers and plastics where some or all of the hydrogen atoms of the hydrocarbon backbone have been replaced with fluorine atoms.
Fluoropolymer	Distinct subset of polymers, namely, those made by (co)polymerization of olefinic monomers, at least one of which contains F bound to one or both of the olefinic carbon atoms, to form a carbon-only polymer backbone with F atoms directly attached to it, e.g., polytetrafluoroethylene
Fluorosurfactant	A substance used to lower aqueous surface tension in which the hydrophobic portion contains F bound to C, often as a perfluoroalkyl moiety, often referred to as ‘‘fluorinated surfactants’’, ‘‘fluorosurfactants,’’ ‘‘fluorinated tensides,’’ or ‘‘fluorotensides’’
Food Contact Material (FCM)	Made with the FCS (food contact substance: any substance that is intended for use as a component of materials used in manufacturing, packing, packaging, transporting, or holding food if such use of the substance is not intended to have any technical effect in such food) and (usually) other substances. It is often (but not necessarily) a mixture, such as an antioxidant in a polymer. The composition may be variable. (https://www.fda.gov/Food/IngredientsPackagingLabeling/Definitions/default.htm)
FPG	Fluoropolymers Product Group, a group within Plastics Europe, the association of Plastics manufacturers.
FRP	Fiberglass Reinforced Plastic
Functional Group Equivalent Weight (FGEW)	Ratio of the molecular weight to the number of occurrences of that functional group in the molecule. It is the weight of substance that contains one formula-weight of the functional group. (40 CFR 723.250(b))
GPC	Gel Permeation Chromatography
HFO-1234yf	2,3,3,3-Tetrafluoropropene
HFP	Hexafluoropropylene: $CF_3CF=CF_2$; 1-propene,1,1,2,3,3,3-hexafluoro-
HFPO	Hexafluoropropylene oxide
HNBR	Hydrogenated Acrylonitrile Butadiene Rubber

Homopolymer	A polymer made with only one monomer
HPFP	Propylene,1-hydropentafluoropropene
HS-GC/MS	Head space gas chromatography/mass spectrometry
ICE	Internal Combustion Engine
IEM	Ion exchange membrane
ISO	International Organisation for Standardization
IXM	Ion Exchange Material
K_{OW}	The octanol–water partition coefficient (Kow) is a criterion to assess chemicals and their environmental and health impact
LEV	Low emission vehicle
LOI	Limiting oxygen index
MFA	PPVE and TFE co-polymer, a perfluoroalkoxy polymer
MMAD	Median mass aerodynamic diameter. The MMAD is the value of aerodynamic diameter for which 50% of some quantity in a given aerosol is associated with particles smaller than the MMAD, and 50% of the quantity is associated with particles larger than the MMAD.
Modified Homopolymer	Polymers containing not more than 1 % by weight of other fluoromonomers. (ASTM D4895 Standard Specification for Polytetrafluoroethylene (PTFE) Resin Produced from Dispersion
NMP	N-Methyl-2-pyrrolidone, a solvent
NMR	Nuclear Magnetic Resonance Spectroscopy
OECD	Organisation for Economic Co-operation and Development
OEM	Original Equipment Manufacturer
Oligomer	A molecule consisting of only a few monomer units (dimer, trimer, tetramer) (40 CFR 723.250(b))
PA	Polymerization Aid. A substance (e.g., catalyst, stabilizer, surfactant) added to the reactor vessel from 0.01% to 0.5% of the weight of water, depending on the rate and degree of reaction
PAFC	Phosphoric Acid Fuel Cell
PAVE	Perfluoroalkyl vinyl ether (generic name) in which the alkyl group is methyl, ethyl or propyl
PCTFE	Polychlorotrifluoroethylene
PDD	2,2-bistrifluoromethyl-4,5- difluoro-1,3-dioxole
PEM	Proton Exchange Membrane
Perfluoroalkyl acid (PFAA)	Perfluoroalkyl acids, include perfluoroalkyl carboxylic, sulfonic, sulfinic, phosphonic, and phosphinic acids which are highly persistent substances, such as PFOA or PFOS. They are released into the environment directly or are formed indirectly from the environmental degradation or metabolism of precursor substances
PEVE	Pentafluoroethyl trifluorovinyl ether

PFA	Perfluoroalkoxy polymer (generic name)
PFAS	A very diverse group, per- and poly-fluoroalkyl substances (PFAS), include the class of polymers (fluoropolymers, perfluoropolyethers, side chain fluorinated polymers) and non-polymers - perfluoroalkyl substances for which all hydrogens on all carbon not associated with functional groups have been replaced by fluorine, and polyfluoroalkyl substances for which all hydrogens on at least one, but not all, carbon have been replaced by fluorine.
PFCA	Perfluorocarboxylic acid: $F(CF_2)_nCOOH$
PFECA	Per- and poly-fluoroether carboxylate
PFP	U.S.-based Performance Fluoropolymer Partnership
PFPE	A perfluoropolyether is a polymer in whose backbone $-CF_2-$, $-CF_2CF_2-$, and possibly -CF(CF3)CF2- units are separated by O atoms
PFSA	Perfluoroalkyl sulfonic acid, $F(CF_2)_n-SO_3H$
PMMA	Polymethylmethacrylate
PMVE	Trifluoromethyl trifluorovinyl ether
Polymer of Low Concern (PLC)	A polymer deemed to have insignificant environmental and human health impacts
PP	Polypropylene
PPA	Polymer Processing Additive - also called Polymer Processing Aid, Extrusion Process Aids or Polymer Processing and Recycling Aids
PPVE	Perfluoropropyl vinyl ether
PRR	Polymer Requiring Registration [URL]
PTFE	Polytetrafluoroethylene
PVDF	Polyvinylidene fluoride
PVF	Polyvinyl fluoride
REACH	Chemical Control regulation in the European Union (Registration, Evaluation, Authorisation and Restriction of Chemicals)
Reactive Functional Group (RFG)	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.
RMOA	Risk Management Option Analyses
SCFP	Side-chain Fluorinated Polymer
SEAC	Committee for Socio-Economic Analysis
SEC	Analytical size-exclusion chromatography (**SEC**), also called Gel Permeation Chromatography (GPC)
Smart Mobility	Smart mobility is the connection of various elements of technology and mobility, a rethinking of the transportation infrastructure used in daily life and business
SOFC	Solid Oxide Fuel Cell
Specific Migration Limit	The maximum permitted amount of substance (e.g., monomer) in food that has been determined to not pose a risk to human health

Sustainable Industry	Related to the development of industrial processes in a sustainable way. The phrase refers to greening of energy intensive industries such as the textiles, steel, cement, and paper industries.
SVHC	Substance of Very High Concern
TCLP	Toxicity Characteristic Leaching Procedure; SW-846 Test Method 1311
TFE	Tetrafluoroethylene
TFE/P	Tetrafluoroethylene Propylene copolymer
TFE/PDD	Tetrafluoroethylene and perfluorodimethylenedioxole co-polymer
TGA	Thermal Gravimetric Analysis (TGA), which determines mass loss over time and temperature of a test substance
THV	1-propene,1,1,2,3,3,3-hexafluoro (HFP) - polymer with 1,1-difluoroethylene (VF2) and tetrafluoroethylene (TFE)
TLCP	Toxicity Characteristic Leaching Procedure
TrFE	Trifluoroethylene
TSCA	Toxic Substance Control Act (TSCA) authorizes the USEPA to regulate and screen all chemicals produced or imported into the United States to prevent unreasonable risks to health and the environment.
USEPA	US Environmental Protection Agency
USP	The United States Pharmacopeial Convention (USP) is a nonprofit scientific organization founded in 1820 in Washington, D.C., that develops and disseminates public compendial quality standards for medicines and other articles
VDF or VF2	Vinylidene fluoride
VF	Vinyl fluoride, CH_2=CHF

2. Table 2 - Fluoropolymer Property and Functionality Descriptions

In this Chapter, text describing the properties and functionalities shown in Table 2 of the paper are elaborated upon.

DURABLE

- Mechanical strength: Mechanical strength gives the information about the strength, ductility, hardness and fracture toughness of the material. Mechanical strength can be determined under many conditions such as impact, fatigue, load, compression, stress, elongation, tension and compression.

(OR)

The strength of a material is its ability to withstand an applied load without failure or plastic deformation.

- Wear resistance: Wear resistance defines the ability to resist the aggressiveness of wearing medium.
- Flexibility: It is defined as the ability of the material to bend without breaking and return to its original shape or position

The order of the elastic modulus is usually as follows:

Fluorelastomers <THV < PTFE < PFA, FEP < ETFE < PVDF < PCTFE

- Low coefficient of friction: Coefficient of friction describes how easily the material slides against another surface.

The coefficient of friction, μ, is a measure of the amount of friction existing between two surfaces. The value of the coefficient of friction is given by

μ=frictional force, (F)/ normal force, (N)

INERT – STABLE

- Resistance to chemicals: Chemical resistance can be defined as the ability of a substance to withstand, resist or endure itself from chemical attack for a specific period of time.
- Weatherability: Weatherability is the ability of a material or structure to withstand, resist or endure harsh atmospheric weather conditions, such as extremely hot or cold temperatures, UV light, humidity, salt air or similar corrosive conditions.
- Cryogenic properties (lower than -50 °C): In general, a measure of how a material maintains it mechanical strength at low temperatures.
- High Operating Temperature Range: Operating temperature range refers to the range of temperature that a material can withstand, while successfully performing its intended operation.
- High limiting oxygen index: Limiting oxygen index (LOI) is the measure of the minimum concentration of oxygen in a mixture of oxygen and nitrogen that is needed to support the flaming combustion of a material. Limiting oxygen index (LOI) is the parameter most frequently used to characterize the improvements in fire retardancy. Note: Also consider that LOI is the

measure of the minimum percentage of oxygen in an oxygen/nitrogen mixture that is required to support the combustion of plastics

FUNCTIONAL

- Electrical insulator - high data transmission rate: A material which does not allow the electricity to pass through them is known as an electrical insulator. A charge does not move freely through an insulating material, providing a high resistivity path to the electric current. Ionic Conductivity: Ionic conductivity is electrical conductivity due to the motion of ionic charge (Instead of electrons in electrical conductivity)
- Piezo-electrical Properties – Piezoelectricity is electric polarization of a film produced by mechanical strain in some crystals, or the reverse induced by electrical energy.
- Barrier properties: It refers to the property of material when the/a specified permeable object transmits from one side to the other (from high density side into low density side).
- Non-stick properties: Inability of a substrate to form bonds at the molecular level with a foreign material

Ultra High Purity Grades for clean applications. Material that is non leaching and has a low water absorption rate which means that the chemicals passing through or over tubing will not diffuse into the tubing or extract (leach) soluble species from the tube material.

- Optical clarity: The clarity or transmittance of a polymer usually increases with decreasing crystallinity, refractive index, compressibility and intermolecular interaction.

  Many of the optical properties of a polymer are related to the refractive index, which is a measure of the ability of the polymer to refract or bend light as it passes through the polymer.

Low refractive index - used for optical effects: The refractive index (RI) of a polymer is the ratio of the speed of light in a vacuum to the speed of light through the polymer. The lower the refractive index, the less the material bends the light, decreasing the focusing power, the reflective effect and the light dispersion. The polymer of an optical plastic must possess lower value of refractive index.

Polymer Processing Additives (PPA) have helped the extrusion of polyolefins or engineering polymers by reducing or eliminating melt fracture and die build up and by reducing melt pressure or enabling increased extrusion rates. They are based on high molecular weight fluoroelastomers or fluorothermoplastics

3. Polymer of Low Concern (PLC) Polymer Hazard Assessment

3.1 PLC is a Useful Tool to Assess Polymer Hazards

Well-established science-based definitions and criteria for Polymers of Low Concern (PLC) have been discussed and elaborated globally for decades to ensure international consistency.

It is important to underline that the PLC criteria were created to facilitate polymer hazard assessment that identifies low risk polymers that in turn assists in prioritizing regulatory activity on high-risk substances. The PLC criteria were established as a useful tool to assess potential hazards resulting from the intrinsic properties of polymers. *PLC was not established as a comprehensive Life Cycle Assessment Tool.*

The science developed over 30 years ago, behind the use of structure-activity relationships and predictive modelling is still valid today independent of their OECD, US or European origin [1,2,3].

These methodologies should be retained because of their tried and tested scientific merit. The definition of PLC criteria by the OECD has enabled identification of chemical, physical, and biological properties predictive of health and environmental effects which are of low concern [4,5].

References

[1] Auer CM, Nabholz JV, Baetcke KP. 1990. Mode of action and the assessment of chemical hazards in the presence of limited data: Use of structure-activity relationships (SAR) under TSCA, Section 5. Environ Health Perspect 87:183–197

[2] National Resource Council, Toxicity Testing: Strategies to Determine Needs and Priorities. National Academy Press, Washington, DC, 1984.).

[3] Wagner PM, Nabholz JV, Kent RJ. 1995. The new chemicals process at the Environmental Protection Agency (EPA): Structure-activity relationships for hazard identification and risk assessment. Toxicol Lett 79: 67– 73.

[4] Organisation for Economic Co-operation and Development. 1993. OECD Expert Group on Polymers. Third Meeting of the Experts on Polymers: Chairman's Report [ENV/MC/CHEM/RD(93)4]; 1993 Apr; Paris

[5] Organisation for Economic Co-operation and Development. 2009. Data analysis of the identification of correlations between polymer characteristics and potential for health or ecotoxicological concern. OECD Task Force on New Chemicals Notification and Assessment, Expert Group Meeting on Polymers; 2007 Mar; Tokyo, Japan. Paris (FR).

References describing the History and origins of polymer hazard assessment and the PLC

- Wagner PM, Nabholz JV, Kent RJ. 1995. The new chemicals process at the Environmental Protection Agency (EPA): structure-activity relationships for hazard identification and risk assessment. Toxicology Letters 79:67-73.
- Auer CM, Nabholz JV, Baetcke KP. 1990. Mode of Action and the Assessment of Chemical Hazards in the Presence of Limited Data: Use of Structure-Activity Relationships (SAR) under TSCA, Section 5. Environmental Healthy Perspectives, Vol. 87, pp. 183-197.
- https://www.epa.gov/tsca-screening-tools/using-predictive-methods-assess-hazard-under-tsca Organisation for Economic Co-operation and Development. (1993). OECD Expert Group on Polymers.

Third Meeting of the Experts on Polymers: Chairman's Report (ENV/MC/CHEM/RD(93)4). https://www.oecd.org/ env/ehs/oecddefinitionofpolymer.htm
- Organisation for Economic Co-operation and Development. (2009). Data analysis of the identification of correlations between polymer characteristics and potential for health or ecotoxicological concern. OECD Task Force on New Chemicals Notification and Assessment, Expert Group Meeting on Polymers.
- BIO by Deloitte. (2015). Technical assistance related to the review of reach with regard to the registration requirements of polymers. European Commission. https://ec.europa.eu/environment/chemicals/reach/pdf/ FINAL%20REPORT%20POLYMER%20SI671025.pdf;
- European Commission. (2012). Review of REACH with regard to the registration requirements on polymers (070307/2011/602175/SER/D3). https://ec.europa.eu/environment/chemicals/reach/pdf/studies_ review2012/report_study9.pdf;
- European Commission. (2020). ENV.B.2—Sustainable chemicals. Scientific and technical support for the development of criteria to identify and group polymers for registration/evaluation under REACH and their impact assessment. https://op.europa.eu/en/publication-detail/-/ publication/1cc811ff-d5fc-11ea-adf7-01aa75ed71a1
- European Centre for Ecotoxicology and Toxicology of Chemicals. (2019). Conceptual framework for polymer safety assessment. http://www. ecetoc.org/mediaroom/conceptual-framwork-for-polymer-safetyassessment
- [USFR] US Federal Register. 1984. Premanufacture Notification Exemptions for polymers; Final rule 49 FR 46066, 1984 Nov 21. FRL-2439-1.

3.2 Polymer of Low Concern (PLC) Hazard Assessment Criteria Descriptions & References

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).

References

- BIO by Deloitte. (2015). Technical assistance related to the review of reach with regard to the registration requirements of polymers. European Commission. https://ec.europa.eu/environment/chemicals/reach/pdf/ FINAL%20REPORT%20POLYMER%20SI671025.pdf;
- [USFR] US Federal Register. 1995. Premanufacture notification exemptions; Revisions of exemptions for polymers; Final rule. Federal Register 60(60):16316–16336. Environmental Protection Agency. 60 FR 16316. 1995 Mar 29. FRL–4929–8.
- [USFR] US Federal Register. 2006. Premanufacture notification exemption for polymers; Amendment of polymer exemption rule to exclude certain perfluorinated polymers. 40 CFR Part 723. 2006 Mar 7. Fed Reg No 06-02152.
- [USFR] US Federal Register. 2010. Premanufacture notification exemption for polymers; Amendment of polymer exemption rule to exclude certain perfluorinated polymers. 40 CFR Part 723. 2010 Jan 27. EPA-HQ-OPPT-2002-0051; FRL-8805-5. RIN 2070-AD58.

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). 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 (>1000–10 000 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 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 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 Mn of <1000 Da and oligomer content of >1 %.

Molecular Weight distribution (MWD) are sometimes characterized by the ratio of different averages, the "polydispersity index". 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.

References

Size

- Leeson, Paul. Drug discovery: Chemical beauty contest. Nature 481, 455–456 (26 January 2012)
- Information to be considered in a weight-of-evidence-based PBT/vPvB assessment of chemicals (Annex XIII of REACH).ECETOC Special Report No.18. Brussels, July 2014.
- Ming-Qiang Zhang and Barrie Wilkinson. Drug discovery beyond the 'rule-of-five'. Current Opinion in Biotechnology 2007, 18:478–488.

Molecular Weight

- Beyer EC, 1993. Gap junctions. Int Rev Cytol 137:2.
- DeMello WC, Ed., Cell-to-Cell Communication, Plenum Press, NY, 1987, p.34.
- Molecular Biology of the Cell, 3rd Ed., Alberts B, Bray D, Lewis J et al., Gaeland Science, NY, 1994, pp 958, 963.
- Organisation for Economic Co-operation and Development. (2009). Data analysis of the identification of correlations between polymer characteristics and potential for health or ecotoxicological concern. OECD Task Force on New Chemicals Notification and Assessment, Expert Group Meeting on Polymers. Pp 9, 37.
- Henry et al., 2018. Integr Environ Assess Manag 2018:316–334. Supplemental Data, page 10.

Molecular weight distribution

- Ebnesajjad, 2011. Introduction to fluoropolymers. In: Kutz M, editor. Applied plastics engineering handbook. New York (NY): Elsevier. p 49–60
- Starkweather Jr HW and Wu S. 1989. Molecular weight distribution in polymers of tetrafluoroethylene. Polymer 30:1669–1674.

Ionic character

Ionic character can be described as anionic or cationic. If the molecule contains both cationic and anionic groups, it is called a zwitterion. Nonionic molecules are in the table marked as "neutral". 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).

References

- Ebnesajjad S. 2011. Introduction to fluoropolymers. In: Kutz M, editor. Applied plastics engineering handbook. New York (NY): Elsevier. p 49–60.
- Auer CM, Nabholz JV, Baetcke KP. 1990. Mode of action and the assessment of chemical hazards in the presence of limited data: Use of structure-activity relationships (SAR) under TSCA, Section 5. Environ Health Perspect 87:183–197.
- [USEPA] US Environmental Protection Agency. 1997a. Chemistry assistance manual for premanufacture notification submitters. Washington (DC). EPA 774-R-97-003. March 1997.
- [NICNAS] National Industrial Chemicals Notification and Assessment Scheme. 2016. NICNAS Handbook Guide for importers and manufacturers of industrial chemicals in Australia. Sydney (AU). [cited 2017 July 12]. http://webarchive.nla.gov.au/gov/20161017033100/https://www.nicnas.gov. au/regulation-and-compliance/nicnas-handbook

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 a ratio between molecular weight of repeating units with functional groups and the molecular weight of the polymer. Depending on the FGEW a polymer can qualify as PLC (USEPA 1997b). The FGEW of a polymer is defined as the ratio of the Mn to the weight 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 higher the potential for health and environmental impact (OECD 2009, p 10).

References

- [USFR] US Federal Register. 2012. Polymers (b). 40 CFR Sect 723.250.
- [USEPA] US Environmental Protection Agency. 2010. Reviewing new chemicals under the Toxic Substances Control Act (TSCA) EPA's Review Process - Chemical categories used to review new chemicals under TSCA: TSCA New Chemicals Program (NCP) Chemical Categories. Washington (DC): USEPA Office of Pollution Prevention and Toxics. [cited 2017 July 12]. http://www.epa.gov/oppt/newchems/pubs/npcchemicalcategories.pdf

Functional Group Equivalent Weight (FGEW) References

- [NICNAS] National Industrial Chemicals Notification and Assessment Scheme. 2016. NICNAS Handbook Guide for importers and manufacturers of industrial chemicals in Australia. Sydney (AU). [cited 2017 July 12]. http://webarchive.nla.gov.au/gov/20161017033100/https://www.nicnas.gov.au/regulation-and-compliance/nicnas-handbook
- [OECD] Organisation for Economic Co-operation and Development. Data Analysis of the Identification of Correlations between Polymer Characteristics and Potential for Health or Ecotoxicological Concern, OECD, Paris, 2009.

Low MW Leachables

Low MW Leachables are chemical molecules, either inorganic or organic, that can be extracted from 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) or additives like stabilizers, plasticizers etc. 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 extractability 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.

References

- BIO by Deloitte. 2015. Technical assistance related to the review of REACH with regard to the registration requirements on polymers Final report prepared for the European Commission (DG ENV), in collaboration with PIEP.
- Ebnesajjad S. 2011. Introduction to fluoropolymers. In: Kutz M, editor. Applied plastics engineering handbook. New York (NY): Elsevier. p 49–60.

Particle size

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

Structural and elemental composition

In the United States, Chemical Categories of Concern (2010) 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). 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 pre-manufacture 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 decision 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.

Structural Similarities to Polymers of Concern or High Concern "Chemical Categories"

- https://www.epa.gov/reviewing-new-chemicals-under-toxic-substances-control-act-tsca/chemical-categories-used-review-new

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 (1×10^{-6} mg/L; 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 mg/L–10 000 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).

Water and Lipid Solubility and the Octanol Water Partition Coefficient

- Organisation for Economic Co-operation and Development. (2009). Data analysis of the identification of correlations between polymer characteristics and potential for health or ecotoxicological concern. OECD Task Force on New Chemicals Notification and Assessment, Expert Group Meeting on Polymers.

The octanol–water partition coefficient (Kow) is another criterion to assess chemicals and their environmental and health impact. The Kow 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 Kow, the more lipophilic the compound. Typically, a Kow >5000 or a log Kow >5 means high lipophilicity and, thus, a high potential to bioaccumulate or bioconcentrate. Numerous studies showed that Kow 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.

References

- [UNEP] United Nations Environment Programme. 2001. Conference of Plenipotentiaries on the Stockholm Convention. UNEP/POPS/CONF/2. [cited 2017 July 12]. http://www.wipo.int/edocs/trtdocs/en/unep-pop/trt_unep_pop_2.pdf

Stability

Stability is resistance to physical, chemical, or biological transformation. Loss of stability can result in the polymer breaking 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.

References

- Drobny JG. 2006. Fluoroplastics. Shropshire (UK): Rapra Technology. p 12.
- Gangal SV, Brothers PD. 2015. Perfluorinated polymers. In: Kirk-Othmer encyclopedia of chemical technology. New York (NY): Wiley. p 1–68.

Abiotic stability

Polymers are generally regarded as 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.

References

- Arkles B. 1973. Recycling polytetrafluoroethylene in polymer science and technology. In: Guillet J, editor. Polymers and ecological problems, Vol. 3. New York (NY): Plenum. p 122.

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.

References

- King MW,Gupta BA,Guidoin R. 2013. Biotextiles as medical implants:15. Vascular prostheses for open surgery. Cambridge (UK): Woodhood. p 434–484.
- Ruwona and Henry 2021. PTFE: Persistence without hazard at environmentally relevant temperatures and durable by design. Fluoros 2021, Providence, R.I.

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."

References

- Puts G, Crouse P, Ameduri B. 2014. Thermal degradation and pyrolysis of polytetrafluoroethylene. In: Smith DW, Iacano TS, Iyer SS, editors Handbook of fluoropolymer science and technology. New York (NY):Wiley. p 81–104.
- [SPI] Society of the Plastics Industry. 2005. SPIs guide to safe handling of fluoropolymers. Washington (DC).
- Drobny JG. 2006. Fluoroplastics. Shropshire (UK): Rapra Technology. p 12.
- Arkles B, Bonnett R. 1974. Method for the depolymerization of polytetrafluoroethylene,US 3832411A

4. Tables 4 and 5 PLC Criteria Data - Methods and References

In this Chapter, methods, references and/or descriptions for each polymer in the study are described as provided by the study participants. These data were used to assess each of the various inputs shown in the main manuscripts Tables 4 & 5.

4.1 Polyvinylidene Fluoride – PVDF and 4.2 PVDF COPOLYMER PVDF Co-polymer

Molecular weight characterization and oligomer content.

Several PVDF samples (100 % solids – pellets or powder form – homopolymer and copolymer) were characterized by SEC analysis (See parameters below*). Typically, 20 to 40 mg of solids were dissolved in DMSO to obtain a 2 g/L concentration of polymer in the solution. Testing was performed according to the following testing methods:

[1] Determination of the Number-Average Molecular Weight and the Molecular Weight Distribution of Polymers Using Gel Permeation Chromatography, OECD guideline for testing of chemicals n° 118, adopted: 14.06.96

[2] Determination of the Low Molecular Weight Content of a Polymer Using Gel Permeation Chromatography, OECD guideline for testing of chemicals n° 119, adopted: 14.06.96

Other solvents may be used (NMP, DMA, DMF) that are able to allow dissolution at room temperature, avoiding heating of the solution at high temperature.

Molecular weight values were determined by calibrating the system against narrow molecular weight PMMA standards.

Depending on the grade (homopolymer or copolymer, content of each of the monomer) and production manufacturing process (i.e. producer) Mn can vary from 70000 to 300000. The Mw/Mn vary from 2 to 3.

Those measurements are similar to the ones defined in several references:

Melting Point Depression and Kinetic Effects of Cooling on Crystallization in Poly(vinylidene fluoride)-Poly(methyl methacrylate) Mixtures. T. Nishi1 and T. T. Wang (1975)

Characterization of Randomly Branched Poly(vinylidene fluoride) : Lotfi Hedhli, Nafaa Mekhilef, Stephane Moyses, and Russell H. Lewis (2007)

By the same technique, percent (%) oligomers have been evaluated. The standard deviation of the method is about 0.3 %. Depending on the grade (and potentially the manufacturer) and knowing the method standard deviation oligomers (Mn<1000Da) content measured on average is 0.5%+/-0.3% and oligomers (Mn<500Da) content measured on average is 0.5%+/-0.3%

Ionic character and Functional groups

Comprehensive Characterization of Chain End Groups of Vinylidene Fluoride Based Polymers (Macromol.Symp.2013,324,41-48)

The PVDF homopolymerization and copolymerization process leads by design to a neutral polymer with neutral end-groups. There is no evidence for cationic groups nor are they to be expected. The PVDF homo and copolymers does not include reactive functional groups by design.

Leachables and Monomer content

The SEC characterization determined the weight fraction below 1000Da to be under 1% maximum and more generally below 0.5% +/- 0.3%. No change of this fraction is significantly seen after different kind of ageing conditions (heat, in water, etc). Water used for ageing shows no detection of Mw<1000 Da with NMR 19F with a limit of detection of less than 500 ppm. Therefore, low molecular weight oligomers that might be present in the polymer are not extractable.
This was confirmed as polymer pellets have no active leachables as tested by USP Class VI and ISO 10993. Additionally, residual monomers were detected under 50 ppb in all polymer samples tested (different grades of homopolymers and copolymers) by Dynamic or Static HS-GC/MS (method selected can change depending on the grade tested). Those methods are not described in detail here as they are considered as company proprietary. The headspace is generated at 150 °C during 20min. The limit of quantification may vary depending on the sample characteristic and the chosen technique adapted to this sample. Several samples demonstrate even a residual monomer content <10pbb w/w. Using the limit of quantification instead of actually detected monomer the ratio of limit of quantification to molecular weight is estimated at or below 10^{-13}.

Physicochemical Properties
The water solubility according to USP 34 NF29 is described as practically insoluble or insoluble. The octanol/water partitioning coefficient does not apply to PVDF as it is not soluble in either octanol or water. PVDF is commercially available in several forms. Particle size varies, depending on the composition of the grade and the production equipment from the manufacturer.

Stability (hydrolysis, light, oxidation, biodegradation, thermal)
PVDF products demonstrate stability properties similar to other fluoropolymers: high stability in numerous harsh environments, e.g. heat, temperature cycling, oxidative and UV exposure.
The very high stability of PVDF has been demonstrated:
Regarding UV exposure, several studies demonstrate that PVDF based coatings are not fading and shows no degradation (visual, mechanical, oxidation) after more than 30 years of exposition to weather in Florida (*Wood.K, 2002. Effect of Fluoropolymer Architecture on the Exterior Weathering of Coatings - XXVI FAPITEC Congress. In HP.Adler; Macromolecular Symposia: Quo Vadis Coatings , 2003; Wiley-VCH.).* In addition, internal lab testing have been performed. Samples of different grades of PVDF (pellets and transformed pieces), have been tested after 1000h UV exposure. The samples have been tested by SEC (similar method than the one mentioned for Molecular Weight characterization). No significant difference before/after ageing has been observed in molecular weight distribution. The same conclusion for the % of Mn<1000 Da, in both cases the value was <0.25 %. The product remains stable and no leachables are generated. Physical properties were unchanged as well.

Similar conclusions are observed after ageing in different conditions of pellets and test pieces for homopolymer and copolymer: 744h @90 °C in air, 744h@140 °C in air, 742h @90 °C in dinitrogen, 744h @60 °C in HCl, 744h @90 °C for homopolymers in water and @60 °C for copolymer in water. The cited testing conditions have demonstrated the stability of the polymer at high T° and in oxidative, acidic environment. In each case, the % of Mw<1000 Da is below 0.25 %. There was no difference in the mass distribution observed when we compare before and after ageing. In addition, when tested in water, the water used for ageing shows no detection of Mw<1000 Da with NMR ^{19}F with a limit of detection of less than 500 ppm.
The hydrolysis resistance was demonstrated via the existence of the ISO10931 standard regarding Plastics piping systems for industrial applications — Poly(vinylidene fluoride) (PVDF) — Specifications for components and the system. Finally, the high resistance of these PVDF polymers to hydrolysis is also mentioned by *Ebnesajjad - 2013 - Introduction to Fluoropolymers Materials, Technology and Applications - Chapter 9 - Introduction to Vinylidene Fluoride*
The thermal degradation resistance has also been demonstrated by
1. S. Zulfiqar and al. Study of the thermal degradation of polychlorotrifluoroethylene, poly(vinylidenefluoride) and copolymers of chlorotrifluoroethylene and vinylidene fluoride, In Polymer Degradation and stability 43(1994) 423-430 - Elsevier
2. Laurence W. McKeen - Book - The Effect of Long Term Thermal Exposure on Plastics and Elastomers - 2014

PVDF is insoluble and with its specific chemical structure it is also non-biodegradable.

PVDF has been tested according to OECD 301F – Aerobic biodegradability for 28 days showing no biodegradation. PVDF has also been tested according to ASTM D5511 – Anaerobic biodegradability demonstrating no biodegradation after 90 days representing 6.25 years of landfill. Those two test methods are state of the art in environmental studies. In addition, in each test no presence of by-products in the environment has been detected.

SEC Parameters
Isocratic pump P600 from WATERS (Milford, MA, US)

- Sample management/injector module WISP717 from WATERS
- Solvent: Dimethyl sulfoxide (DMSO) from Alfa Aesar (Heyshame, Lancashire, United Kingdom)
  - stabilized with 0.1 M sodium nitrate (NaNO3) from Merck (Darmstadt, Germany)
  - Dissolution at 95 °C for 4h
  - Flow rate: 1mL/min
  - Column Temperature: 50 °C
  - A set of three columns: 300x8mm 7µm PFG 4000 Å (ref. PFA0830074E3) 300x8mm 7µm PFG
  - 1000Å (ref. PFA0830071E3) and 300x8mm 7µm PFG 100Å (ref. PFA0830071E2) columns
  - from Polymer Standards Service (Mainz, Germany). Maximum nominal molecular weight of these column set is 3,000,000

- Sample concentration: 2 g/L
- Injection volume: 200 µL
- Refractive Index Detector (RID) –2414 model from WATERS
- RID temperature: 50 °C
- Polymethylmetacrylate (PMMA) standards calibration with molecular weights ranging from
- 1900000 to 1102 g/mol (1900000 to 1850 from Varian, Inc. (Palo Alto, CA, US), and 1102 from
- Polymer Standards Service). 3rd order fit for the calibration curve
- Data treatment: PSS WinGPC Unity version SR1 Build 5403 from Polymer Standards Service

4.3 Ethylene Chlorotetrafluoroethylene Copolymer- ECTFE and 4.4 ECTFE TERPOLYMER

Molecular weight characterization and oligomer content.

Copolymer and terpolymer ECTFE, both in pellet form, were characterized with GPC using internal company resources.

Equipment conditions

Measurement Instrument: Agilent PL220 high temperature GPC system
Detector: RI
Solvent: 1-chloronaphthalene
Column (maker, model no.): 2x PL Gel mixed B, 10 µm, 300 x 7.5 mm + PLgel mixed guard column 5 µm
Temperature: 210 °C
Flow rate: 0.7 mL/min
Injection System, Injection Volume and Test Concentration: 200 µL, 3 mg/mL
Data Processing: Cirrus GPC

Polystyrene standards from Agilent Technologies with certified molecular weights were used.
Method and criteria: Cubic calibration assigning the retention times at the peak to the certified Mp value of the calibration standards.
Injection volume and concentration of the calibration standards: 200 µL, 0.6 – 3.2 mg/mL.

Test method

Polymer molecular weight distribution and averages were measured according to OECD TG 118 guideline.

Ionic character, reactive functional groups, functional group equivalent weight

The ECTFE copolymerization and terpolymerization processes lead by design to a neutral polymer with neutral end-groups. There is no evidence for cationic groups nor are they to be expected.

Low molecular weight leachables

No molecular weight fractions < 1000 Da are observed on the GPC chromatogram of ECTFE copolymer and terpolymer that could be associated with any leachable compound either able to enter biological cells or overall.

Residual Monomers

Residual monomers were detected at levels less than 50 ppb w/w in all polymer samples tested (different grades of homopolymers and copolymers) by Dynamic or Static HS-GC/MS (method selected can change depending on the grade tested). Those methods are not described in detail here as they are considered company proprietary. The headspace is generated at 150 °C during 20min. The limit of quantification may vary depending on the sample characteristic and the chosen technique adapted to this sample.
Ratio of residual monomers to molecular weight is estimated at or below 10^{-13}.

Particle size distribution

To determine the particle size distribution of ECTFE in powder form, the diffraction laser technique was used. Method ISO 13320
Instrument: Beckmann Coulter Laser granulometer LS 13 320 with dry module
Laboratory Instrumentation
Dry ECTFE SOP
Measurement of D10% - D50% - D90% based on ISO 13320

Physicochemical Properties

Similarly, to other high molecular weight fluoropolymers (e.g. PVDF), ECTFE can be considered practically insoluble in water. The octanol/water partitioning coefficient does not apply to ECTFE fluoropolymers as they are not soluble in either n-octanol or water.

Stability (hydrolysis, light, oxidation, biodegradation, thermal stability)

Similarly to other fluoropolymers, ECTFE products demonstrate high stability in numerous harsh environments, e.g. heat, temperature cycling, oxidative and UV exposure.
Some relevant literature on ECTFE properties:
(1) Encyclopedia of polymer science and engineering Vol.3, John Wiley & Sons, WlLEY-INTERSCIENCE PUBLICATION (1985); page 480 – onward Primary Reference
(2) Halar ® ECTFE Design & Processing Guide, Solvay Specialty Polymers Primary Reference https://www.solvay.com/sites/g/files/srpend221/files/2018-07/halar-ectfe-design-and-processing-guide-en.pdf
(3) Halar® ECTFE Electrostatic Powder Coating - Processing Guide
(4) Halar ECTFE - Typical Properties https://www.solvay.com/en/brands/halar-ectfe/properties
(5) TDS_Halar_copolymer_500LC https://www.solvay.com/en/product/halar-500-lc
(6) TDS_Halar_terpolymer_6014 https://www.solvay.com/en/product/halar-6014

4.5 Polychlorotrifluoroethylene – PCTFE

Molecular weight

PCTFE can be dissolved in 1,1,3-trifluoropentachloropropane, 2,5-dichlorobenzotrifluoride, or o-chlorobenzotrifluoride at high temperatures. Molecular weight can be measured by the osmometry method. Kaufmann et. al. proposes the formula which express the relationship between extreme viscosity and molecular weight. The average molecular weight of commercial PCTFE grade is considered to range from 70000 to 400000 units.

Formula: [η]=6.15×10^-5×M^0.74

(E.K. Walsh and H.S. Kahfman, J. Polymer Sci. A1 833 (1963))

("PCTFE". *Fluoropolymer handbook*, edited by Takaomi Satokawa, Nikkan Kogyo Shimbun, **1990**, pp. 340-341).

Data has been obtained for the 2 PCTFE grades by melt viscoelastic method (Parallel plate rheometry) at 250 °C. Mn were 810000 and 950000

Molecular weight distribution

Data has been generated for the 2 PCTFE grades by melt viscoelastic method (Parallel plate rheometry) at 250 °C. Mw/Mn was around 3.

Oligomer Content

Negligible. Based on multiple 8-hr reflux extractions using polymer pellets with various solvents. Internal CTFE M400H FDA 177.1380 Data

Ionic Character

The polymerization process leads by design to a neutral polymer with neutral or anionic end-groups. There is no evidence for cationic groups nor are they to be expected.

Reactive Functional group (RFG)

The fluoropolymer does not include reactive functional groups like acrylates, isocyanates, anhydrides or aziridines by design.

Functional Group Equivalent Weight (FGEW)

Due to the lack of functional groups the term "equivalent weight" is not applicable.

Low Molecular Weight Leachables

Negligible. Same extraction methods as noted for Oligomer Content

Residual Monomers

Negligible. CTFE monomers has a boiling point of -27.8 °C (-18 °F). In the process of extrusion for pelletizing and drying in manufacturing process of PCTFE, all the residual monomers are volatilized.

Ratio of Residual Monomers to Molecular Weight

Less than 10^{-5}

Structural Similarities to RFG of Concern
None

Reference Standards
ASTM D7194-12
ASTM D1430-17
ASTM D3595-14
ASTM D7211-13

Water Solubility
Negligible. Method used: pellets with 100 milliliters of distilled water at reflux temperature for 8 hours (CTFE M400H FDA 177.1380 Data)

Octanol/Water Partition Coefficient, Kow
N/A. PCTFE is not soluble in water and n-octanol

Particle Size
Pellet 2-4 mm
Flake 0.5-4 mm
Powder 5-300 micron

Oxidation, Hydrolysis Stability
The chemical resistance of PCTFE is slightly inferior to PTFE, but superior to other polymeric materials. PCTFE exhibits good chemical resistance to strong acids, strong alkalis, mixed acid, oxidized agents, etc.
("PCTFE". *Daikin Fluoropolymer handbook*, Daikin Industries, LTD., **2011**, pp.99-101).

Biodegradation
There is no data that directly indicates biodegradation.
Note that the first step of biodegradation is depolymerization in the environment (heat, sunshine, and acid rain). PCTFE has resistance against severe environments. Therefore, the first step does not proceed.
("PCTFE". *Daikin Fluoropolymer handbook*, Daikin Industries, LTD., **2011**, pp.99-101).

Light Stability
PCTFE shows little degradation depending on UV rays. Company internal data shows mechanical properties (TS/EL) are kept after 3000 hr Sunshine Carbon Ark exposure (63 centigrade, 60 %RH).
("PCTFE". *Fluoropolymer handbook*, edited by Takaomi Satokawa, Nikkan Kogyo Shimbun, **1990**, pp. 346).

Thermal Stability

The melting point of PCTFE is affected by crystallinity and is roughly 212 °C to 217 °C. The glass transition temperature exists around 50 °C. PCTFE results in degradation with weight loss above 300 °C.
("PCTFE". *Fluoropolymer handbook*, edited by Takaomi Satokawa, Nikkan Kogyo Shimbun, **1990**, pp. 342).

Maximum Continuous Usage Temperature
Use max temperature: 120 °C
("PCTFE". *Daikin Fluoropolymer handbook*, Daikin Industries, LTD., **2011**, pp.10).

Recommended Molding Temperature/Use Temperature
Molding temperature:230-330 °C
Use max temperature:120 °C
("PCTFE". *Daikin Fluoropolymer handbook*, Daikin Industries, LTD., **2011**, pp.10, 106).

4.6 Fluoroethylene Alkyl Vinyl Ether - FEVE

FEVE resins are polymers consisting of alternating **f**luoro**e**thylene and alkyl **v**inyl **e**ther segments. 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. Thus, FEVE resins are used to make ultra-weatherable coatings for architectural, aerospace, automotive, bridge and industrial maintenance markets.

Molecular weight characterization and oligomer content
Several uncured FEVE resin samples were characterized by SEC analysis. Approximately 100 mg of solid was dissolved in THF to obtain a 10 g/L concentration of polymer in the solution. The following test methods were used to characterize FEVE fluoropolymer resins:
[1] Determined Number-Average Molecular Weight and Molecular Weight Distribution by using Gel Permeation Chromatography, OECD guideline for testing of chemicals n° 118, adopted: 14.06.96
[2] Determined the Low Molecular Weight Content using Gel Permeation Chromatography by using OECD guideline for testing of chemicals n° 119, adopted: 14.06.96
Molecular weight values were determined by calibrating the system against narrow molecular weight polystyrene standards.
Depending on the grade, Mw can vary from 7,000 to 46,000. These values are for uncured FEVE resins. It is expected that the cured resins will have significantly higher molecular weight. Due to their insolubility, the actual MW cannot be accurately determined. The molecular weight distribution was determined to vary between 2.0 – 4.0 depending on the grade of FEVE.

The same technique was used to determine the % of oligomers. Depending on the uncured grade, the content of oligomers with Mn<1000 Da is reported as <3.5 % and the content of oligomers with Mn<500 Da is reported to be <0.7 %.

GPC Conditions
(1) Apparatus: TOSHO GPC HLC-8320
(2) Pump: HLC-8320 combined unit

(3) Detector: RI
(4) Solvent: THF
(5) Columns : Manufacturer, model no. : Shodex GPC KF-802 x 1, GPC KF-806M x 2
(6) Temperature: 40 ℃
(7) Flow rate: 1.0mL/min
(8) Injection volume and concentration of sample: 30μ, 1% conc.

The cured FEVE resins are expected to have negligible oligomer content.
The residual monomers are largely from the non-fluorinated monomer component used in the manufacturing process.

Ionic character and functional groups
The polymerization process leads by design to a polymer with neutral or anionic end-groups. There is no evidence for the formation of cationic groups nor would they be expected.
FEVE resins contain hydroxyl and carboxyl functional groups. Hydroxyl or carboxyl functional group equivalent weight may vary $>10^2$. These functional groups are classified as low concern RFG by the US EPA. (and OECD: https://www.oecd.org/env/ehs/risk-assessment/42081261.pdf). Therefore, the FGEW is not of concern for these polymers.

Leachables
The SEC characterization determined the weight fraction below 1000 Da to be under 5 % for FEVE having the smallest molecular weight. Generally, FEVEs are used after crosslinking, therefore the resins are expected to have a very low oligomer content below 1000 Da after cross-linking/curing.

Liquid or emulsion type FEVE resins contain some quantities of residual monomers. The residual monomers present are dominated by the non-fluorinated monomers, which account for greater than 99 % of the residual monomers. The weight fraction may vary under 2 wt %. Testing for residual monomers was based on Gas Chromatography.

Physicochemical Properties
FEVE resins are insoluble in water. Since the FEVE resins are insoluble in both water and n-octanol, determination of a Kow is not possible and therefore is not applicable.
FEVE resins are commercially available in several forms: as a solution in an organic solvent, as flakes or as a water-based dispersion.

Stability
FEVE based coatings provide outstanding stability in a variety of harsh environments.
UV exposure studies demonstrate that FEVE based coatings do not fade and show no degradation after more than 30 years of exposition. (S. Ochi, T. Takayanagi ” The Progress of Weathering Performance using Fluoro-polymer Topcoat System For around 30 years exposure” NACE international’s corrosion Conference 2019). In addition, FEVE based coatings exposed for 15,000 hour of UV exposure in Weather-meter retain their gloss and colors. (L.Capino

"FLUORO-URETHANES COATINGS WITH EXTREME EXTERIOR DURABILITY" PACE2007 *Paint* and *Coatings* Expo)
Additional data and discussion is provided on hydrolysis and oxidation in the following reference: Robert Parker and Kristen Blankenship, ASM Handbook, Volume 5B, Protective Organic Coatings K.B. Tator, editor; 2015; pp 88-95

Biodegradation: No direct data is provided on biodegradation. However, the properties exhibited by FEVE do lead to the conclusion that cured FEVE is not expected to biodegrade.

Thermal Stability:

The thermal decomposition temperature begins at 220 °C which is the point at which 1 % decomposition occurs. This value has been determined by TGA. Graphical representation of these data has been provided and verified.

Recommended Processing/Application Temperature (°C):

Typical curing temperature for solvent grades is room temperature to 180 °C and for powder grades it is 200 °C. See ASM Handbook reference cited above.

4.7 EFEP

Molecular Weight and **Molecular Weight Distribution** were determined by the parallel plate rheometry method. The details and references of this method are given below.
Calculation method of Mw and Mn by parallel plate rheometry method:

(1) Measure the viscosity at 1 rad / sec every 5 °C and measure the relationship between temperature and viscosity.

(2) Omit the high temperature part where the influence of thermal decomposition is seen and Omit the low temperature part where the influence of the phase transition is seen.

(3) Apply the temperature dependence to the formula of Ln (η0) = (A) + (B) x 1000 / K and obtain the coefficients (A) and (B). (A) is a parameter that depends on the molecular weight, and (B) is a parameter that depends on the resin skeleton. K is the absolute temperature

(4) In principle, when (A) and (B)are obtained, the viscosity at the desired temperature can be estimated.

(5) Zero shear viscosity approximation: When melt-viscosity converges at 0.01 rad/sec or more, zero shear viscosity should be converged complex viscosity. When melt-viscosity does not converge, zero shear viscosity should be complex viscosity at 0.01 rad /sec.

(6) Obtain the weight-average molecular weight (Mw) from the relational expression (1) between the zero-shear viscosity and the weight-average molecular weight.

(7) Calculate the value of molecular weight distribution (Mw/Mn) from the frequency dependence of the storage elastic modulus at 270 ℃ by the method of Tuminnello's literature (ref 2).

(8) Calculate Mn from Mw and Mw / Mn

For EPEP the Mw was calculated to be 130,000 and the MWD was determined to be 4.

Method references:

(1) S. Wu, Macromolecules, Vol. 18, No. 10, 1985

(2) W. H. TUMINELLO, POLYMER ENGINEERING AND SCIENCE, MAY 1989, Vol. 29, No. 10

Oligomer Content
Negligible
0.1 wt % at most based on the weight loss of the polymers at the condition of 165 °C x 1hr

Ionic Character
The polymerization process leads by design to a neutral polymer with neutral or anionic end-groups. There is no evidence for cationic groups nor are they to be expected.

Reactive Functional group (RFG)
The fluoropolymer does not include reactive functional groups like acrylates, isocyanates, anhydrides or aziridines by design.

Functional Group Equivalent Weight (FGEW)
Due to the lack of functional groups the term “equivalent weight” is not applicable.

Low Molecular Weight Leachable
Negligible. Based on multiple 8-hr reflux extractions using polymer pellets with various solvents.

Residual Monomers
Negligible.
TFE monomers has a boiling point of -76.3 °C (-105.3 °F).
HFP monomers has a boiling point of -29.4 °C (-20.92 °F).
Ethylene monomers has a boiling point of -104 °C (-155.2 °F).
In the process of drying in manufacturing process of EFEP, all the residual monomers are volatilized.

Ratio of Residual Monomers to Molecular Weight
Less than 10^5

Structural Similarities to RFG of Concern
None

Reference Standard: ASTM D7472

Water Solubility
Negligible. Method used: pellets with 100 milliliters of distilled water at reflux temperature for 8 hours (*Fluoropolymer handbook*, JFIA, **2020**, pp.172).

Octanol/Water Partition Coefficient, Kow
N/A because EFEP is not soluble in water and n-octanol

Particle Size
Pellet 2-4 mm

Oxidation, Hydrolysis Stability
The chemical resistance of EFEP is similar to ETFE. EFEP exhibit good chemical resistance to strong acids, strong alkalis, mixed acid, oxidized agents, etc,
("EFEP". *Daikin Fluoropolymer handbook*, Daikin Industries, LTD., **2011**, pp.86).

Biodegradation
Stable because this material exhibits heat and strong acid resistance.
("EFEP". *Daikin Fluoropolymer handbook*, Daikin Industries, LTD., **2011**, pp.86).

Light Stability
EFEP shows little degradation depending on UV rays because of minimal absorption of UV light.
("Neoflon EFEP". Brochure, Daikin Industries, LTD**., 2003**, pp. 4).

Thermal Stability
EFEP provides relatively low melting point (160-190 ℃) and high decomposition temperature (357-380 ℃) .
("EFEP". *Daikin Fluoropolymer handbook*, Daikin Industries, LTD., **2011**, pp.86).

Maximum Continuous Usage Temperature
Use max temperature: 130 ℃
Based on company-owned data

Recommended Molding Temperature/Use Temperature
Molding temperature:200-280 ℃
Use max temperature:130 ℃
("EFEP". *Daikin Fluoropolymer handbook*, Daikin Industries, LTD., **2011**, pp.87).

4.8 CPT

Molecular Weight and **Molecular Weight Distribution** were determined by the parallel plate rheometry method.

For CPT the Mw was calculated to be 200,000-300,000 and the MWD (Mw/Mn) was determined to be between 2-5.

Oligomer
Negligible. 0.1 wt % at most based on the weight loss of the polymers at the condition of 185 °C x 1hr

Ionic Character
The polymerization process leads by design to a neutral polymer with neutral or anionic end-groups. There is no evidence for cationic groups nor are they to be expected.

Reactive Functional group (RFG)
The fluoropolymer does not include reactive functional groups like acrylates, isocyanates, anhydrides or aziridines by design.

Functional Group Equivalent Weight (FGEW)
Due to the lack of functional groups the term “equivalent weight” is not applicable.

Low Molecular Weight Leachables
Negligible. Based on multiple 8-hr reflux extractions using polymer pellets with various solvents.

Residual Monomers
Negligible.
CTFE monomers has a boiling point of -27.8 °C (-18 °F).
TFE monomers has a boiling point of -76.3 °C (-105.3 °F).
In the process of drying in manufacturing process of PCTFE, all the residual monomers are volatilized.

Ratio of Residual Monomers to Molecular Weight
Less than 10^{-5}

Structural Similarities to RFG of Concern
None

Reference Standard
ASTM D7471

Water Solubility
Negligible.

(*Fluoropolymer Handbook*, JFIA, **2020**, pp.172).

Octanol/Water Partition Coefficient, Kow
N/A because the polymer is not soluble in either water or n-octanol

Particle Size
Pellet 2-4 mm

Oxidation, Hydrolysis Stability
CPT exhibit good chemical resistance to strong acids, strong alkalis, mixed acid, oxidized agents, etc.
("CPT". *Daikin Fluoropolymer handbook*, Daikin Industries, LTD., **2011**, pp.59).

Biodegradation
Stable because this material exhibits heat and strong acid resistance.
("CPT". *Daikin Fluoropolymer handbook*, Daikin Industries, LTD., **2011**, pp.59).

Light Stability
CPT shows little degradation because of minimal absorption of UV light.
("CPT". *Daikin Fluoropolymer handbook*, Daikin Industries, LTD., **2011**, pp.60).

Thermal Stability
EFEP provides relatively low melting point (239-251 °C) and high decomposition temperature (more than 400 ℃) *handbook*, Daikin Industries, LTD., **2011**, pp.58).

Maximum Continuous Usage Temperature
Use max temperature: 200 °C
("CPT". *Daikin Fluoropolymer handbook*, Daikin Industries, LTD., **2011**, pp.58).

Recommended Molding Temperature/Use Temperature
Molding temperature:310-330 °C
Use max temperature:200 °C
("CPT". *Daikin Fluoropolymer handbook*, Daikin Industries, LTD., **2011**, pp.58,61).

4.9 THV

THV is a fluorothermoplastic product family with similar but somewhat different compositions. Some products are soluble in organic solvents and are used as example since they can be characterized by typical polymer characterization methods. Other THV grades are insoluble in typical organic solvents.

Molecular Weight Characterization

Six fluoropolymer samples (100% solids) were characterized by SEC analysis. Approximately 50 mg of solids were dissolved in 10 mL of THF (inhibited with 250 ppm BHT). The resulting

solution was run through a 0.45 micron syringe filter and analyzed by SEC. All samples were prepared and analyzed in duplicate.

SEC Conditions:

The SEC system was operated under the following conditions:

Sample:	100 mL Injection @ 5 mg/mL Tetrahydrofuran-inhibited
	*Sample filtered through 0.45 micron membrane
Mobile Phase:	Tetrahydrofuran-uninhibited, EMD OmniSolv or equivalent grade
Flow Rate:	1.0 mL/min
System:	Reliant
Detector:	ACS 950/14 Mass Detector; 60 °C
Columns:	PL-Gel-4 Columns; 300x7.8 mm each (104, 103, 500, 100 Å)
Standards:	Polystyrene, narrow dispersity; ranging 377,400 - 580 Mp;

(3rd order polynomial fit)

Molecular weight values were determined by calibrating the system against narrow molecular weight polystyrene standards. Tabulated below are the relative molecular weight and polydispersity values. The results are averages of duplicate injections.

THV Polymers

Sample Name	Mw	Mn	Mz	Mw/Mn	W% < 2500 Da
Lot #1	2.558E+05	1.445E+05	4.001E+05	1.77	0.0
Lot #2	2.455E+05	1.343E+05	3.904E+05	1.83	0.0
Lot #3	2.335E+05	1.266E+05	3.689E+05	1.85	0.0
Lot #4	2.401E+05	1.349E+05	3.723E+05	1.78	0.0
Lot #5	2.250E+05	1.206E+05	3.544E+05	1.87	0.0
Lot #6	2.246E+05	1.258E+05	3.404E+05	1.79	0.0

As a representation of the polymer the averages of the five lots from the table above are chosen for the main document: Mn = 131,000 and Mw/Mn = 1.8

Functional groups

The polymerization process leads by design to a neutral polymer with neutral or anionic end-groups. There is no evidence for cationic groups nor are they to be expected. THV does not include reactive functional groups like acrylates, isocyanates, anhydrides or aziridines by design. Due to the lack of functional groups the term “equivalent weight” is not applicable. No structural similarities to reactive functional groups of concern (RFG of Concern) are known.

Leachables

The SEC characterization determined the weight fraction below 1000 Da to be 0.0 wt%. Polymer pellets have no active leachables as tested by USP Class VI and ISO 10993. Additionally, no residual monomers were detected, but due to the limits of quantification an upper limit of 91 ppb for the sum of all monomers was set. Using the limit of quantification instead of actually detected monomer the ratio of limit of quantification residual (<91 ppb) to molecular weight (Mn=130000) is estimated at or below 10^{-13}. The testing for residual monomers was based on heated headspace GC/MS. Approximately one gram of each sample was weighed into a 20 mL headspace vial, and then capped with an aluminum crimp cap that had a PTFE-lined septum. The headspace vials were loaded into an Agilent Model 7694 headspace autosampler for analysis. The headspace-GC/MS system included an Agilent 6890 gas chromatograph and an Agilent Model 5973 Mass Selective Detector (MSD). For each analysis, the sample vial was heated at 200 °C for 30 minutes, and then a 1 mL volume of the headspace was injected into the gas chromatograph for analysis

Physicochemical Properties

The water solubility according to USP 34 NF29 is described as practically insoluble or insoluble. The octanol/water partitioning coefficient does not apply since THV is not soluble in either octanol or water. THV is commercially available in several forms: as melt pelletized pellets, as a coarse powders or as a water-based dispersion. Powders for use as additives are available in a particles size range from 400-750 µm. *Lavallée, C., Chapter 4: “Polymer Processing Additives (PPA)”, in Macnamara Jr., James (ed.), Film Extrusion Manual – Process, Materials, Properties, 3rd Edition, TAPPI Press, Atlanta, pp. 291–302 (2020) and*

Stability

THV is used in architectural application in fabric laminates which require long term stability under outdoor weathering conditions. S. Zehentmaier RFP 3/2015 Vol 10, 198 ff. (https://multimedia.3m.com/mws/media/1119313O/article-fluorothermoplastics-in-film-applications.pdf; https://www.3m.co.uk/3M/en_GB/p/d/b40070075/ and Laurence W. McKeen “The Effect of UV Light and Weather on Plastics and Elastomers” 4th ed. 2019 Plastics Design Library Elsevier pg. 384.). This illustrates the stability against hydrolysis, light, oxidation and biodegradation. The Danish Environmental Protection agency concluded that fluoropolymers cannot lead to the formation of long-chain PFCAs (Danish Environmental Protection Agency (2013). Survey of PFOS, PFOA and other perfluoroalkyl and polyfluoroalkyl substances. Part of the LOUS-review. *Environmental Project No. 1475, 2013. Danish Ministry of*

the Environment, The Danish Environmental Protection Agency. Pg. 27 ff https://www2.mst.dk/Udgiv/publications/2013/04/978-87-93026-03-2.pdf).

THV products demonstrate stability against hydrolysis in damp heat, temperature cycling, humidity freeze and UV exposure (Test Conditions: 121 °C, 2 bar pressure and 100 % RH. Samples were exposed until inner PET layer cracked. 3M™ Scotchshield™ Backsheet Film. The THV fluoropolymer barrier layer remains intact and well adhered and maintains its smooth surface structure. *https://multimedia.3m.com/mws/media/1128326O/3m-scotchshield-solar-backsheet-film.pdf?fn=10748%20Solar%20Backsheet%20Brochure%209).*

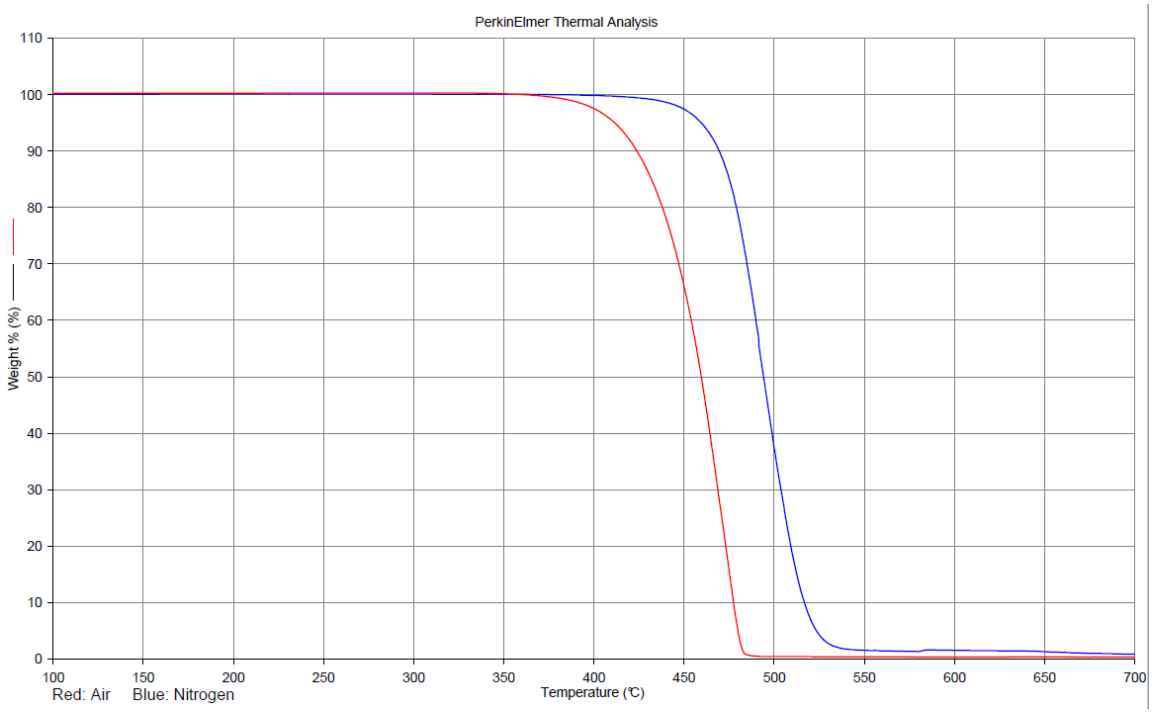
THV films are used in demanding safety glass applications due to their clarity and the fire performance – additionally demonstrating light stability. *https://www.3m.co.uk/3M/en_GB/design-and-specialty-materials-uk/applications/film-and-sheet/extruded-film/*

Excellent thermal stability and oxidative stability are also evident by the following application tests: 3M™ THV exhibits after 11,112 hours (1.27 years) at 200 °C virtually no degradation. The Limiting Oxygen Index (LOI) of 65 % was determined by ASTM 2863 and clearly exceeds the oxygen content in normal air *(https://multimedia.3m.com/mws/media/571351O/fluoroplastic-granules-thv-221gz-data-sheet.pdf also in "THV Fluoroplastics" in "Modern Fluoropolymers" Ed. By John Scheirs Wiley 1997, D.E. Hull; B.V. Johnson; I.P. Rodricks and J.B. Staley pg. 259).*

Recommended processing temperatures range from 200 – 270 ^{o}C melt temperature. (https://fluoropolymers.plasticseurope.org/application/files/6216/3178/0517/Fluoropolymers_Safe_Hand_EN__June_2021.pdf). Individual processing profiles are available at:

https://www.3m.co.uk/3M/en_GB/design-and-specialty-materials-uk/resources/download_and_services/

Based on the TGA sweeps in air and under nitrogen atmosphere below the polymer is stable up to 350 ^{o}C in air and up to 400 ^{o}C in nitrogen:


PerkinElmer Thermal Analysis
Weight % (%)
110
100
90
80
70
60
50
40
30
20
10
0
100
150
200
250
300
350
400
450
500
550
600
650
700
Temperature (°C)
Red: Air
Blue: Nitrogen

4.10 FEPM

FEPM is a fluoro rubber category described in ASTM D1418 as a fluoro rubber of the polymethylene type only containing one or more of the monomeric alkyl, perfluoroalkyl, and/or perfluoroalkoxy groups, with or without a cure site monomer. TetraFluoroEthylene-Propylene (TFE-P) is a major fluoroelastomer in this category

Molecular Weight Characterization and **Oligomer Content**

Three grades of FEPM were characterized by 2 different methods of GPC analysis.

[1] The samples 100H and 100S were dissolved in 1,2,4-trichlorobenzene (TCB) with 0.5 mg/mL 2,6-di-tert-butyl-4-methylphenol (BHT). The insoluble portion (extreme high molecular weight portion) of the samples were gravimetrically analyzed to calculate the actual sample concentrations in the solutions used for GPC analysis. The calibration and its accuracy were achieved by running a liner Polyethylene standard that was obtained from National Institute of Standards and Technology.

GPC conditions:

Samples were monitored using a HT-GPC Module 350A detector array by VISCOTEK, Data acquisition and handling were made with VISCOTEK software.

SOLVENT: Trichlorobenzene (TCB)/0.5 mg/mL BHT
FLOW RATE: 1.0 mL/min
INJECTION VOLUME: 200 uL
COLUMN TEMPERATURE: 160 degrees C and sample holder 150 degrees C
CONCENTRATION: ~ 2.5 mg/mL
COLUMN: 2 x Varian PLGel Mixed-B LS 30cm x 7.5mm
RUN TIME: 60 minutes
INTEGRATION METHOD: Known dn/dc
[2] The sample 150P was dissolved in THF. The sample and standards (known polystyrene) were dissolved and filtered in mobile phase.
GPC conditions:
SOLVENT: THF
FLOW RATE: 1.0 mL/min
INJECTION VOLUME: 150 uL
COLUMN TEMPERATURE: 40 degrees C
CONCENTRATION: 1.0 mg/mL
COLUMN: AM GPC Gel: Two Linear
DETECTOR: Waters 150C(64/25)
DATA MODULE: GPC Pro 3.13
Number of fraction total: 451

The results are tabulated below.

	Lot#	Mn	Mw	Mz	Mw/Mn	*Last 0.01wt% fraction
100H	H108016	198,116	274,819			
100S	S001007	140,265	222,836			
150P	P311003	44,000	145,900	406,850	3.32	Mw:4930

*The last fraction from a total 451 fractions was taken as last 0.01 wt% detection of injected sample amount, and the calculated Mw of the last fraction was described. It is concluded that a portion of Mw<4930 was less than 0.01 wt% of the sample.

Leachables

The GPC characterization determined the fraction which represent 4930 of molecular weight to be less than 0.01 wt%. It proved the weight fraction below 1000 Da to be far less than 0.01 %. FEPM polymer have no active leachables. FEPM fluoroelastomer was tested and had been certified as USP Class VI material.

Physicochemical Properties

The water solubility is described as practically insoluble.

FEPM is commercially available in several forms: as sheet, pellets, crumb, and latex as a water based dispersion. Particle size vary, depending on the composition of the grade and production equipment from the manufacturer.

Stability

As is a natural processing step for rubber, FEPM must be crosslinked. The outstanding heat and oil resistance of fluoroelastomers compared to other elastomers are discussed in the Fluoroelastomers Handbook: The Definitive User's Guide published by Jiri George Drobny. It classifies fluoroelastomer as 200 degrees C continuous service temperature material. It discloses that TFE and propylene monomers will be copolymerized with strong alternating tendency and commercial TFE-P elastomers are made slightly rich in TFE to avoid continuous propylene units that would tend to give lower thermal stability. TFE-P has outstanding steam and hot water resistance which demonstrates its stability against hydrolysis.

Ionic Character

The fluoroelastomer can have a few carboxylate end groups, however end groups in high molecular weight polymers do not change the ionic character of the polymer. Some grades have a small degree of unsaturation in their backbone due to the dehydrohalogenation that takes place during the process. This is how they can crosslink. See Appendices A & B

RFG's

The copolymer can have either double bonds or reactive sites in the backbone to enable thermal vulcanization. A few grades containing neither double bonds nor reactive sites can be cured by electron beam. Appendix C also shows FT-IR charts as Figure 4. None of the RFG's are considered high concern on the EPA list.

FGEW

FGEW can be optimized by dosage of double bonds or reactive sites by electron beams or by certain peroxides.

Residual Monomers

TFE and propylene monomers and both are gases at ambient temperature. Therefore, it is unlikely that they remain in the polymer matrix after processing and potential heating cycles. Samples of an FEPM grade were extracted in methylene chloride to evaluate whether any unreacted or residual compounds were present in the polymer product. No unreacted or residual components were detected in the methylene chloride extracts of product.

Particle Size

FEPM is provided in crumb (>2 mm) or sheet (10 mm thick) or pellet (>8 mm) form.

Hydrolysis

Highly stable to hydrolysis. Data available against steam and hot water resistance. See Appendix E.

Light

Appendix D "It provides good resistance to radiation and excellent resistance to weathering and ozone."

Oxidation

Appendix D "It provides good resistance to radiation and excellent resistance to weathering and ozone."

Biodegradation

It is not biodegradable.
It is also a safe material and is listed as USP class VI and FDA FCN 1958

Thermal Stability

Appendix D "the TFE/P elastomer provides long term service at 200 ℃"

Recommended Processing Temperature

Also supported by Appendix D "the TFE/P elastomer provides long term service at 200 ℃"

References cited:

Appendix A ： A New Fluoroelastomer derived from Tetrafluoroethylene and Propylene, G. Kojima, Rubber Chemistry and Technology(1977)50(2):403-412
Appendix B ： Fluoroelastomers Handbook_The Definitive Users Guide, P23
Appendix C ： Studies of AFLAS Fluoroelastomers. Catherine A Byrne, July 1989, US Army Materials Technology Laboratory report. AD-A213 046.
Appendix D ： Tetrafuoroethylene-Propylene Copolymer (Aflas): New Technology, New Uses. D.E.Hull, Xenox, Inc.
Appendix E ： AGC Chemicals Americas Website: https://www.agcchem.com/products/fluoropolymer-resins/fluoroelastomers/#

4.11 FKM

In Tables 1 and 2, the properties and functional benefits of FKM covering the breadth of this class of fluoropolymers. This chapter will provide a detailed look at two examples step by step to support and compliment the assessment as Polymer of low Concern as made in the main paper.

The main paper describes FKM as a family of fluoroelastomers. Cross-linked (cured) polymers are by definition very high or infinite molecular weights and are typically insoluble in any solvent. FKM are further described as VDF containing copolymers with a variety of comonomers. Typical comonomers are VDF-HFP or VDF-HFP-TFE as referenced by the CAS numbers in Table 2 – at times also including cure site monomers. Two different examples of uncured VDF-HFP copolymers - both described by CAS# 9011-17-0 - were selected for the review. Both VDF-HFP copolymers in the following identified as #1 and #2 are soluble in THF which simplifies the characterization according to PLC criteria:

Five fluoroelastomer samples of composition #1 and 3 samples of composition #2 (both 100 % solids) were received for SEC analysis. Approximately 50 mg of solids were dissolved in 10 mL of THF (inhibited with 250 ppm BHT). The resulting solution was run through a 0.45 micron syringe filter and analyzed by SEC. All samples were prepared and analyzed in duplicate.

Table 4.11

	FKM uncured #1	FKM uncured #2	FKM	FKM
CAS#	9011-17-0	9011-17-0	9011-17-0	9011-17-0 25190-89-0
Supplement ID	**4.11a**	**4.11b**	**4.11c**	**4.11d**
Polymer Composition	Yes	Yes	Yes	Yes
Molecular Weight Mn	81,000 Da (narrow PS Standard)	77,000 Da (narrow PS Standard); 340,000 Da (Light Scattering)	60,000-120,000 Da	30,000-200,000 Da
Molecular Weight Distribution	2.1	2.4 (narrow PS standard); 1.9 (Light scattering)	No data	1.2-2.0
wt% oligomer	wt.% < 1000: 0%	wt.% < 1000: 0.1%	<1%	< 1%
Ionic Character	Neutral	Neutral	Neutral	Neutral
Reactive Runctional Groups (RFGs)	None Expected	None Expected	<1%	None Expected
Functional Group Equivalent Weight (FGEW)	Not Applicable	Not Applicable	$>10^4$	$>10^5$
Low Molecular Weight Leachables	TCLP test results 0.6 ppm inorganic fluoride and <0.6ppm total organic fluorine extracted in water	TCLP test results <0.9 ppm inorganic fluoride and <0.4ppm total organic fluorine in water	No active leachables	< 1 ppm
Residual Monomers	VDF was not detected; < 3.25 ppm for sum of the monomers	No Residual Monomer Detected; <0.06 ppm for the sum	No data	< 1 ppm
Ratio of Residual Monomers to Molecular Weight	$\sim 10^{-11}$	$\sim 10^{-12}$	No data	$> 10^{-5}$
Structural Similarities to RFG of Concern	None	None	No data	None
Reference Standard	ASTM D 1418	ASTM D 1418	ASTM D 1418	ASTM D 1418

Physical-Chemical Properties				
Water Solubility	practically insoluble	practically insoluble	practically insoluble	practically insoluble
Octanol/Water Partition Coefficient, Kow	N/A	N/A	N/A	N/A
Particle Size	~ 300-350 µm	~ 300-350 µm	sheet or block	sheet form, 1 cm thick pellet - 3-5 mm powder - refer to published reference
Stability				
Hydrolysis	Stable	Stable	No data	Stable
Light (hv)	Stable	Stable	No data	Stable
Oxidation	Stable	Stable	No data	Stable
Biodegradation (aerobic and anaerobic)	Stable	Stable	Stable	Stable
Thermal Stability at Normal Foreseeable Use Maximum Continuous Temp (°C)	Continuous use is expected ~room T. <100C as Host resin melts at 120 ^{o}C). Cured elastomers are used up to 180 ^{o}C No Expected degradation. Fluoropolymer degrades >350°C by TGA.		300°C	3,000h at 232°C (450°F) 1,000 at 260°C (500°F) 240h at 288°C (550°F) 48h at 316°C (601°F)
Meets PLC criteria (Y /N)	Yes	Yes	Yes	Yes
Additional Information				
Fluorinated Polymerization Aid Used ? (Y or N)	N	N	N	Y and N
Recommended Processing / Application (Use) Temperature (T°C)	Melt Processing: <300C Application: <100C (LLDPE)	Melt Processing: <300C Application: <100C (in LLDPE)	160-200 C (Crosslnking Temperature)	See Thermal Stability

Table 4.11 Continued

4.11a and 4.11b FKM - Uncured

Molecular weight, molecular weight distribution and oligomers:

SEC Conditions:

Sample: 50 µL Injection @ 5 mg/mL Tetrahydrofuran-inhibited
*Sample filtered through 0.45 micron membrane
Mobile Phase: Tetrahydrofuran-UV Grade, uninhibited; EMD OmniSolv or equivalent
Flow Rate: 1.0 mL/min
System: Reliant (Waters e2695 pump/autosampler, system MAID #1221)
Detector: Waters 2414 evaporative light scattering detector; 70°C drift tube, 30 psi nitrogen flow, 30°C nebulizer temperature, MAID #1120)
Columns: 2 PLGel 10 µm Mixed-B (nominal MW range 500-1e7 Daltons), 7.8x300 mm
1 PLGel 5 µm Mixed-D (nominal MW range 200-400,000 Daltons), 7.8x300 mm
Columns are held at 40 °C
Standards: Polystyrene, narrow dispersity; (6.87e6 - 580 Mp); (3rd order polynomial fit)
Syringe filter: 0.45 micron PTFE

Molecular weight values were determined by calibrating the system against narrow molecular weight polystyrene standards.

Table 1 contains the relative molecular weight and polydispersity values for the samples. Each result is the average of duplicate injections. Note: Lot 66706 should be 4000066706 (same lot in next table)

Table 1: Fluoropolymer Results Summary

Sample Name	Mw	Mn	Mz	Polydispersity	%<2500	%<1000
FKM #1 Lot 31525	1.676E+05	7.975E+04	2.811E+05	2.10	0.06	0.00
FKM #1 Lot 34067	1.665E+05	7.930E+04	2.776E+05	2.10	0.06	0.00
FKM #1 Lot 34068	1.699E+05	8.414E+04	2.789E+05	2.02	0.04	0.00
FKM #1 Lot 34069	1.693E+05	8.045E+04	2.827E+05	2.10	0.06	0.00
FKM #1 Lot 31603	1.705E+05	8.332E+04	2.783E+05	2.05	0.05	0.00
FKM #2 Lot 34003	1.647E+05	7.413E+04	4.474E+05	2.22	0.01	0.00
FKM #2 Lot 66706	2.609E+05	8.090E+04	1.799E+06	3.22	0.02	0.00
FKM #2 Lot 35006	1.810E+05	7.880E+04	4.730E+05	2.30	0.00	0.00

FKMs were additionally characterized by GPC with multi-angle light scattering detector: GPC with light scattering detection is used in order to measure their *absolute* or standardless molecular weight.

Sample Description:
Uncured FKM #1 and #2 Copolymers of Vinylidene fluoride and hexafluoropropylene
Lots 34015, 34016, 34017, 4000064934, 4000066755, 4000066756, 4000066706, 4000045557
Data:
Table 1. Molecular weight results. Results are averages from duplicate injections.

M_n = Number-average molecular weight
M_w = Weight-average molecular weight
$Đ$ = Dispersity = M_w/M_n
dn/dc = differential refractive index increment (of sample in tetrahydrofuran)

Sample Name	dn/dc	M_n	M_w	$Đ$
	mL/g	g/mol	g/mol	
FKM #1 Sample 1	-0.02	1.45E+05	3.24E+05	2.23
FKM #1 Sample 2	-0.02	1.48E+05	3.26E+05	2.20

Sample·Name¤	dn/dc¤	M_n¤	M_w¤	$Đ$¤
¤	mL/g¤	g/mol¤	g/mol¤	¤
FKM·#2·Lot·34015¤	-0.017¤	2.97E+05¤	5.78E+05¤	1.95¤
FKM·#2·Lot·34016¤	-0.018¤	3.65E+05¤	6.64E+05¤	1.82¤
FKM#2·Lot·34017¤	-0.018¤	3.48E+05¤	6.48E+05¤	1.86¤
FKM#2·Lot·4000064934¤	-0.019¤	3.24E+05¤	6.19E+05¤	1.92¤
FKM#2·Lot·4000066755¤	-0.017¤	3.48E+05¤	6.69E+05¤	1.92¤
FKM#2·Lot·4000066756¤	-0.018¤	3.23E+05¤	6.46E+05¤	2.01¤
FKM#2·Lot·4000066706¤	-0.018¤	3.93E+05¤	6.99E+05¤	1.78¤
FKM#2·Lot·4000045557¤	-0.019¤	3.36E+05¤	6.91E+05¤	2.06¤

This method measures Mw directly and Mn is calculated indirectly under the assumption that the quality of the separation is such that each time slice is monodisperse (and thus $M_n = M_w$) thus the uncertainty propagates in M_n at ≈ ± 25%.

Sample Preparation Method / Test Method:
Submitted samples were prepared and tested in duplicate. Solutions of known concentration were prepared by weighing sample and solvent (tetrahydrofuran stabilized with 250 ppm BHT); the volume of solvent was calculated using its density – the volume of solute was assumed to be negligible (this assumption is valid for dilute solutions like the prepared for this analysis). The

samples were allowed to dissolve while swirling for at least 16 hours. The solutions were then filtered through 0.45 µ PTFE syringe filters and analyzed by GPC.

GPC conditions:

Instrument:	Agilent 1100 LC
Column set:	2 x Waters Styragel® HR 5E, 300 mm length x 7.8 mm I.D.
Col. Heater:	40 °C
Eluent:	Tetrahydrofuran (stabilized with 250 ppm BHT) at 1.0 mL/min
Injection volume:	60 µL
Detector (s):	Wyatt DAWN® HELEOS® II - 18 angle Light Scattering detector Wyatt Optilab® rEX Differential Refractive Index (DRI) detector

Data were collected and analyzed using software ASTRA® version 6 from Wyatt Technology Corporation. The dn/dc of the samples in tetrahydrofuran was measured using a Total Recovery Approach.[1]

In comparison, the absolute molecular weight measurement of FKM #2 the Polystyrene calibration delivers significantly lower molecular weight results which might lead to the conclusion that data based on a polystyrene calibration is conservative for these polymers and underestimates true molecular weights.

Functional groups:
The polymerization process leads by design to a neutral polymer with neutral or anionic end-groups for FKM #1 and #2. There is no evidence for cationic groups nor are they to be expected. The fluoroelastomers do not include reactive functional groups like acrylates, isocyanates, anhydrides or aziridines by design. Due to the lack of functional groups the term “equivalent weight” is not applicable.

Low molecular weight leachables:
The TCLP (Toxicity Characteristic Leaching Procedure) is designed to determine the mobility of both organic and inorganic analytes present in liquid, solid, and multiphasic wastes (https://www.epa.gov/hw-sw846/sw-846-test-method-1311-toxicity-characteristic-leaching-procedure: SW-846 Test Method 1311)
TCLP testing of mixtures containing about 30 % of FKM #1 and about 50% of FKM #2 were completed: Extraction of polymer blend with buffered acetic acid solution according to EPA SW-846 Test Method 1311. 100 g of polymer mixture tumbled for 18 hrs with 2L acetic acid/sodium acetate (pH 4.93). Instrumental Analysis of Leachate for PFCA (C4-C13), PFSA (C4, C6, C8) and TOF (total organic fluoride and inorganic fluoride) are presented in the tables below:

Sample Description	PFBA Conc. (ng/mL)	PFPeA Conc. (ng/mL)	PFHxA Conc. (ng/mL)	PFHpA Conc. (ng/mL)	PFOA Conc. (ng/mL)	PFNA Conc. (ng/mL)	PFDA Conc. (ng/mL)	PFUnA Conc. (ng/mL)	PFDoA Conc. (ng/mL)	PFTrA Conc. (ng/mL)	PFBS Conc. (ng/mL)	PFHS Conc. (ng/mL)	PFOS Conc. (ng/mL)
Filtered Leachate from Fluorelastomer #2	<0.0250	<0.0250	<0.0250	<0.0250	<0.0240	<0.0250	<0.0250	<0.0250	<0.0250	<0.0250	<0.0250	<0.0250	<0.0232
Filtered Leachate from Fluorelastomer #2	<0.0250	<0.0250	<0.0250	<0.0250	<0.0240	<0.0250	<0.0250	<0.0250	<0.0250	<0.0250	<0.0250	<0.0250	<0.0232
Laboratory Blank	<0.0250	<0.0250	<0.0250	<0.0250	<0.0240	<0.0250	<0.0250	<0.0250	<0.0250	<0.0250	<0.0250	<0.0250	<0.0232
Laboratory Blank	<0.0250	<0.0250	<0.0250	<0.0250	<0.0240	<0.0250	<0.0250	<0.0250	<0.0250	<0.0250	<0.0250	<0.0250	<0.0232
Filtered Leachate from Fluorelastomer #1	<0.0250	<0.0250	<0.0250	<0.0250	<0.0240	<0.0250	<0.0250	<0.0250	<0.0250	<0.0250	<0.0250	<0.0250	<0.0232
Filtered Leachate from Fluorelastomer #1	<0.0250	<0.0250	<0.0250	<0.0250	<0.0240	<0.0250	<0.0250	<0.0250	<0.0250	<0.0250	<0.0250	<0.0250	<0.0232
Laboratory Blank	<0.0250	<0.0250	<0.0250	<0.0250	<0.0240	<0.0250	<0.0250	<0.0250	<0.0250	<0.0250	<0.0250	<0.0250	<0.0232
Laboratory Blank	<0.0250	<0.0250	<0.0250	<0.0250	<0.0240	<0.0250	<0.0250	<0.0250	<0.0250	<0.0250	<0.0250	<0.0250	<0.0232

Sample Description	PFBA Conc. (ng)	PFPeA Conc. (ng)	PFHxA Conc. (ng)	PFHpA Conc. (ng)	PFOA Conc. (ng)	PFNA Conc. (ng)	PFDA Conc. (ng)	PFUnA Conc. (ng)	PFDoA Conc. (ng)	PFTrA Conc. (ng)	PFBS Conc. (ng)	PFHS Conc. (ng)	PFOS Conc. (ng)
Unfiltered Leachate from Fluorelastomer #2	<0.250	<0.250	<0.250	<0.250	<0.240	<0.250	<0.250	<0.250	<0.250	<0.250	<0.250	<0.250	<0.232
Unfiltered Leachate from Fluorelastomer #2	<0.250	<0.250	<0.250	<0.250	<0.240	<0.250	<0.250	<0.250	<0.250	<0.250	<0.250	<0.250	<0.232
Unfiltered Leachate from Fluorelastomer #1	<0.250	<0.250	<0.250	<0.250	<0.240	<0.250	<0.250	<0.250	<0.250	<0.250	<0.250	<0.250	<0.232
Unfiltered Leachate from Fluorelastomer #1	<0.250	<0.250	<0.250	<0.250	<0.240	<0.250	<0.250	<0.250	<0.250	<0.250	<0.250	<0.250	<0.232

The PFTrA results should be considered qualitative as the LCSs average recoveries were <50%

Sample Description	Total Fluoride (µg/mL)	Inorganic Fluoride (µg/mL)	Total Organic Fluoride (µg/mL)
Lab Blank Sample	<0.286	0.144	<0.286
Sample containing FKM#1; Rep3; Filtered Leachate	1.27	0.61	0.656
Sample containing FKM#1; Rep4; Filtered Leachate	1.17	0.599	0.574
Lab Blank Sample	<0.286	0.146	<0.286
Sample containing FKM#2; Rep3; Filtered Leachate	1.29	0.854	0.438
Sample containing FKM#2; Rep4; Filtered Leachate	1.25	0.869	0.383

6

Based on these results, all specific PFCA and PFSA analytes listed above are below LOQ (25 ng/L) in filtered leachate for both samples containing uncured FKM #1 and #2.
Filtered leachate contained low levels of inorganic Fluoride (IF) (0.61 ppm in uncured fluoroelastomer #1 and 0.86 ppm in uncured elastomer #2) and Total Organic Fluoride (TOF) (0.58 ppm in in uncured fluoroelastomer #1 and 0.41 ppm in uncured fluoroelastomer #2) [average of replicates].

Low molecular weight leachables:
Testing for residual monomers was conducted for FKM #1 via headspace gas chromatography with mass spectrometry detection. The samples were heated in sealed vials to 200 °C for 30 minutes prior to analysis via GC-MS.
Samples were prepared in triplicates. Approximately 1 g of samples subdivided into smaller pieces (25-100 mg each) were weighed into a 20 ml headspace vial. Each vial was capped with an aluminum crimp cap with a PTFE lined septum. The vials were heated for 30 minutes prior to instrumental analysis. The instrument was calibrated by a series of gas standard mixtures prepared in gas bulbs and known aliquots of the gas standards injected into sealed head space vials. Spiking experiments were conducted to validate the use of external standards and to establish limits of quantification.

Averages of triplicates	VDF average in ppm (µg/g)	HFP average in ppm (µg/g)	Modifier Average in ppm (µg/g)
FKM #1 Sample A	below LOQ of 0.009	3.19	N./A.
FKM #1 Sample B	below LOQ of 0.009	3.23	N./A.
FKM #1 Sample C	below LOQ of 0.009	0.058	N./A.
FKM #2	0.032	below LOQ of 0.02	below LOQ of 0.02

Physicochemical properties:
Fluoroelastomers are practically insoluble in water and also practically insoluble in octane. Fluoroelastomers form a separate solid phase and K_{OW} is not applicable. Fluoroelastomers are typically provided in slab form. For applications such as polymer processing additives, there are also powder blends with synergist and separating agent with particle sizes of about ~ 300-350 µm available.

Stability:
Hydrolysis testing according to OECD 111 was performed to confirm hydrolytic stability:
Hydrolysis testing was performed based on OECD Method 111 “Hydrolysis as a Function of pH” A preliminary Tier 1 test was performed at pH’s 4,7,9 at 50 °C for 5 days. The test material concentration was 100 g/L. Testing included replicate samples for each condition and preparation and evaluation of analytical control samples. Following the incubation period, samples were prepared for LC/MS/MS analysis by dilution of an aliquots with methanol and filtration. Results with recovery outside of 100 +/- 30 % were not reported.

SUPPLEMENTAL DATA

Summary of the %Hydrolysis of 30% FKM #1 blend - calculated after 5 days of incubation (PFBA value at pH 9 likely artefact since it was detected in only 1 of 4 replicates)			
Analyte	Percent Hydrolysis		
	pH=4	pH=7	pH9
PFBS	0.00%	0.00%	0.00%
PFHxS	0.00%	0.00%	0.00%
PFOS	0.00%	0.00%	0.00%
PFBA	0.00%	0.00%	0.000000337%
PFPeA	0.00%	0.00%	0.00%
PFHxA	0.00%	0.00%	0.00%
PFHpA	0.00%	0.00%	0.00%
PFOA	0.00%	0.00%	0.00%
PFNA	0.00%	0.00%	0.00%
PFDA, PFUnA, PFDoA, PFtrA	not reported	not reported	not reported
TOF	0.00%	0.00%	0.00%

Summary of Percent Hydrolysis of blend with about 50% FKM #2 Calculated from the Total Fluorine of Total Fluorine of Measured PFAAs after 5 days of incubation			
Analyte	Percent Hydrolysis		
	pH 4	pH 7	pH 9
PFBS	0.00%	0.00%	0.000000202% (5)
PFHxS	0.00%	0.00%	0.00%
PFOS	0.00%	0% (4)	0.00%
PFBA	0.00%	0.00%	0.00%
PFPeA	0.00%	0.00%	0.00%
PFHxA	0.00%	0.00%	0.00%
PFHpA	0.00%	0.00%	0.00%
PFOA	0.00%	0.00%	0.00%
PFNA	0.00%	0.00%	0.00%
PFDA (1)	NR	NR	NR
PFUnA(1)	NR	NR	NR
PFDoA(1)	NR	NR	NR
PFTrA(1, 2)	NR	NR	NR
PFAAs	0.00%	0.00%	0.000000202%
TOF(3)	0.00%	0.00%	0.00%
(1) Results not reportable due to loss of OFAA too reaction vessel (2) Results not reportable due to QA failure (3) See Attachment A for TOF details (4) Percent hydrolysis based on the day 5 results only (5) One of four replicates was above the LLOQ			

Rugg et.al (2) and Logothetis(3) describe the stability to light and UV light. Logothetis (3) and Lewis et al (4) attest to the oxidative stability. Additionally, Worm et al and Hintzer et al highlight the thermal stability of cross-linked fluoroelastomers.
Two FKM #1 samples (not cross-linked) were analyzed via TGA-FTIR at different temperatures over 3 hours. At 250 °C, HF was detected. At 300 °C, HF and trifluoromethane were detected. If used as additive to polyolefins continuous use is expected near room temperature. (likely <100 °C as host resin melts at 120 ^{o}C). Cured elastomers are used up to 200 ^{o}C without expected degradation. Fluoropolymer themselves degrade at temperatures above 350 C based on TGA testing.

References:
(1) Podzimek, Stepan. Light Scattering, Size Exclusion Chromatography and Asymmetric Flow Field Flow Fractionation: Powerful Tools for the Characterization of Polymers, Proteins and Nanoparticles. John Wiley & Sons, Inc.: Hoboken, New Jersey, 2011. pp 65-72.

(2) Rugg, J. S.; Stevenson, A. C. “Viton-A, a new fluorine-containing rubber” in Rubber Age (New York) (1958), 82, 102-4;
(3) A.L. Logothetis in "Organofluorine Chemistry" Ed. R.E. Banks, B.E. smart and J.C. Tatlow Plenum Press New york and London 1994 pg. 384f.
(4) DOI: 10.107/978-1-4684-2148-4 "Flame-Retardant Polymeric Materials" Menachem Lewis, S.M. Atlas and Eli M. Pearce Plenum Press New York & London 1975;
(5) A.T. Worm, W. Grootaert, “Fluorocarbon Elastomers” in Encyclopedia of Polymer Science and Technology, Wiley 2003 (Vol 2) pp 577-590
(6) K. Hintzer, T. Zipplies, D.P. Carlson, W. Schmiegel “Fluoropolymers, Organic” in Encyclopedia of Industrial Chemistry 7th edition pp 41-46

4.11c FKM – Cured Product

Molecular Weight Characterization:
What does MW mean for any crosslinked elastomer? It is essentially a continuous network. See the Figure 5.8 referenced below.

Molecular Weight Distribution:
Mw/Mn of FKM varies 1.2 to 8 or more depending on the distribution set by the polymerization process and operating conditions.
Japanese literature written by Mr. Tatemoto. Fig.1 shows that Mw or Mn was calculated in equivalents of polystyrene.
U.S. Patent 5,077,359 also states that GPC was used.
See reference: https://www.jstage.jst.go.jp/article/koron1974/49/10/49_10_765/_pdf

The portion having a molecular weight <1000 Da is practically negligible.
("Fluoroelastomers Handbook 2nd Edition” Jiri George Drobny. **2016**, pg. 70-71).

Wt % Oligomer

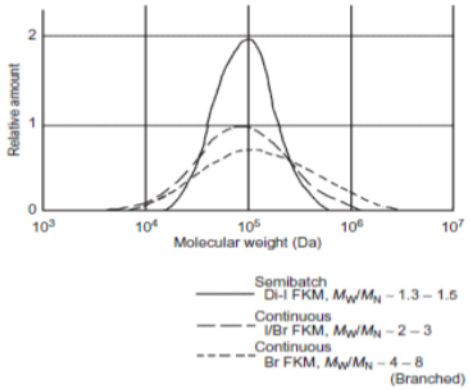


Figure 5.8 Fluoroelastomer molecular weight distribution.

See FE Handbook page 71, Fig 5.8

Ionic Character

Neutral. There is no cationic character.

Reactive functional groups (RFGs):

Functional group in FKM fluoroelastomers could include -OH, -COOH,- CH3, CF2H with some of ester groups coming from chain transfer agents, or iodide as Cure Site Monomers (CSM).

Ref1) Maurizio Pianca et al, Endgroup in Fluoropolymers, Journal of Fluorine Chemistry(1999), pg82-83

Ref2) "Fluoroelastomers Handbook 2nd Edition" Jiri George Drobny. 2016, pg. 71

See reference: https://www.sciencedirect.com/science/article/pii/S0022113998003042

Functional Group Equivalent Weight (FGEW):

According to the literature (==>please see the link), the functional groups corresponding to FGEW are listed in Table 4 on pg26, and all the functional groups are not applicable for FKM which has OH or COOH end groups and CSM (Iodide) .

See Reference: https://www.epa.gov/sites/default/files/2015-03/documents/polyguid.pdf

Low MW Leachables:

No direct data is available, but standard FKMs are in compliance with FDA regulation 21 CFR 177.2600 (e.g. please see the link for Viton FKM).

See reference: https://www.newmangasket.com/PDF%20files/Viton%20A201%20Spec%20Sheet..pdf

Residual monomers:

The value <50 ppt is company internal data measured by a third party analysis company. The measurement conditions are 200 °C / 20 minutes /under N2 atmosphere, and the volatiles generated from raw gum by heating is quantified by the GC/MS-SIM method.

Ratio of Residual Monomers to Mw:

Outgas: 1 μg/g = 10^{-6}

Average Mw = 10^{5}

Outgas / Mw = 10^{-11} Since the above representative data is 0.05 ppb.

Structural Similarities of RFG of Concern:

According to the PLC criteria listed in the reference link below, polymer-terminated carboxylates might be classified as low risk. And considering the Mw is 10^{5}-10^{7} Da, the ratio of functional groups is negligibly small.

See reference: https://www.industrialchemicals.gov.au/help-and-guides/polymer-low-concern-plc-criteria

Water Solubility:

FKM's are insoluble in water.
See reference: https://www.missionrubber.com/wp-content/uploads/2017/07/sds-fkm-chemical-resistant-couplings.pdf

Octanol/Water partition coefficient, Kow:
FKM (fluoroelastomers) are insoluble in water and n-octanol, therefore Kow is not applicable

Stability References:
Hydrolysis:
FKM is extremely resistant to hydrolysis. e.g HiFluor® FB(FKM) is in a compliance with 21 CFR 177.2600.
See reference: https://www.parker.com/literature/Praedifa/Brochures/Compounds-for-Food-and-CPI_PTD3029_EN.pdf

Light:
FKM has a chemical structure that's virtually unbreakable and impervious to attack by oxygen, ozone, UV light and harsh chemicals.
See reference: https://www.easternseals.co.uk/viton-fkm-vs-nitrile/

Oxidation:
Figure 9 in the scientific paper referenced below shows high stability with almost no difference in molecular weight before and after exposure to ozone water.
See reference: https://www.jstage.jst.go.jp/article/gomu/85/3/85_81/_pdf/-char/ja

Biodegradation:
There is no data that directly indicates biodegradation.
FKM shows the best performance in harsh environments.
See reference: https://www.osti.gov/pages/servlets/purl/1236238

Particle Size

Many FKM products forms are "block", so that particle size is not applicable. If the FKM needs to be processed in a particular molding application, the block could be processed into a granular form which would depend on the downstream application.

Elastomer products can also have amorphous shape, so some SDS describe FKM as 'crumb'. see ref https://multimedia.3m.com/mws/media/634781O/3m-dyneon-peroxide-cure-perfluoroelastomer-pfe-90-data-sheet.pdf

Thermal stability at normal foreseeable use maximum continuous temp (°C):

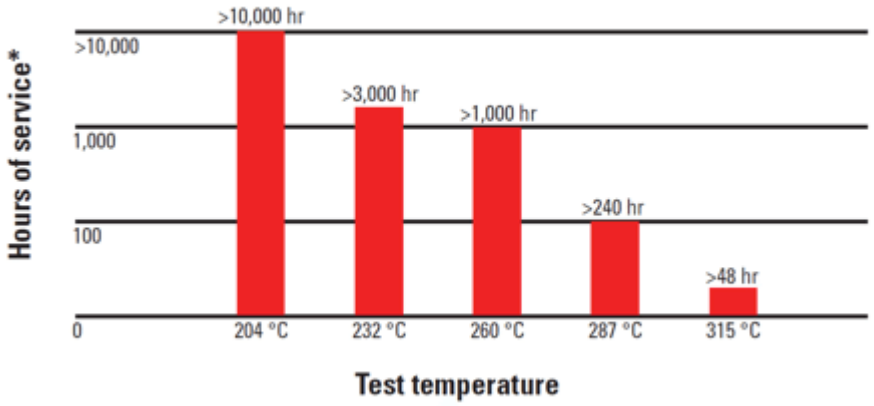
Other thermal stability data.

Figure 5 (see below) in the polycomp reference below. is very straightforward that FKMs shows thermal stability at 204 °C for >10,000 hrs and at 232 °C for >3000 hrs. So, 200 °C is reasonable temperature when considering continuous thermal stability.

See reference: https://www.polycomp.nl/fkm-advantages/

And https://www.osti.gov/servlets/purl/1254690

Figure 5 from polycomp ref. cited above



Recommended Processing / Application (Use) Temperature (T°C):

Maximum processing temperature depends on the crosslinking system. Peroxide curable grades are usually post cured and have a maximum service temperature of 200 °C. Bisphenol curable grades require 230-250 °C post curing and their upper limit of service temperature is 230 °C.

4.11d FKM Uncured

Molecular weight, molecular weight distribution:

The molecular weight range and molecular weight distribution (M_w/M_n) for commercial FKM fluoroelastomers have been reported by Drobny 2015 and are 60,000 – 120,000 and 1.2 – 8 respectively. For the substance assessed in this study, the molecular weight distribution was 1.2-2.0.

Reactive Functional Groups (RFGs), Functional Group Equivalent Weight (FGEW):

No cationic or reactive functional groups like acrylates, isocyanates, anhydrides or aziridines are introduced nor created in the manufacture of fluoroelastomers.

The monomers polymerized to synthesize FKM result in polymer with neutral and/or anionic end-groups. Therefore, functional equivalent weight, computed based on the presence of a neutral or anionic end group on a polymer chain of molecular weight 60,000-120,000 would therefore be $>10^5$.

Residual Monomers

Residual monomers were determined by placing a polymer sample in a vial which was then heated to generate a headspace which was then analyzed by GC-MS SIM mode analysis. Calibration curves with 4 points were generated for the monomers. The monomers are all gases.

Substance	CAS #	Boiling Point (°C)
Hexafluoropropene (HFP)	116-15-4	-29
Vinylidene difluoride (VF2)	75-38-7	-84
Tetrafluoroethene (TFE)	116-14-3	-76

Multiple determinations showed less than 0.2ppm for all monomers.

Oligomers and Low Molecular Weight Leachables:

Extraction of solid polymer matrices for the purpose of targeted quantitation was conducted. The resulting extracted solutions were analyzed using appropriate LC/MS/MS methods (e.g. ISO 25101 Method). Less than 1ppm of low molecular weight substances were observed to demonstrate conformance to regulatory criteria (e.g., European Commission).

Equipment:

- Cryogrinder (SPEX SamplePrep 6875 Freezer/Mill, or equivalent)
- Heated Sonicator (Branson CPX2800H, or equivalent)
- Centrifuge (Eppendorf 5430 Microcentrifuge with F-35-6-30 Rotor, or equivalent)
- Balance capable of measurement to two decimal places
- Digital thermometer
- Oven

Consumables / Reagents:

[Note: Avoid using glass. All samples should be prepped and stored in HDPE or PP containers; do not use caps or other items containing PTFE. Part numbers are provided below, but substitutions of similar products can be made.]

- 50 mL free-standing centrifuge tubes: VWR P/N 82018-048
- Cryo storage vials: Greiner (through VWR), P/N 127263
- Transfer pipets: Globe Scientific (through VWR), P/N 134050
- LC/MS grade methanol

Extraction Procedure:

1. Pellets or cubes should be cryoground prior to extraction with liquid nitrogen. A visual inspection of the cryoground product must be performed; an acceptable product has homogenous particle size with the consistency of a flaky powder.
2. Weigh approximately 8 g of polymer into a 50 mL centrifuge tube; record weight to 2 decimal places. Weigh a second 8 g aliquot to prepare a duplicate sample.
3. Add approximately 25 mL (19.8 g, density = 0.792 g/mL) of LC/MS grade methanol into each duplicate tube.

4. Tightly cap tubes and shake briefly to mix. Place tubes in a rack into the sonicator, also filled with water and pre-heated to 60°C.
5. Allow to incubate with heated sonication for 6 hours. During the incubation period, monitor temperature periodically to ensure heat remains ±5 °C of the 60 °C setpoint.
6. After 6 hours, remove centrifuge tubes and allow to cool to room temperature.
7. Centrifuge scintillation vials for 15 minutes at 5000 rpm.
8. Transfer 15 mL (11.88 g) of the methanol extract into a clean centrifuge tube. Label the tube with the extraction number.
9. Add a fresh 15 mL aliquot of methanol to the original (polymer-containing) tube in an equal amount to the weight removed in Step 8. Shake and vortex to break up packed polymer.
10. Repeat Steps 4 through 9 for a total of three sequential extractions per sample. After the final extraction, the extracted polymer and original tube may be discarded.

Physicochemical properties:

Fluoroelastomers are practically insoluble in water and organic solvents including octanol. Additionally, fluoroelastomers form a separate solid phase in water and octanol making K_{OW} not able to be determined nor applicable. Fluoroelastomers are available in various forms: sheet (1cm thickness), pellet (3-5mm) and powder.

Stability (a,b,c,d,e)

In the references provided, hydrolysis, light, oxidation and biodegradation stability as well as the thermal stability and recommended use temperatures of fluoroelastomers are documented (a,b,c,d,e). Fluoroelastomers are not soluble in water or hydrocarbons (e.g., octanol) and are chemically and biologically stable.

A fluorinated polymerization aid is used in the manufacture of some, not all fluoroelastomers.

References

(a) Drobny, J. G., 2015, Fluoroelastomers Handbook - The Definitive User's Guide, 2nd Edition. Plastics Design Laboratory, Elsevier. http://doi.org/10.1016/B978-0-323-39480-2.00001-4
(b) Worm, A. T.; Grootaert, W., 2015. Fluorocarbon Elastomers. Encyclopedia of Polymer Science & Engineering. pp. 577-590. https://doi.org/10.1002/0471440264.pst137
(c) Hintzer, et al., 2013. Fluoroelastomers, Chapter 3, in Organic Fluoropolymers, Ullmann's Encyclopedia of Industrial Chemistry, Wiley-VCH, Weinheim.
(d) A.L. Logothetis, 1994. Fluoroelastomers. In, Organofluorine Chemistry, Ed. R.E. Banks, B.E. smart and J.C. Tatlow, Plenum Press, New York.
(e) Viton™ Fluoroelastomers, Selection Guide, C-11021.
https://www.viton.com/en/products/product-selection

4.12 FFKM - Perfluoroelastomer

Molecular weight Characterization

The estimated molecular weight is in excess of 100 000 as the TFE/PMVE copolymer is created via an emulsion polymerization with a free radical initiator.
("NMR Study of radiation-Induced Cross-Linking of Poly(tetrafluoroethylene-co-perfluoromethyl vinyl ether" Macromolecules, J.S.Forsythe et al. **1997**, 30, pg. 8103).

Molecular Weight Distribution

Estimated from FKM, which has similar monomers and polymerization methods. Mw/Mn of FKM varies 1.2 to 8 or more depending on the distribution set by the polymerization process and operating conditions. The portion having a molecular weight <1000 Da is practically negligible.
("Fluoroelastomers Handbook 2nd Edition" Jiri George Drobny. **2016**, pg. 70-71).

Wt % Oligomer

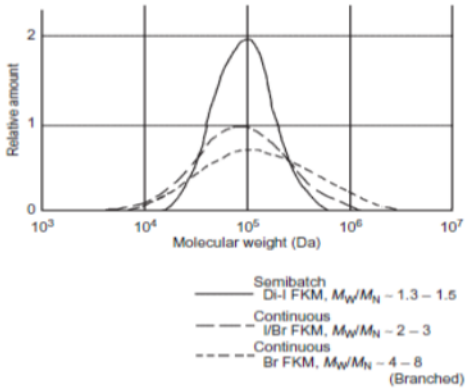


Figure 5.8 Fluoroelastomer molecular weight distribution.

See FE Handbook page 71, Fig 5.8

Ionic Character

FFKM polymers are neutral polymers based on the building blocks or monomers. Some FFKM polymers may carry neutral or ionic end-groups but this does change the character as a neutral polymer.

Reactive functional groups (RFGs)

TFE/PMVE copolymers contains CSM (Cure site monomer) which has nitrile group or halogen. CSM is consumed during the polymerization process, and eventually disappears. There are no RFG's in the FFKM product.
("Fluoroelastomers Handbook 2nd Edition" Jiri George Drobny. **2016**, pg. 94-97).

Residual monomers

PMVE, which has the lowest vapor pressure among FFKM monomers, has a boiling point of -23 °C (-9 °F). Therefore, in the process of drying in manufacturing process of FFKM, all the residual monomers are volatilized.

Ratio of residual monomers to molecular weight (typical value)

Outgassing property: see reference: ("Valqua Technology News No.23 SUMMER, Masanori Okazaki, **2012** pg 10- 11). *Japanese only.* https://www.valqua.co.jp/wp-content/uploads/pdf/technical/23/vtn023-04.pdf Table 1 in reference shows measurement results by GC-MS (Dynamic Headspace Method). FFKM 'FLUORITZ®-HS' shows that the amount of released gas is below the detection limit, no released gas is detected.

Test conditions:

Analyzer: GC-MS (Dynamic Headspace Method)

Heating conditions: 250 °C x 30 min

Amount of released gas: Amount of released gas when converted to pentadecane

Lower limit of detection: 1 μg/g

Calculated from the above data that outgas: 1 μg/g = 10^{-6} and average Mw = 10^{5} Da, Outgas / Mw = 10^{-11} is a reasonable value.

Structural similarities to RFG of concern

Persulfate initiation results in carboxylate end groups in TFE/PMVE perfluoroelastomers. Therefore, FGEW are listed in Table 4 on pg 26 of reference) are not applicable for FFKM. ("Fluoroelastomers Handbook 2nd Edition" Jiri George Drobny. 2016, pg. 71).

Octanol/Water partition coefficient, Kow

TFE/PMVE based FFKM (Perfluoroelastomers) are insoluble in all solvents except certain perfluorocarbons and chlorofluorocarbons. The FFKM fluoroelastomers are not soluble in either water or n-octanol. Therefore, a Kow cannot be calculated.
("Fluoropolymers, Organic" Klaus Hintzer, Tilman Zipplies, D. Peter Carlson, Walter Schmiegel **2014**, pg.527).

Hydrolysis, light (hv), Oxidation, Thermal stability

The perfluoroelastomer backbone provides the unique combination of properties, e.g. high thermal stability, chemical inertness, excellent weatherability, low water absorptivity, low flammability.
FFKM is extremely resistant to hydrolysis.
FFKM has a chemical structure that is impervious to attack by oxygen, ozone, UV light and harsh chemicals.

("Developments in perfluorocarbon elastomers" A. L. Logothetis, International rubber conference **1985** Kyoto Japan, pg.74).
Perfluoroelastomers that match the oxidative, thermal and chemical inertness of PTFE are currently based on copolymers of TFE and perfluoroalkyl vinyl ethers.
("Chemistry of fluorocarbon elastomers" Anestis L. Logothetis, Prog. Polym. Sci., Vol.14, **1989**, pg.279).

Thermal stability

TFE/PMVE copolymers are usable at temperature up to 315 °C (600 °F).
FFKM is usable up to 315 °C (200-300 °C meant considering the effect of the structure of the crosslinks.) Please see the technical data from Parker-Hannifin Corporation (need reference), according to the data, the maximum service temperature ranges from 220 °C to 325 °C depending on the grade. These differences in operating temperature are due to additives, not to decomposition of FFKM polymer. The polymer itself can withstand at least 350 C. "Evaluation of Elastomers for Geothermal Well Applications" E. M. Redlinea, T. Sugamab, T. Pyatinabshows that FFKM have extremely high thermal stability up to at least 350 C.
("Fluoroelastomers Handbook 2nd Edition" Jiri George Drobny. **2016**, pg. 94).

Stability References:

https://www.parker.com/literature/Praedifa/Brochures/Compounds-for-Food-and-CPI_PTD3029_EN.pdf
https://dpseals.com/wp-content/uploads/2017/02/Affordable_FFKM.pdf
https://www.parrinst.com/wp-content/uploads/downloads/2011/07/Parr_DuPont-Kalrez-O-ring-Materials-Corrosion-Info.pdf
https://www.osti.gov/pages/servlets/purl/1236238
https://www.parker.com/Literature/Praedifa/Brochures/Parofluor_PTD3026-EN.pdf
https://www.osti.gov/servlets/purl/1254690

Particle Size

Elastomer products have amorphous shape, so some SDS is described as 'crumb'. see ref https://multimedia.3m.com/mws/media/634781O/3m-dyneon-peroxide-cure-perfluoroelastomer-pfe-90-data-sheet.pdf

4.13 Amorphous Fluoropolymers

Amorphous (CAS# 37626-13-1, CAS 101182-89-2 and 37626-13-4)

CAS# 37626-13-4

Amorphous fluoropolymers are specialty polymeric materials, manufactured in small volumes, and used in high performance applications where their extremely unique optical and physical-chemical properties are required and provide benefits. The product is provided as a resin (pellet form) or in an inert fluorinated solvent.

CAS# 37626-13-4 is produced by free-radical polymerization in aqueous media of tetrafluoroethylene and (TFE) and perfluoro-2,2-dimethyl-1,3-dioxole (PDD) using a fluorinated polymerization aid. (a, b, c, e, f) Safe handling and use guidance is provided for commercial products (e).

Molecular weight, molecular weight distribution:

A molecular weight between 10^4-10^6 and molecular weight distribution for several amorphous fluoropolymers was estimated based on their rheological properties (Hoffman and Shields, 2009).

More recent determination of molecular weight (M_w) and molecular weight distribution (M_w/M_n) based on viscosity measurements for CAS# 37626-13-4 solutions in a perfluorinated solvent versus polystyrene standards yielded M_w between 250,000-300,000 and molecular weight distribution (M_w/M_n) between 1.4-1.8.

Reactive Functional Groups (RFGs), Functional Group Equivalent Weight (FGEW):

No cationic or reactive functional groups like acrylates, isocyanates, anhydrides or aziridines are introduced nor created in the manufacture of CAS# 37626-13-4.

The monomers polymerized to synthesize CAS# 37626-13-4 result in polymer with neutral and/or anionic end-groups (a, b). Therefore, functional equivalent weight, computed based on the presence of a neutral or anionic end group on a polymer chain of molecular weight 250,000-300,000 would therefore be $>10^5$.

Residual Monomers

Residual monomers in a polymer sample were determined by placing a polymer sample in a vial which was then heated to generate a headspace which was then analyzed by GC-MS SIM mode analysis. Determination showed less than 0.2ppm for all monomers.

Oligomers and Low Molecular Weight Leachables:

Extraction of solid polymer matrices for the purpose of targeted quantitation was conducted. The resulting extracted solutions were analyzed using appropriate LC/MS/MS methods (e.g. ISO 25101 Method). Less than 1 ppm of low molecular weight substances were observed to demonstrate conformance to regulatory criteria (e.g., European Commission).

Equipment:

- Cryogrinder (SPEX SamplePrep 6875 Freezer/Mill, or equivalent)
- Heated Sonicator (Branson CPX2800H, or equivalent)
- Centrifuge (Eppendorf 5430 Microcentrifuge with F-35-6-30 Rotor, or equivalent)
- Balance capable of measurement to two decimal places
- Digital thermometer
- Oven

Consumables / Reagents:

[Note: Avoid using glass. All samples should be prepped and stored in HDPE or PP containers; do not use caps or other items containing PTFE. Part numbers are provided below, but substitutions of similar products can be made.]

- 50 mL free-standing centrifuge tubes: VWR P/N 82018-048
- Cryo storage vials: Greiner (through VWR), P/N 127263
- Transfer pipets: Globe Scientific (through VWR), P/N 134050
- LC/MS grade methanol

Extraction Procedure:

Pellets should be cryoground prior to extraction with liquid nitrogen. A visual inspection of the cryoground product must be performed; an acceptable product has homogenous particle size with the consistency of a flaky powder.

Weigh approximately 8 g of polymer into a 50 mL centrifuge tube; record weight to 2 decimal places. Weigh a second 8 g aliquot to prepare a duplicate sample.

Add approximately 25 mL (19.8 g, density = 0.792 g/mL) of LC/MS grade methanol into each duplicate tube.

Tightly cap tubes and shake briefly to mix. Place tubes in a rack into the sonicator, also filled with water and pre-heated to 60 °C.

Allow to incubate with heated sonication for 6 hours. During the incubation period, monitor temperature periodically to ensure heat remains ±5 °C of the 60 °C setpoint.

After 6 hours, remove centrifuge tubes and allow to cool to room temperature.

Centrifuge scintillation vials for 15 minutes at 5000 rpm.

Transfer 15 mL (11.88 g) of the methanol extract into a clean centrifuge tube. Label the tube with the extraction number.

Add a fresh 15 mL aliquot of methanol to the original (polymer-containing) tube in an equal amount to the weight removed in Step 8. Shake and vortex to break up packed polymer.

Repeat extraction steps for a total of three sequential extractions per sample. After the final extraction, the extracted polymer and original tube may be discarded.

Physicochemical properties:

CAS# 37626-13-4 is insoluble in water and organic solvents including octanol. K_{OW} cannot be determined nor is it applicable. CAS# 37626-13-4 is provided in a solution of an inert fluorinated solvent.(e)

Stability (a, c, e)

CAS# 37626-13-4 is transparent to visible light. In the references provided, hydrolysis, light, oxidation and biodegradation stability as well as the thermal stability and recommended use temperatures are documented (a, c, e). CAS# 37626-13-4 is not soluble in water or hydrocarbons (e.g., octanol) and is thermally, chemically and biologically stable.

A fluorinated polymerization aid is used in the manufacture of CAS# 37626-13-4.

References

(a) Gangal, S. V.; Brothers, P. D., Perfluorinated Polymers, 2002. Tetrafluoroethylene–Perfluorodioxole Copolymers. In, Encyclopedia of Polymer Science and Technology, John Wiley & Sons, Inc. New York, NY. http://doi.org/10.1002/0471440264.pst420.pub2.

(b) Bekarian, et al. 1990, Process for the Stabilization of Fluoropolymers, US 4,946,902.

(c) Korinek, P. M., 1994. Amorphous fluoropolymers - a new generation of products. Macromolecular Symposia, 82(1):61-65. https://doi.org/10.1002/masy.19940820108

(d) Hoffmann and Shields, 2009. Rheological Properties & Molecular Weight Distributions of Four Perfluorinated Thermoplastic Polymers. (LLNL-CONF-410869), ACS Polymer Symposium, August 2009, Washington, D. C.

(e) Teflon™ AF Fluoropolymer Solutions. Teflon™ AF Amorphous Plastic Resins. https://www.teflon.com/en/products/resins/amorphous-fluoropolymer

(f) Hintzer, et al., 2013. Amorphous Fluoropolymers Chapter 2.10, in Organic Fluoropolymers, Ullmann's Encyclopedia of Industrial Chemistry, Wiley-VCH, Weinheim.

4.14 Fluorinated Ionomers

Molecular weight, molecular weight distribution:
The polymer is insoluble. The molecular weight has been estimated at 10^5-10^6 Da (a, b, c). More recent determination of molecular weight (M_w) and molecular weight distribution (M_w/M_n) based on melt flow for both sulfonate and carboxylate ionomers versus similar polymers yielded M_w between 120,000-130,000 and molecular weight distribution (M_w/M_n) near monodispersity, 1.0.

The Equivalent Weight (EW) and material thickness are used to describe most commercially available fluorinated ionomer membranes. The EW is the number of grams of dry ionomer per mole of acid groups in the acid form, e.g., -SO_3H, CO_2H (c). Values between 960EW-1200EW are representative for sulfonated polymers (c, g).

Reactive Functional Groups (RFGs), Functional Group Equivalent Weight (FGEW):
No cationic or reactive functional groups like acrylates, isocyanates, anhydrides or aziridines are introduced nor created in the manufacture of fluorinated ionomers. The acid functional groups are in the ionic form, -SO_3^- or CO_2^-, not the acidic, protonated form.

Therefore, functional equivalent weight, computed based on the presence of a neutral or anionic end group on a polymer chain of molecular weight 120,000 would therefore be >10^5.

Residual Monomers
Residual monomers were determined by placing a polymer sample in a vial which was then heated to generate a headspace which was then analyzed by GC-MS SIM mode analysis. Determinations showed less than 0.2ppm for all monomers.

Monomers (anionic), Oligomers & Low Molecular Weight leachables:
Extraction of solid polymer matrices for the purpose of targeted quantitation was conducted. The resulting extracted solutions were analyzed using appropriate LC/MS/MS methods (e.g. ISO 25101 Method). Less than 1ppm of low molecular weight substances were observed to demonstrate conformance to regulatory criteria (e.g., European Commission).

Equipment:

- Cryogrinder (SPEX SamplePrep 6875 Freezer/Mill, or equivalent)
- Heated Sonicator (Branson CPX2800H, or equivalent)
- Centrifuge (Eppendorf 5430 Microcentrifuge with F-35-6-30 Rotor, or equivalent)
- Balance capable of measurement to two decimal places
- Digital thermometer
- Oven

Consumables / Reagents:

[Note: Avoid using glass. All samples should be prepped and stored in HDPE or PP containers; do not use caps or other items containing PTFE. Part numbers are provided below, but substitutions of similar products can be made.]

- 50 mL free-standing centrifuge tubes: VWR P/N 82018-048
- Cryo storage vials: Greiner (through VWR), P/N 127263
- Transfer pipets: Globe Scientific (through VWR), P/N 134050
- LC/MS grade methanol

Extraction Procedure:
Pellets or membrane should be cryoground prior to extraction with liquid nitrogen. A visual inspection of the cryoground product must be performed; an acceptable product has homogenous particle size with the consistency of a flaky powder.
Weigh approximately 8 g of polymer into a 50 mL centrifuge tube; record weight to 2 decimal places. Weigh a second 8 g aliquot to prepare a duplicate sample.
Add approximately 25 mL (19.8 g, density = 0.792 g/mL) of LC/MS grade methanol into each duplicate tube.
Tightly cap tubes and shake briefly to mix. Place tubes in a rack into the sonicator, also filled with water and pre-heated to 60 °C.
Allow to incubate with heated sonication for 6 hours. During the incubation period, monitor temperature periodically to ensure heat remains ±5 °C of the 60 °C setpoint.
After 6 hours, remove centrifuge tubes and allow to cool to room temperature.
Centrifuge scintillation vials for 15 minutes at 5000 rpm.
Transfer 15 mL (11.88 g) of the methanol extract into a clean centrifuge tube. Label the tube with the extraction number.
Add a fresh 15 mL aliquot of methanol to the original (polymer-containing) tube in an equal amount to the weight removed in Step 8. Shake and vortex to break up packed polymer.
Repeat extraction steps for a total of three sequential extractions per sample. After the final extraction, the extracted polymer and original tube may be discarded.

Physicochemical properties:
Fluorinated ionomers are practically insoluble in water and organic solvents including octanol.
Fluorinated ionomers are available as membranes, resins and aqueous dispersions (e).

Stability (a, b, c, d, e, f)
In the references provided, hydrolysis, light, oxidation and biodegradation stability as well as the thermal stability and recommended use temperatures of fluorinated ionomers are documented (a, b, c, d, e, f). Fluorinated ionomers are not soluble in water or hydrocarbons (e.g., octanol) and are chemically and biologically stable.

A fluorinated polymerization aid is used in the manufacture of some, not all fluorinated ionomers.

References
(a) Grot, W., 2011. Fluorinated Ionomers. PDL Handbook Series, Elsevier Inc. http://dx.doi.org/10.1016/C2010-0-65926-8.

(b) Heitner-Wirguin, 1996. Recent advances in perfluorinated ionomer membranes: structure, properties and applications. J. Membrane Sci., 120:1-33. http://doi.org/10.1016/0376-7388(96)00155-X
(c) Mauritz, 2004. State of Understanding of Nafion™. Chemical Reviews 104(10):4535-4586. https://doi.org/10.1021/cr0207123
(d) Nafion™, 2015. In, Encyclopedia of Polymer Science & Technology, John Wiley & Sons. https://doi.org/10.1002/0471440264.pst633
(e) Nafion™ Membranes, Dispersions and Resins. https://www.nafion.com
(f) Kusoglu, A.; Weber, A. Z., 2017. New Insights into Perfluorinated Sulfonic-Acid Ionomers. Chemical Reviews 117(3):987-1104. http://dx.doi.org/10.1021/acs.chemrev.6b00159
(g) Jalani, et al. 2005. The effect of equivalent weight, temperature, cationic forms, sorbates, and nanoinorganic additives on the sorption behavior of Nafion®. Journal of Membrane Science, 264(1-2):167-175. http://doi.org/10.1016/j.memsci.2005.04.047

5. Fluoropolymers: Benefits, Features and Alternatives Assessment

5.1 PVDF and 5.2 PVDF Copolymer

(main reference : https://www.extrememateriales-arkema.com/en/product-families/kynar-pvdf-family/download-performance-characteristics-data-brochure/

Polyvinylidene fluoride (PVDF) is a tough engineering thermoplastic that offers a balance of performance properties. It has the characteristic stability of fluoropolymers to resist harsh thermal, chemical and ultraviolet environments. PVDF, in addition to being readily melt-processed by standard methods, can be dissolved in polar solvents, such as organic esters and ketones, for coating applications. PVDF can be produced by homopolymerization or copolymerization, providing a full range of products with different molecular architecture along with different ranges of properties. Some of the important properties of PVDF homopolymers and copolymers are a function of the crystalline content and type of crystalline structure, both of which are affected by the processing methods and conditions.

Features

- Outstanding resistance to sunlight/UV exposure
- Tremendous chemical resistance to a wide range of aggressive chemicals
- Radiation resistance
- Excellent burn characteristics / flame and smoke properties (low flame spread and low quantity of smoke generated)
- Easy processing on industry-standard equipment and easy post-processing, such as welding and fabrication
- Extremely high purity for the most demanding applications
- Extremely high electrochemical stability
- Excellent abrasion resistance
- High temperature rating: RTI 150 °C

Applications

- Chemical Processing: Due to its high temperature resistance, low permeability and high mechanical strength, PVDF is used as a contact surface for the production, storage and transfer of corrosive fluids (chemically resistant to halogens and acids). PVDF resin is used in mechanical components, fabricated vessels, tanks, pumps, valves, filters, heat exchangers, tower packing, piping systems, and many other applications.
- Wire and Cable: PVDF has excellent fire, abrasion, chemical and impact resistance. Depending on the test method, it can have up to a 150°C rating and can be irradiated for even higher ratings.
- Electricity and Electronics: Its fire resistance, abrasion resistance, low-smoke emission, chemical and mechanical properties make PVDF resin suitable for protective sheathing, plenum and communications wiring insulation and binder resin for battery manufacture.
- High Purity: As semi-conductor and pharmaceutical production require increasingly pure materials, high purity PVDF resin grades meet industry needs (low extractables values). PVDF resin regulatory compliances include food and water use certifications (in FDA 177.2510 and/or 177.2600 compliance, NSF Standard 51 – Food Equipment Materials, NSF Standard 61 – Drinking Water System Components) as well as compliance for use in industries such as healthcare (USP Class VI approval).
- Transportation: PVDF resin is used in both public and private transport vehicles as a barrier liner for automotive fuel line and gas station fuel pipes, in decorative films, as a binder in HEV/EV batteries, as molded and thermoformed body components (weathering, anti-grime/graffiti), and as tank trailer linings for corrosion protection. PVDF resin has strength, flame resistance, durability and versatility that make it a preferred material in automotive wiring harnesses, general coatings, and plastic optical fibers.
    - Focus on Battery: PVDF polymers are used in the battery industry as binders for cathodes and anodes in lithium-ion batteries, and as battery separators in lithium-ion polymer batteries. PVDF is helping to design thinner and smaller lithium-ion batteries.
- Architecture: The excellent outdoor aging and weathering properties of PVDF resin lead to its use in long-lasting 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 anti-grime and anti-graffiti surfaces with excellent weathering properties.
- Photovoltaic: PVDF Film is used in the protection of back sheet and for front sheet glazing. Those films provide exceptional solar transmittance and also have excellent dirt shedding and fire resistance properties.
- Membrane: PVDF resin is a respected membrane material for applications ranging from bioprocess separations to water purification because it is extremely chemically resistant and well suited to aggressive chemical environments. PVDF tolerates ozone and chlorine (an oxidant increasingly used for water purification) very well. Grades with FDA and/or NSF compliance, are compatible with food and/or beverage contact applications. It is used to manufacture flat sheet, hollow fiber, and TIPS process membranes, and/or enclosed shapes that cannot be lined or coated in a conventional manner.
- Fabrics: Woven and non-woven fabrics can be produced using specific PVDF grades. These fabrics offer excellent chemical resistance, stability to sunlight, and flame retardant properties.

General physical and mechanical properties

PVDF homopolymers and copolymer resin grades give the option to combine rigid and flexible materials when processing. As a material of construction for pumps and pipe, PVDF exhibits excellent resistance to abrasion. PVDF can also be manufactured in thin, flexible and transparent films, filament, and tubing. Sunlight has little to no effect on PVDF resins.

- Strength & toughness: PVDF fluoropolymers are inherently strong and tough as reflected by their tensile properties and impact strength. An ambient temperature tensile strength at yield of 35-55 MPa (5,000-8,000 psi) and an unnotched impact strength of no break offered by select resins emphasize this. These characteristics are retained over a wide range of temperatures
- (Flexural creep: Compared to many thermoplastics and fluoropolymers tensile yield of 15-55 MPa (2,200-8,000 psi), PVDF polymers have excellent resistance to tensile creep and fatigue also at elevated temperatures. Likewise, the short-term flexural creep resistance of PVDF homopolymer resins reflects superior load bearing performance.
- Tensile creep: Compared to many thermoplastics and fluoropolymers tensile yield of 15-55 MPa (2,200-8,000 psi), PVDF polymers have excellent resistance to tensile creep and fatigue also at elevated temperatures. PVDF resins are able to maintain a low tensile creep when subjected to constant stress even at high temperatures.
- Flexural creep: PVDF is rigid and resistant to creep under mechanical stress and load. Likewise, the short-term flexural creep resistance of PVDF homopolymer resins reflects superior load bearing performance.
- Thermal properties: PVDF resins exhibit high thermal stability. Prolonged exposure of some PVDF grades at 250 °C (482 °F) in air does not lead to weight loss. No oxidative or thermal degradation has been detected during continuous exposure at 150 °C (302 °F) for a period of ten years. In testing, select resins have been given an RTI of 150 °C. PVDF resins thermally decompose at temperatures greater than 375 °C (707 °F). However, the melt processing range of unfilled PVDF homopolymer resins is very broad – from slightly above the melting point of 155 - 170 °C (311-338 °F) up to 300 °C (572 °F).
- Electrical properties: PVDF combine high dielectric strength and excellent mechanical properties over a broad temperature range. This has led PVDF resin to be used for thin-wall primary insulation and as a jacket for industrial control wiring. With proper shielding, PVDF resin can be used as jacketing for high frequency plenum-rated data cables because of its excellent flame and smoke performance.
- Stability to weather & UV effects: Many years of outdoor exposure in direct sunlight have little effect on the physical properties of PVDF. Some increases in tensile strength and reduction in elongation do occur over time.
- Ozone resistance: Ozone is a powerful oxidizing agent characterized by a high degree of chemical instability. PVDF offers excellent chemical resistance to ozone exposure.

5.3 ECTFE Copolymer and 5.4 ECTFE Terpolymer

Poly-Ethylene/Chlorotrifluoroethylene (ECTFE) is a semi-crystalline and melt-processable fluoropolymer obtained by the copolymerization of the two monomers ethylene and chlorotrifluoroethylene, with an essentially 1:1 alternating structure.

Because of its chemical structure, ECTFE offers a unique combination of properties including excellent chemical resistance, high thermal rating and very good mechanical properties. Enhanced stress cracking performances can also be achieved with chain structure modifications of the polymer. ECTFE is widely used in anti-corrosion applications such as coating or in self-supporting constructions (pipes) and architectural films.

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, roto and transfer molding. Powder coating methods are also applicable.

ECTFE resins are available in a wide range of melt viscosities to suit virtually every processing technique. ECTFE resins are extremely pure polymers and they are suitable for high purity systems in the biotech and pharmaceutical industries, as well as a lining and coating for ultra-pure water systems in the semiconductor industry.

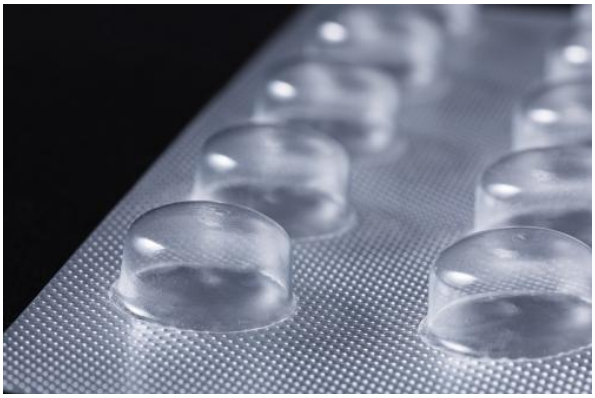
ECTFE embodies an excellent trade-off among general properties, offering high chemical and mechanical resistance combined with easy processing of the resin.

In addition, it exhibits much lower surface roughness when compared with most other plastics. This is extremely important in high purity applications as it helps limiting foreign particle trapping.

5.5 PCTFE

Overview

PCTFE is a homopolymer of chlorotrifluoroethylene. PCTFE is melt processible and can be extruded or molded. PCTFE has excellent mechanical properties, especially hardness, and chemical resistance next to PTFE and PFA. Therefore, PCTFE has been widely applied to the semiconductor industries, or aerospace industries. In addition to excellent thermal and chemical stability, it has very low moisture absorption and permeation and hence, it is applied to pharmaceutical package industry. It also is highly resistant to cold flow, is very rigid, is tough, has excellent dimensional stability and extremely good low temperature properties. It is especially applicable as a valve component material in cryogenic fluid service. PCTFE Films excels in water vapor barrier, transparency, chemical resistance and electric insulation as a plastic film. It exerts optimal moisture prevention out of the plastics. Moreover, it has highly transparent value of Haze less than 1%.
It shows excellent durability to chemicals for a long time under solutions of acid, alkali and organic.
Wetting property is improved by applying corona treatment on one side of the film.



PCTFE Features:

- A melt processable resin of chlorotrifluoroethylene with physical and mechanical properties.
- Excellent mechanical properties, especially hardness.
- It is one of the best class water vapor barrier property among resins.
- Excellent dimensional stability and low temperature characteristics.

PCTFE Applications:

PCTFE fluoropolymers are used in semiconductors, chemicals, electronic components and medical. It is also utilized as component materials for cryogenic fluids.

-Blister package
- Sealing materials (packing, gasket)
- Pump parts (casing, impeller, valve body, plug)
- Chemical tube
- Cryogenic parts (valve, fitting, gasket, filter housing)
- Excellent in mechanical properties, although it is slightly inferior to PFA and FEP in heat resistance and chemical resistance.

General physical mechanical properties

PCTFE is a long chain-like crystalline polymer made up of repeating CF2-CFCl-units. And it has high gas barrier property, high hardness, high mechanical strength and high transparency due to chlorine atom.

- Compression molding and extrusion molding are suitable. Increasing the molecular weight of PCTFE will improve stress crack resistance.

5.6 FEVE

FEVE fluoropolymer resins are polymers consisting of alternating **f**luoro**e**thylene and alkyl **v**inyl **e**ther segments. They were developed in 1982 as the first solvent-soluble fluoropolymers in the world. The alternating fluorinated segments provide outstanding UV stability, weather and chemical resistance, while the vinyl ether segments provide solvent compatibility and cross-linking sites. FEVE resins are used to make ultra-weatherable coatings for architectural, aerospace, automotive, bridge and industrial maintenance markets. These resins can be used to make both clear and pigmented coatings. They can be formulated with a wide range of gloss (from high gloss to flat finishes) and colors. The FEVE polymer is a platform chemistry that is supplied in various forms including solvent-based liquid for easy application, water based resins for low VOC (Volatile Organic Compound) and low odor coatings, and a flake for sustainable powder coatings. FEVE powder coating materials are environmentally friendly providing zero VOC and HAPS (Hazardous Air Pollutants) free coatings.

FEVE coatings protect steel, aluminum and other metals as well as concrete from degradation by UV light, wind and rain, and corrosion. Because of their ultra-weatherability, FEVE based coatings offer substantial life cycle cost savings over conventional coatings. They can be used in the field for re-coating of structures, or in the shop to manufacture pre-coated panels. FEVE resin chemistry allows for use in coatings that cure at ambient or low temperatures. This is important for use over heat-sensitive substrates like vinyl and fiberglass. Solvent based and water based FEVE resins may be

used to create highly weatherable coatings for vinyl and fiberglass building materials that allow for a cure process that meets the specific needs of these sensitive substrates.

High performance FEVE coatings can extend the lifetime of bridges and water tanks and reduce the frequency of maintenance, by helping to prevent coating degradation at the hands of UV radiation, salt, and water. These coatings contain anti-corrosive properties that help maintain the coating's structural integrity for decades. Costs associated with bridge downtime, including increased traffic congestion, are also significantly reduced over the life of the coating.

FEVE resins have outperformed even the best acrylic urethane coatings on steel, aluminum, magnesium and plastics like ABS, polyurethane, FRP, PVC, polyethylene, polypropylene and polycarbonate enabling transportation manufacturers to create and maintain the appearance for years. FEVE-based topcoats have been shown to yield over five times the lifespan of acrylic urethane coatings typically used in the transportation industry. FEVE resins can also be blended with traditional resins like acrylics to significantly increase their performance. For example, FEVE-based coatings can reduce maintenance costs in the aerospace market by as much as 50 % over the life of the plane, in addition to substantially reducing the loss of revenue during scheduled repainting. Aircraft coated with FEVE resin typically require no repainting for at least eight years, maintaining outstanding appearance and a durable surface that allows for easy cleaning. In contrast, acrylic urethanes begin to fade and chalk after only three years and require repainting after five.

FEVE Alternatives Assessment

The two main alternatives for an FEVE-based coating are polyurethanes and polysiloxanes. Urethanes have a long performance history and are still widely used as durable coatings. In general, polyurethanes will usually start to chalk and change color within 5-10 years. Due to degradation, the coating thickness of urethanes starts to decrease and after 15-25 years will no longer act as a barrier against corrosion. Polysiloxanes come in two types, epoxy and acrylic.

Siloxanes have a couple of advantages. First, they don't require an isocyanate crosslinker; they crosslink via a moisture cure mechanism. Second, they can be used as a two-coat system consisting of a zinc rich primer and a higher film build of siloxane (usually around 6-8 mils). This saves time especially in fabrication shops. Neither coating system discussed above will weather as well as LUMIFLON. A typical FEVE coat system will retain color and gloss for 25+ years and can prevent corrosion for up to 60 years, depending on the environment. Outdoor testing done in Japan over a 16-year period showed that a 25 µm FEVE-based coating retained 21 µm of thickness after 16 years. A 75 µm (3 mil) topcoat, typical thickness in a coating project, has a theoretical life of >100 years. In that same test, a 25 µm polyurethane coating was gone after 12 years. We have 30-year test results from bridges in Japan where gloss retention of the FEVE-based coating was 80% with a very small color change. In terms of corrosion protection, we've determined that a FEVE-based coating is about the same as a urethane or siloxane coating. However, we have test results that show that FEVE-based coatings retain their protective properties for a longer period than either of the other coatings. This makes sense in that the main purposes of the topcoat are to preserve its

initial appearance for as long as possible, and to act as a barrier film to corrosion initiators like chloride, water, and oxygen.

5.7 EFEP

EFEP is a terpolymer of ethylene, tetrafluoroethylene and hexafluoropropylene that provides both outstanding chemical and mechanical performance. EFEP also has outstanding transparency and because of its lower processing temperatures it can be coextruded with conventional thermoplastic polymers such as polyamide, EVOH, and modified polyethylene. It can be extruded, injection molded and blow molded and is used in many applications exemplified below. (Daikin Fluoropolymer Handbook)

EFEP was developed with outstanding moldability and with ease of polymer processing in mind with the goal to increase production efficiency and reduce manufacturing costs, while maintaining a low melting point, strong mechanical performance and chemical resistance. EFEP has a melting point of 160-200 ℃ and a high decomposition temperature (357 to 380 ℃) and can therefore be molded over a wide temperature range. Due to the residing ethylene units in the backbone, this leads to increased tensile and elongation performance as compared to other fluoropolymer resins._EFEP has many fluorine molecules on the backbone which help to increase the resistance of the polymer to chemicals like strong acids and bases. The table (1) below shows a comparison of EFEP to PFA with both weight change % and physical property % retention after soaking in various chemicals.

Comparison of Chemical Resistance of Neoflon EFEP and PFA
(Holding Ratio of Weight and Tensile Characteristics)

Immersed at 60°C for one month

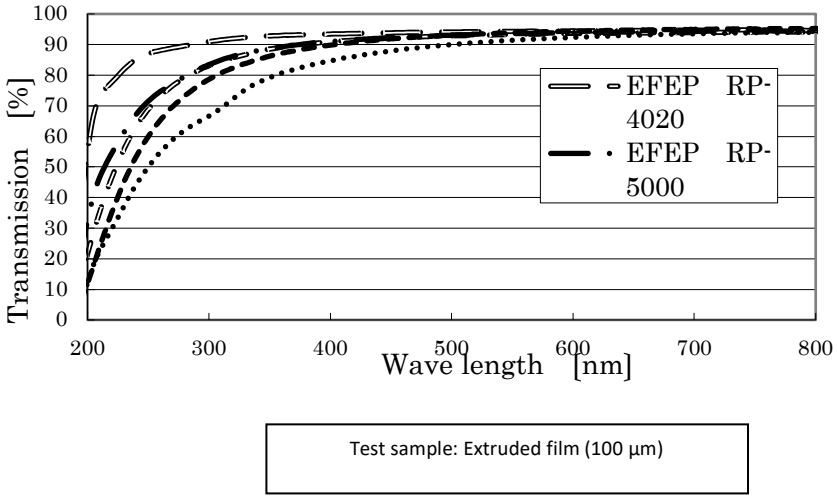
		EFEP			PFA		
		Weight holding ratio	Holding ratio (%) Tensile strength	Holding ratio (%) Tensile elongation	Weight holding ratio	Holding ratio (%) Tensile strength	Holding ratio (%) Tensile elongation
Acids	Hydrochloric acid (35%)	100	102	103	100	92	92
	Nitric acid (95%)	100	98	94	100	95	95
	Sulfuric acid (60%)	100	100	99	100	93	94
Bases	Sodium hydroxide (50%)	100	101	100	100	92	94
	Ammonium hydroxide (28%)	100	102	104	100	89	96
Solvents	Acetone	98	97	103	100	94	97
	Methyl alcohol	100	90	92	100	95	97
	Chloroform	99	96	100	100	93	94
	Ethyl acetate	98	91	98	100	97	104
	Toluene	100	99	98	100	97	99
	Diethylamine	99	88	94	100	90	91

Appearance change: EFEP Acetone: Pale brown Diethylamine: yellowing
PFA Acetone: Pale brown

Table 1

There are several additional beneficial properties to be observed for EFEP. Again, due to the fluorine content, EFEP shows excellent weatherability for use in outdoor applications. EFEP also shows excellent optical transparency in the lower wavelength regions (200-400nm) as compared to other fluoropolymers. The transparency to light has been improved by roughly 30% by using an EFEP. The figure (1) below represents the % transmission of EFEP as compared to other materials like PFA and FEP.

Figure 1



Finally, like most fluoropolymers the dielectric constant and loss tangent are also low compared to other non-fluorine containing polymers. As mentioned above, EFEP has bonding capability to other materials making it attractive for multi-layer constructions. Certain specific grades of EFEP provide outstanding barrier properties towards hydrocarbons such as fuel vapor.

EFEP Applications

As mentioned above, EFEP has excellent transparency. This makes the material and excellent choice in applications in which visual control is required. Examples include chemical solution piping and liquid level gauges, etc. A common application for RP-4020 is for perfume bottle tubes due to the same refractive index as most perfume solutions making it near invisible to the naked eye.

Due to EFEP's strong resistance to fuel permeation, it finds a common use in automotive fuel hoses. EFEP can be laminated on the inside of a polyamide tube which helps reduce the tube's overall fuel migration throughout. Recent initiative to use fuels derived from plants in place of petroleum-based fuel for environmental reasons are expanding throughout the world. Therefore, chemical resistance and fuel vapor barrier performance have become important properties in automotive fuel-line design. The chart below shows the results of chemical resistance of Daikin EFEP compared with non-fluoropolymer resins commonly used for fuel lines.

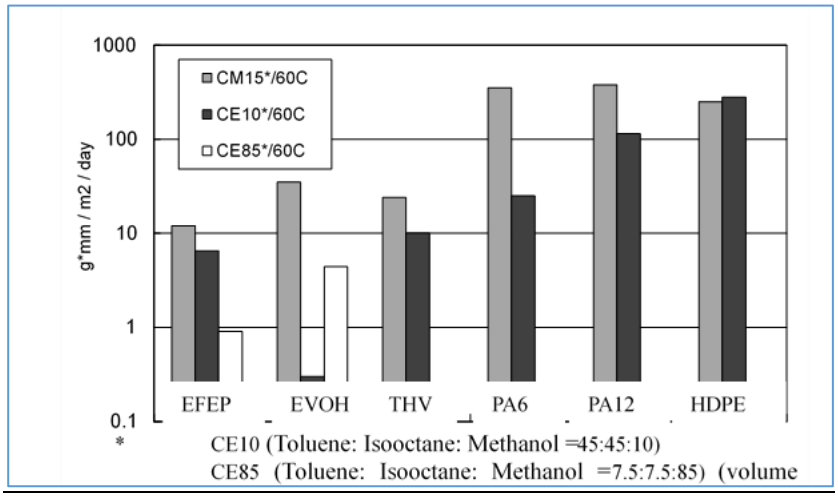


Table 3

Table 3 shows the fuel permeability coefficient (g* mm/m^2/day) (60°C) of each resin against CM15 and CE10 as well as CE85. Before fuel permeability transparency was regulated, polyamide 12 single-layer tube was used as fuel piping, but as compared to polyamide 12, EFEP exhibits outstanding fuel permeability resistance. In addition, when EFEP is compared with EVOH, the larger the alcohol content in the fuel, the more outstanding is EFEP in fuel permeability resistance.

EFEP can also be used in catheter applications due to its mechanical strength and strong chemical resistance. Other common applications for EFEP include cables: mono-wall electrical cable and sheaths of optical cables, film applications that include multilayer antifouling film and multilayer bags, and multilayer blow molded bottles. EFEP can also be filled with materials to provide greater mechanical strength or to modify conductivity performance.

References

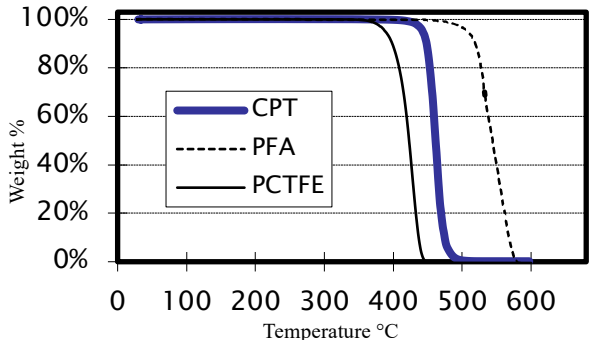
Daikin Fluoropolymer handbook, Daikin Industries, 2011, PP.84-93.

5.8 CPT

CPT is a Terpolymer of chlorotrifluoroethylene, tetrafluoroethene and perfluoroalkyl-vinyl-ether. The polymer is a modified PFA-type fluoropolymer that is melt processible. The processing of CPT is done by common extrusion molding techniques, such as, injection and compression molding.

The addition of the third monomer chlorotrifluoroethylene provides a unique property to the polymer resulting in low permeability as compared to PFA. Being a hybrid polymer, it has many outstanding properties coming from both the PFA and PCTFE.

CPT possesses valuable thermal stability properties. CPT has a melting point similar to FEP (~255 ℃) and a continuous service temperature of up to 200 ℃ allowing it to find use in applications requiring higher thermal stability. The heat-weight reduction curve of the hybrid CPT as compared to PFA and PCTFE is shown in figure 1.



Heat-weight reduction curve of Neoflon CPT
Figure 1

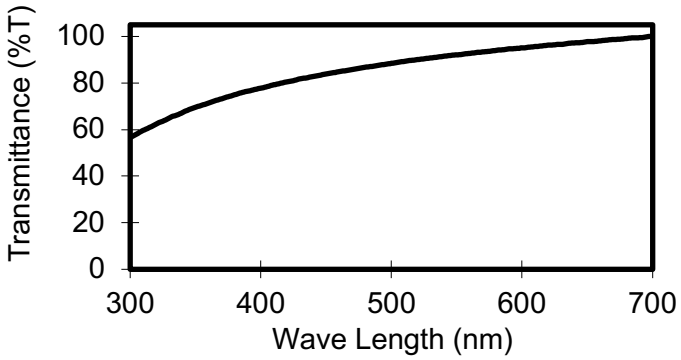
CPT provides excellent chemical resistance and does not swell in contact with most solvents. As mentioned above, CPT also has excellent barrier properties that prevents the permeation of gases and chemical solutions throughout the molded article. Table 1 below shows the chemical performance of CPT when exposed to various acids, bases, and common solvents as compared to PFA and FEP.

Table 1

Chemicals		Mass change (%)		
		Neoflon CPT	Neoflo n PFA	Neoflon FEP
Hydrochloric acid	35%	0.0	0.0	0.0
Nitric acid	60%	0.0	0.0	0.0
Hydrofluoric acid	50%	0.0	0.0	0.0
Ammonia water	28%	0.0	0.0	0.0
Methyl alcohol		0.0	0.0	0.0
Acetone		0.1	0.0	0.0
Methyl ethyl ketone		0.1	0.0	0.0
Carbon tetrachloride		0.0	0.0	0.0
Toluene		0.0	0.0	0.0
Ethyl acetate		0.0	0.0	0.0
Ethanolamine		0.0	-	-
Diethylamine		-	0.0	0.0
Dimethylformamide		0.0	-	-

Note) Immersing conditions: 25 °C × 7 days

There are several other unique properties of CPT polymers. CPT has an outstanding modulus and strength that is superior to PFA and FEP. Like most fluoropolymers, CPT is considered a noncombustible material that does not generate smoke and is free of any dripping below the critical oxygen index of 90 % volume. As with most fluoropolymers, the fluorine content on the backbone allows for outstanding electrical/insulation properties. Like most fluoropolymers, CPT also provides outstanding optical transmittance in the ultraviolet to visible light region. Figure 2 shows the transmittance scan for CPT at various wavelengths.

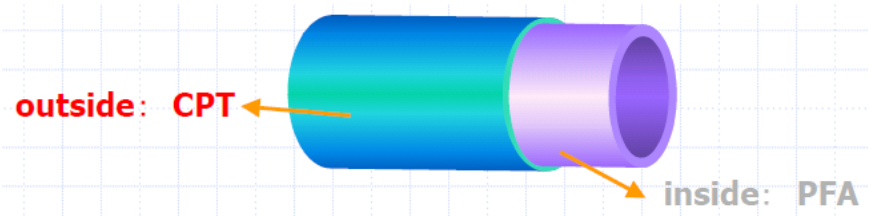


Optical transmittance of Neoflon CPT

Figure 2

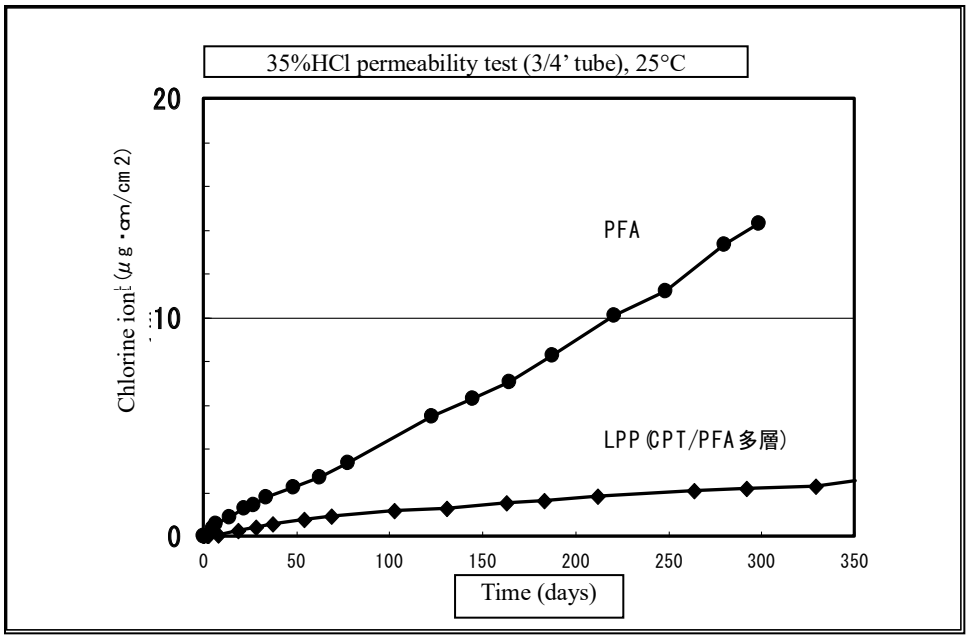
Applications of CPT:

There are numerous commercial, technical, and industrial applications for CPT polymers. Due to the superior permeation resistance towards gasoline and that CPT can also be bonded to various types of specific recipes of rubber by cross-linking, it can be used in filler neck fuel hose applications where the material needs to meet LEV III requirements (U.S. environmental protection regulations in automotive applications). CPT also has excellent barrier properties against many kinds of organic solvents and strong acids especially for HF, HCl and HNO3. This is very useful for semiconductor application. Since it has a wider processing window, CPT can be co-extruded with other fluoropolymers like PFA and FEP. This leads to increased barrier property performance to many plastics by utilizing the co-extrusion process. Figure 3 below shows an example of a tubing construction using CPT as the outer layer in a multilayer tube containing PFA. Materials used in the semiconductor must have good resistance to strong acids and bases used in the etching process. Figure 4 represents the differences of acid permeation of a tube made with PFA compared with a multilayer LPP tube using CPT. The LPP tube shows much better permeation resistance to hydrochloric acid as compared to the tube using only PFA.



LPP Tube Construction

Figure 3



Hydrochloric Acid Permeability of LPP Tube

Figure 4

References

Daikin Fluoropolymer Handbook, Daikin Industries, PP.58-62.

Daikin Industries Homepage. https://www.daikinchemicals.com/solutions/products/fluoropolymers/neoflon-cpt.html?_ga=2.257391307.1754525417.1636603879-520575968.1622167042

5.9 THV

THV is a group of fluorothermoplastic polymers composed of tetrafluoroethylene, hexafluoropropylene, and vinylidene fluoride (1, 2, 3). Different THV grades exhibit excellent high flexibility, high transparency, bondability to fluorinated and non-fluorinated 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 multi-layer construction (1,4). "The high transparency of the special film makes the film the ideal adhesive film for laminated glass and the optimal protective film for surfaces. Also for lamination with fabrics (textile, glass, nylon, fluoropolymers, etc.) and as a sealing film, the high-performance film NOWOFLON THV is used" (5). Some specialty THV grades are designed as Polymer

Processing Additives to reduce defects during melt extrusion of other engineering and standard polymers (6).

THV grades compete against other fluorothermoplastic materials for applications that require transparency and low refractive index as well as with fuel barrier materials. Commercial non-fluorinated materials cannot be used as substitutes for THV in many applications: PMMA is used in conjunction with THV to provide differences in refractive index to create total reflection needed for polymer optical fibers (7). Transparent polymers like PMMA or Polycarbonate do not have the same chemical resistance or UV resistance to compete directly with THV. On the fuel barrier side polyvinyl alcohols or nylon materials may be good barrier materials to hydrocarbons but cannot provide barrier properties to alcohol containing fuels. There are other fluorothermoplastic materials competing with THV as fuel barrier materials.

References

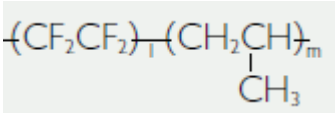
(1) D. E. Hull, B. V. Johnson, I. P. Rodricks and J. B. Staley in "Modern Fluoropolymers" Edited by John Scheirs 1997 Wiley & Sons Chichester England pp 257ff. ISBN-13: 978-0471970552
(2) K. Hintzer, T. Zipplies, P. Carlson, W. Schmiegel "Fluoropolymers, Organic" in Ullmann's Encyclopedia of Industrial Chemistry 2014 Seventh Edition pg. Chapter 2.11 pg. 36 ff.
(3) H. Domininghaus, "Tetrafluorethylen/Hexafluorpropylen/Vinylidenfluorid-Terpolymer" in "Kunststoffe, Eigenschaften und Anwendungen" Springer 2005 5th edition Chapter 2.1.7.4 pg. 564f.
(4) R. Dams, K. Hintzer "Industrial Aspects of Fluorinated Oligomers and Polymers" in "Fluorinated Polymers Volume 2: Applications" Edited by B. Ameduri and H. Sawada Royal Society of Chemistry Cambridge pg. 16 and pg. 19f.
(5) https://www.nowofol.com/en/products/nowoflon-thv/
(6) C. Lavallée, Chapter 4: "Polymer Processing Additives (PPA)", in Macnamara Jr., James (ed.), Film Extrusion Manual – Process, Materials, Properties, 3rd Edition, TAPPI Press, Atlanta, pp. 291–302 (2020).
(7) Eun-Ju Park, In-Cheol Park, Min Park, Moo Sung Lee "Preparation of Cladding Polymers for Plastical Optical Fibers – miscibility and Interfacial Adhesion of PMMA/THV blends" textile Science & Engineering, 364ff. January 2008
(8) Denis Duchesne, Dennis Hull and Attila Molnar "THV Fluorothermoplastics in Automotive Fuel Management Systems" SAE Transactions Vol. 108, Section 5: JOURNAL OF MATERIALS & MANUFACTURING (1999), pp. 442-450 (9 pages)
(9) https://multimedia.3m.com/mws/media/93162O/permeation-of-dyneontm-fluoropolymers.pdf

5.10 FEPM

Overview:

Curable FEPM polymers (based on Tetrafluoroethylene-Propylene, TFE-P) were first introduced to the market in the 1970's. They are unique fluoroelastomers that do *not* include vinylidene fluoride and are therefore *not* FKMs.

Commercial polymers are classified into two types: TFE-P copolymer type and TFE -P-CSM (Cure Site Monomer) copolymer type.

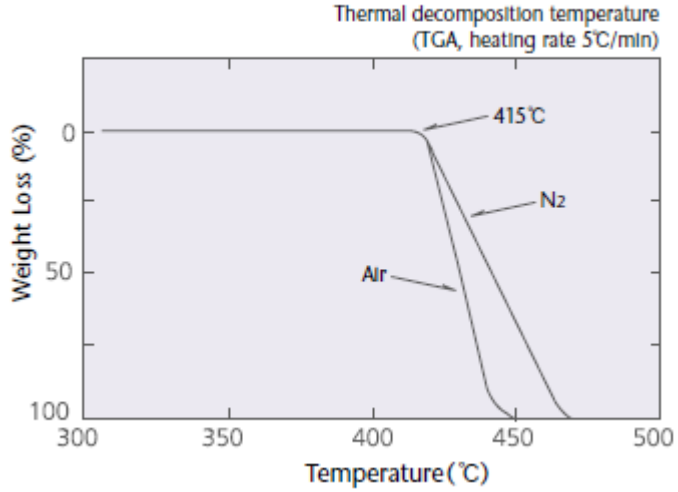


The polymer structure gives unique properties which offers excellent heat resistance, with a continuous service temperature of 200 ℃, and a maximum peak exposure temperature of 250 ℃, outstanding chemical resistance with no or little deterioration even in contact with strong acids and bases at high temperatures, and high electrical resistivity of the order of 10^15～10^16 Ω・cm.

Heat Resistance:

The TFE-P structure provides excellent thermal stability. The copolymer only starts to decompose in open-air or nitrogen gas at 415 ℃. The composition ratio of the copolymer is TFE/P=55/45. Uniquely, the lower fluorine content of 57% does not hinder the performance of TFE-P FEPM grades due to the lack of vinylidene fluoride, and relatively low or no saturation in the polymer backbone.

■Typical Thermogravimetric Curves



Standard Formulation and Vulcanization:

FEPM Fluoroelastomers can be compounded by conventional processing equipment, such as Banbury mixers and open 2-roll mills. Various articles can be produced by means of compression molding, extrusion, injection molding and calendering. They can be vulcanized by organic peroxides with the aid of an appropriate coagent, such as TAIC (triallyl isocyanurate).

Grades are mainly classified according to Storage Modulus, G'(as determined by a Rubber Process Analyzer, RPA) which measures a relative representative of molecular weight.

Standard Formulations and Properties (High-to-Low Mw, L-to-R):

Formulation	Polymer	100	100	100	100
	MT-Carbon (N990)	30	30	30	30
	TAIC*	5	5	5	5
	Peroxide A**	1	1	1	1
	Peroxide B***	—	—	—	—
	MgO (highly active)	—	—	—	—
	Sodium Stearate	1	1	1	1
	Zinc Stearate	—	—	—	—
Mooney Viscosity (121℃)	ML1+4	122	93	58	38
	ML1+10	114	85	51	35
Cure Condition	Press Cure	170℃/20min	170℃/20min	170℃/20min	170℃/20min
	Post Cure	200℃/4hrs	200℃/4hrs	200℃/4hrs	200℃/4hrs
Properties	Tensile Strength (MPa)	21	20	17	13
	Tensile Elongation (%)	300	230	280	360
	100% Modulus (MPa)	6	7	5	5
	Hardness (ShoreA)	72	72	70	70
	Compression Set (%, 200℃X70hrs)	35	26	29	32

* triallylisocyanurate (100%liquid)
** 1,3Bis (t-buthylperoxy isopropyl) benzene (100%active)
*** Di t-buthylperoxide (100%active)

Heat Resistance:
(High (Left)) and Medium (Right) Mw shown)

Heat Resistance	200℃	200hrs	Retention of Tensile Strength(%)	95	96
			Retention of Tensile Elongation(%)	88	93
			Change in Hardness (points)	+1	+1
		500hrs	Retention of Tensile Strength(%)	110	114
			Retention of Tensile Elongation(%)	87	93
			Change in Hardness (points)	+5	+5
		1000hrs	Retention of Tensile Strength(%)	101	102
			Retention of Tensile Elongation(%)	91	93
			Change in Hardness (points)	+3	+2
	230℃	200hrs	Retention of Tensile Strength(%)	88	89
			Retention of Tensile Elongation(%)	107	114
			Change in Hardness (points)	-1	0
		500hrs	Retention of Tensile Strength(%)	74	72
			Retention of Tensile Elongation(%)	122	132
			Change in Hardness (points)	-4	-3
	250℃	96hrs	Retention of Tensile Strength(%)	78	73
			Retention of Tensile Elongation(%)	106	116
			Change in Hardness (points)	0	0

Base Resistance:

Chemical Volume		Immersion Conditions		Retention(%)			Hardness Change (points)	Hardness Change (%)
		Temp(℃)	Time(day)	Tensile Strength	Tensile Elongation	100% Modulus		
Sodium Hydroxide	50%	180	3	102	91	86	+1	1.5
		180	7	96	94	81	0	-0.3
		180	30	117	81	126	+2	-0.1
		100	3	101	116	96	-1	1.1
		70	7	103	90	112	0	0.0
		70	30	105	84	123	0	0.1
		R.T.	7	108	116	75	+2	1.2
		R.T.	30	—	—	—	-1	0.3
		R.T.	90	—	—	—	—	0.7
		R.T.	180	—	—	—	—	0.5
	20%	100	3	95	117	92	-3	2.0
		R.T.	7	85	104	100	-1	-0.3
		R.T.	30	—	—	—	+1	-0.1
Aqueous Ammonia	28%	70	3	82	116	116	-1	3.2
		70	7	100	88	94	-2	1.5
		70	30	105	81	100	-1	2.0
		R.T.	7	—	—	—	0	1.3
		R.T.	30	—	—	—	+1	0.8
		R.T.	90	—	—	—	—	1.0
		R.T.	180	—	—	—	—	2.5
	7%	140	30	87	107	68	-8	16.1
Urea Solution	30%	100	7	107	94	94	0	2.8
Ethylene Diamine		25	7	105	108	108	+5	1.0

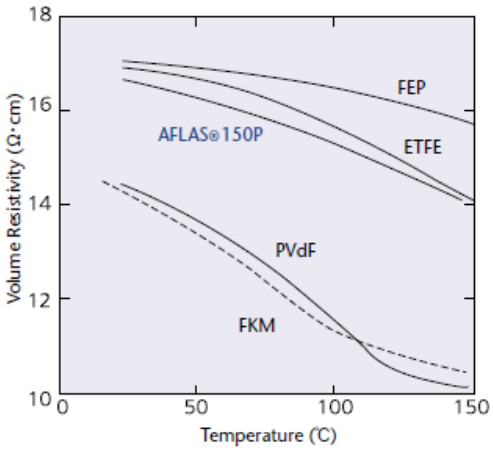
Broad Chemical, Hot Water, and Steam Resistance:

FEPM (TFE-P) Fluoroelastomers perform very well in strong acids, hot water, steam, bleaching liquors, bromides, formates, amines, phosphate esters, etc. They also perform well in polar solvents, but caution is advised when using with non-polar solvents where swelling would be of concern.

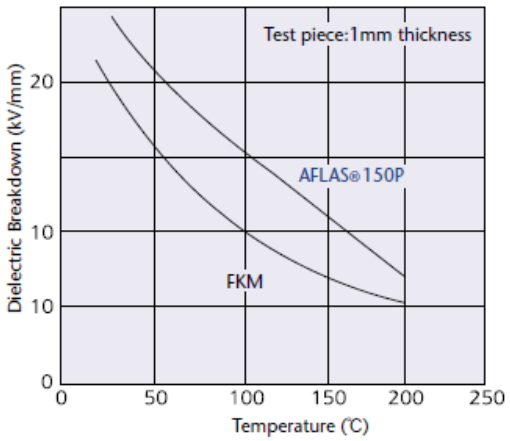
They also have very good oil resistance. High retention of properties are realized in sealing engine oil (SJ), Diesel oil (CD), automatic transmission fluid (ATF), gear oils and pinion fluids, brake fluid, heavy oils, etc.

Electrical Properties:

■Volume Resistivity vs. Temperature (pure rubber compound)



■Dielectric Breakdown vs. Temperature (pure rubber compound)



Other Properties:
The copolymers of FEPM are also highly resistant to radiation, gas permeation, ozone, have very good weather and flame resistance. They have very low odor retention and several grades have FDA Food Contact Notification status (FCN1958).
Typical Applications: is used in a range of applications including, thermal power plants, the oil and gas industry, ocean development, chemical and nuclear plants, the automotive industry, electronics and machinery.

Packings and O-Rings - excellent heat resistance and chemical resistance and is used in chemical plants, downhole applications.
Engine gaskets - excellent resistance to both engine oils and engine coolants.
Wire & Cable - excellent electrical properties, even at high temperatures, and therefore are suitable for insulation jacketing of cables, including High Voltage and EV fast-charging cables.
Shaft Seals - excellent chemical resistance to engine oil additives, for example, dispersants, oxidation inhibitors and abrasion inhibitors.
Thin Sheet - suitable for extrusion and calendaring for the manufacture of extremely thin sheet.
Sponge – filtration and thermal management membranes
Latex - aqueous dispersion of polymer suitable for use as a binder or coating material.

5.11 FKM and 5.12 FFKM

Overview
Fluoroelastomer products provide excellent high temperature and aggressive fluids resistance for sealing and fluid transport applications in automotive, oil and gas, chemical processing, small engine, and other harsh sealing environments. Seals and hoses made from FKM enable equipment manufacturer to meet and exceed evaporative emission standards while providing durability and requiring low maintenance.

Features of fluoroelastomer

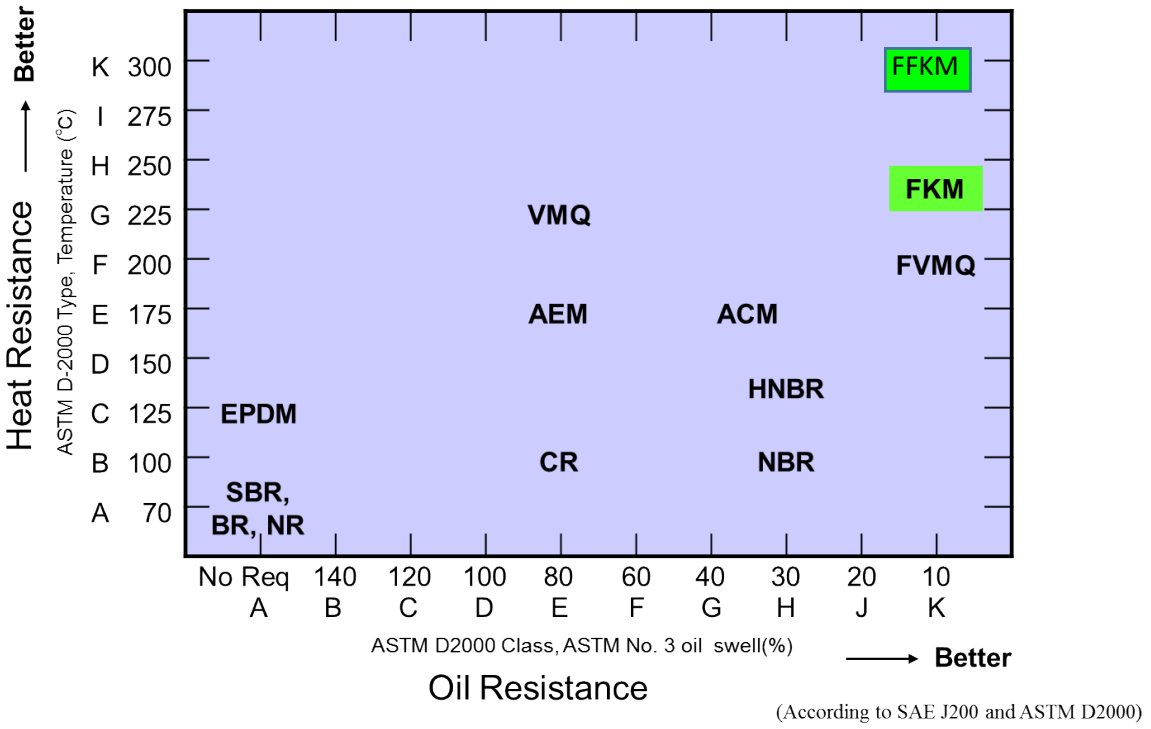
Fluoroelastomer (FKM and FFKM) products excel in high temperature resistance and low volume swell in oil compared to other elastomers as shown in the graph below. They also combine the most effective stability to all sorts of chemicals (lists are available on manufacturers websites) and fluids such as oil, diesel, ethanol mix or body fluid. With low permeation rate, fluoroelastomer allow meeting stringent automotive regulations about gas emission by reducing leakage significantly.

The complex polymer design allows stable extrusion and molding processes for various types of technical rubber parts and fitting in a wide range of processing constraints, reducing the risk of failures and increasing productivity and covers the full range of copolymers and terpolymers for bisphenol and peroxide curing as well as specialty elastomers and ready to use compound.

Application

- Automotive: OEMs continue to increase fuel efficiency, reduce emissions, eliminate fluid leaks and improve the efficiency of their systems.
- Chemical plants: Aggressive chemicals, steam, acids, bases and organic or inorganic solvents or gases require sealing materials with above average fluid resistance and long-term operability
- Oil & Gas: Drilling processes and other downhole fluids contain additives likely to degrade standard rubber.
- Consumer and wearable: Soft, flexible, non-reactive materials which don't degrade in contact with oils and perspiration are required
- Aerospace: high operating temperatures and high altitudes require superior heat resistance and low-temperature performance

Comparison among rubbers: Fluoroelastomer (FKM and FFKM) products excel in high temperature resistance and low volume swell in oil compared to other elastomers. The graph visualizes the unique performance characteristics of fluoroelastomers and perfluoroelastomers. At the same time it becomes apparent that there are no direct alternatives to fluorelastomers and perfluorelastomers.



(According to SAE J200 and ASTM D2000)

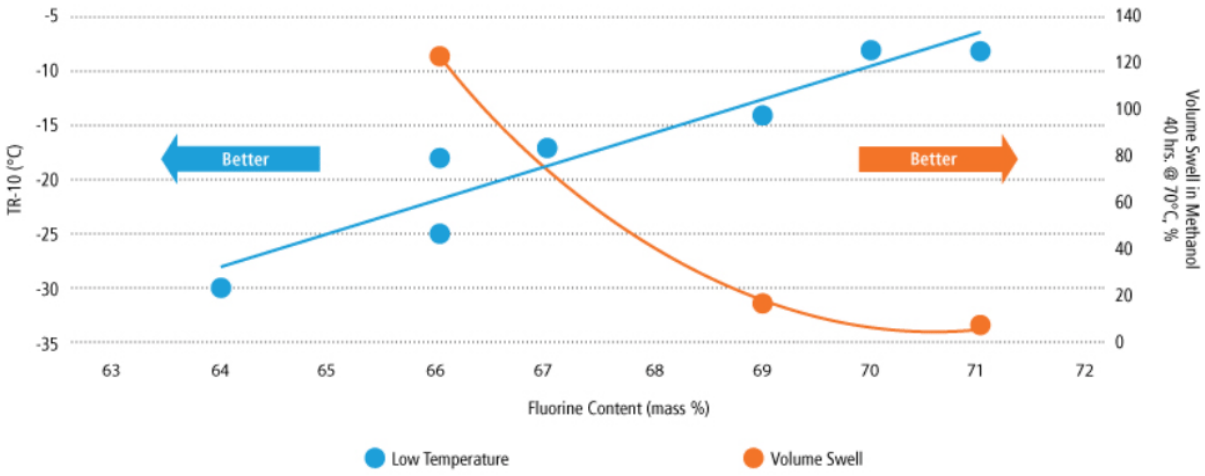
Effect of Fluorine Content

The fluorine content of a fluoroelastomer affects many things, especially low temperature resistance and fluid resistance.

In general, the lower the service temperature and volume swell of a compound, the better. However, as the chart below depicts, when selecting a fluoroelastomer there is generally a tradeoff between the two properties.

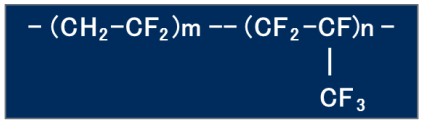
For low temperature operating conditions, consider selecting a fluoroelastomer copolymer grade. For sealing against aggressive fluids or other media, consider a 71 % fluorine terpolymer or even a perfluoroelastomer.

Effect of Fluorine Content on Solvent and Low Temperature Resistance



Copolymer (Fluorine: 66%)

(Vinylidene Fluoride – Hexafluoropropylene)

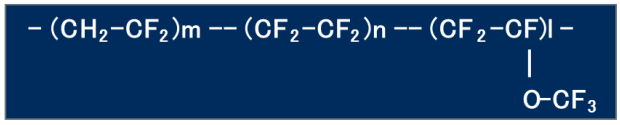


Terpolymer (Fluorine: 66%-71%)

(Vinylidene Fluoride – Hexafluoropropylene - Tetrafluoroethylene)

Low Temperature Type Polymer (Fluorine 64%-67%)

(Vinylidene Fluoride –Tetrafluoroethylene – Perfluoroalkyl vinyl ether)



GRADES & FEATURES

GRADES			
Type	**Curing System**	**Features**	**Typical Applications**
Copolymer	Bisphenol Curable	Compression set resistance, sealing property	Seals (oil, crank shaft, valve system, bearing), Fuel hose
	Peroxide Curable	Mechanical properties, chemical resistance, acid resistance, steam resistance, anti-flex fatigue	
Terpolymer	Bisphenol Curable	Strong polar solvent resistance, compression set resistance, sealing property	Turbo charger hose, O-ring

	Peroxide Curable	Strong polar solvent resistance, chemical resistance, acid resistance, steam resistance	
	Diamine Curable	Strong polar solvent resistance, mechanical properties	
Low Temperature type polymer	Peroxide Curable	Excellent low temperature sealing properties and mechanical properties, acid resistance, anti-flex fatigue	Injector O-ring Diaphragm
Base Resistant Elastomer	Peroxide Curable	Excellent mechanical properties, base resistance, coolant resistance, engine / transmission oil resistance Acid resistance, excellent anti-flex fatigue	Seal (oil, bearing ,coolant packer), Turbo charger hose, O-ring
Specialty Elastomer	Liquid Elastomer	Improvement of processability Reduction of hardness	Process aid
	Thermoplastic fluoroelastomer	At room temperature, it shows elasticity, and at high temperature over melting point, it shows good flowability like thermoplastics.	Semiconductor O-ring
Fluoroelastomer Compound	Bisphenol Curable Peroxide Curable	Available through custom compounders	
Fluoroelastomer Color Compound	-	Color ability, durability, supple touch, low friction	Wearables Consumer goods

<u>Fluoroelastomer Application Examples:</u>

Automotive: fuel hoses, needle tips, fuel pump diaphragm, engine wiring, crankshaft seals, O-rings for fuel injection systems, valve stem seals, filler hoses, bearing seals, O-rings for car air-conditioners, EGR hoses 1Intake gaskets, CAC valves

Office equipment: cleaning blades for copying machines, rollers for copying machines, computer gaskets, cooling hoses for main frame computers

Electrical: insulation oil caps for bullet train and other transportation lines, venting seals for liquid seal transformers, jackets for oil well cables, oil and heat resistant electric wiring

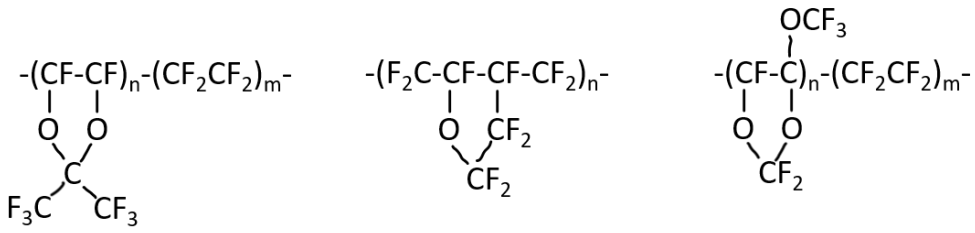
Chemical & mechanical systems: O-rings for chemical pumps, seals for hydraulic and lubricating equipment, seals for chemical pumps, flowmeters and piping, seals for dry cleaning equipment, seals for gas piping, seals for automatic packaging equipment, packing for high-temperature vacuum dryers, wringers for acid pickling, rollers for dyeing, robot cables, coating for plating tools, solvent rollers

Food & Pharmaceuticals: sanitary pipe packing, packing for insulated containers, packing for pressure cookers, seals for plate-style heat exchangers, solenoid valve seals for automatic vending machines, seals for water boiling vessels, tubes

Shipping & Aircraft: stern tube seals, valve seats for butterfly valves, fuel hoses and gaskets, seals for rotating shafts, gaskets for hydraulic equipment, firewall seals

Polyolefin film polymer processing: used as a polymer processing additive in small amounts (50-2000ppm) dispersed in polyolefins such as high-density polyethylene (HDPE) and linear low-density polyethylene (LLDPE) significantly improve 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 (Shell 2020). Selected FKM are approved for use in food-contact polyolefin films (Shell 2020).

5.13 Amorphous Fluoropolymers



(1) (2) (3)

Amorphous fluoropolymers are copolymers of tetrafluoroethylene (TFE) and specialty monomers that yield linear, high molar mass non-crystalline polymers (Resnick and Buck 1997, 1999; Gangal and Brothers 2010; Hintzer et al. 2013). The three commercial types (see URL links 1, 2 and 3 below) are shown in the graphic above. Amorphous fluoropolymers have the outstanding chemical and thermal stability and surface properties of semicrystalline fluoropolymers such as PTFE and also the unique properties associated with amorphous materials such as excellent optical clarity. The optical properties are outstanding and unmatched by any other substances, with >90 % transmission, and thereby low dissipation, over a wide range of wavelengths (e.g., 200-2,000nm). TFE/PDD copolymers (1) have the lowest refractive index known for a solid organic polymer (Groh and Zimmerman 1991). This unique combination of properties make amorphous fluoropolymers unmatched for their combination of properties for uses in fiber optics, photolithography, antireflective coatings, passivation and protective coatings for medical, military and aerospace devices as well as electronic applications (Gangal and Brothers 2010; Hintzer et al. 2013)

(1) https://www.teflon.com/en/products/resins/amorphous-fluoropolymer

(2) https://www.agc-chemicals.com/jp/en/fluorine/products/detail/index.html?pCode=JP-EN-F019

(3) https://www.solvay.com/en/brands/hyflon-perfluoropolymers/hyflon-ad

5.14 Fluorinated Ionomers

Fluorinated ionomers offer a unique combination of properties and enable significant advances in a broad range of applications in a number of industries. The important role of fluorinated Ion Exchange Materials (IXMs) in electrochemical processing, energy production and hydrogen production were described in the main paper. In addition, they support critical applications in the medical, water filtration and purification, electronics and semiconductors, energy storage, and chemical industries. Fluorinated ionomers provide industry with viable solutions in creating a more capable and sustainable world.

- Fluorinated ionomers, when in pellet form, can be melt processed to manufacture tubing for medical device applications. Their excellent barrier properties, chemical resistance, and stability at high temperatures make them desirable in this application.

- Fluorinated ion exchange resins are used in a variety of different separation, purification, and decontamination processes. Examples of these processes include water softening and water purification, used in desalination by electrodialysis (Chemours, Economic and Environmental Improvements with Versatile Membranes).

- Electroplating is a process for plating metal onto a substrate to create an extremely durable, protective barrier. Properties such as excellent thermal and chemical resistance, selectivity, mechanical strength, and insolubility in water make IEMs effective in transmitting metal ions and therefor desirable for electroplating semiconductor substrate (US Patent 7,128,823 B2).

- IEMs play an important role in semiconductor manufacturing by their ability to produce ultra-high purity chemicals, cost effectively. Additional properties like high ionic conductivity and selectivity and excellent mechanical and chemical stability, make them highly desirable in this application.

- IEMs have excellent mechanical properties, high ionic conductivity and selectivity, and chemical stability, making them highly desirable for energy storage technologies such as the flow battery. Flow batteries are a type of electrochemical battery that convert chemical energy into electricity. During this process, the job of the IEM is to keep the electrolytes separated and allow only the desired charge carrier ion to cross the membrane (https://www.nafion.com/en/applications/energy-storage).

- Fluorinated ionomers can be used as catalysts for organic synthesis in a number of applications, including isomerization and alkylation. Their high acid strength and exceptional chemical and thermal stability make them desirable for catalytic applications (Grot, 2011).

Fluorinated ionomers have significantly contributed to technological advances in a wide variety of industries. This includes the renewable energy industry, enabling growth in both hydrogen and energy production, in the pursuit of “clean” energy sources (http://www.sciencenter.org/climatechange/d/cart_activity_guide_energetic_electrolysis.pdf).

They also provide (a solution to eliminating hazardous legacy chemicals and) reduced energy consumption in chemical and industrial processes. There are no viable alternative chemistries that offer the combined performance characteristics of fluorinated ionomers that many critical applications require.

- In the chlor-alkali industry, IEMs replaced the use of hazardous materials (such as mercury and asbestos. The inhalation of mercury is known to be toxic to both the central and nervous systems and may be fatal (https://www.who.int/news-room/fact-sheets/detail/mercury-and-health. The negative health effects of asbestos exposure, such as lung cancer and mesothelioma, are well documented by the CDC (https://www.atsdr.cdc.gov/asbestos/health_effects_asbestos.html).)

- In electrolysis plants, the use of IEMs requires less energy consumption to decompose brine in the manufacture of sodium hydroxide, potassium hydroxide, chlorine, and hydrogen-basic chemical products. Their performance is unmatched by alternatives in their ability to minimize the influence of brine impurities and continuously maintain a high electrical current efficiency. (https://www.agcchem.com/products/forblue-membranes/flemion/)

- Fluorinated ionomers, when used in solid form as a reusable catalyst, eliminate the need for disposable liquid organics such as hydrofluoric acid or sulfuric acid in the chemical industry. These acids generate large volumes of chemical waste that require treatment prior to disposal or “energy-intensive regeneration” (https://www.solvay.com/en/brands/aquivion-ion-conducting-polymers/applications).

- Water electrolysis, utilizing PEM technology to separate hydrogen from oxygen, offers an environmentally safe way to generate large amounts of “green” hydrogen without emitting CO2 (ROMA), a known greenhouse gas. PEM water electrolyzers deliver high energy efficiency, exhibit a low gas crossover rate which yields high purity product, and can operate without the use of corrosive chemicals (https://www.nafion.com/en/-/media/files/nafion/water-electrolysis-white-paper.pdf?la=en). Alternatives include Alkaline electrolysis, Anion Exchange Membrane (AEM) electrolysis, and steam or oil reforming. Alkaline electrolysis yields lower purity product, is not suitable for intermittent power sources like renewables, and uses corrosive chemicals in their operation. AEM electrolysis utilizes membrane chemistries with poor durability due to chemical instability and have lower energy efficiencies. Steam or oil reforming emit significant amounts of greenhouse gases to generate “grey” hydrogen. These alternative technologies cannot match the combined performance characteristics of the PEM water electrolyzers and would result in both reduced performance and product quality.

- Fluorinated ionomers are a key component of the PEM fuel cell, a crucial technology required to meet the European Green Deal (RMOA), by the conversion of hydrogen into electricity. In comparison to the alternative Internal Combustion Engine (ICE) that is only 25% energy efficient, fuel cells typically achieve an energy efficiency of 60% (FlouroCouncil

SEA). Additionally, the only output of the PEM fuel cell is water and heat, therefor not contributing to carbon dioxide emissions (https://www.energy.gov/eere/fuelcells/fuel-cells). Additional alternatives include the Solid Oxide Fuel Cell (SOFC) and Phosphoric Acid Fuel Cell (PAFC), both of which exhibit high temperature corrosion and breakdown of cell components and are not suitable for transportation applications.

- Energy storage solutions, such as the flow battery, rely on PEMs enabled by fluorinated ionomers. Flow batteries are scalable, easy to maintain, nonflammable, safe with a low environmental footprint and offer a long-life cycle of 20+ years. Alternative rechargeable batteries include lithium-ion, lead-acid, and sodium-sulfur batteries. These batteries have varying disadvantages including the use of hazardous and combustible materials, environmental and fire safety issues, and short life cycles (Chemours, The evolution of energy storage).

Fluorinated ionomers play an important role in supporting economic growth in the transportation, chemical and industrial, and energy sectors. They contribute significantly to these sectors in terms of revenue, investment, and employment. They provide crucial performance characteristics to products or production processes globally, creating socio-economic value in the industry itself and downstream applications. Fluorinated ionomers are vital to the sectors and industries that they serve.

- Fluorinated ionomers are key components in fuel cells and flow batteries for electric vehicles, significantly contributing to the transportation sector. The transportation sector employs greater than 13 million people in the EU with a total value of 300 (m€) (see paper reference FPG 2021a).

- Fluorinated ionomers play an important role in the chemical and industrial sectors by enabling the production of critical commodity chemicals for the entire European industry including chlorine, caustic soda, and caustic potash. The chemical industry is the fourth largest producing sector in Europe, employing 1.2 million people (RMOA).

- In the energy sector, fluorinated ionomers enable flow batteries that have the ability to support large-scale grids and save surplus energy, significantly contributing to energy supply and demand. As with fuel cells, renewable hydrogen created via PEM water electrolyzers enabled by fluorinated ionomers, are expected to play a key role in the policy goals of the European Green Deal (EC 2021).

- Research and development have a significant role in driving economic growth through the investment in technological advances. Fluorinated ionomers have enabled innovations in the transportation, chemical and industrial, and energy sectors. Socio-economic benefits from these innovations include lower production costs, lower emissions, and lower environmental/health implications.

6. Fluoropolymers vs. Side-chain Fluorinated Polymers (SCFPs)

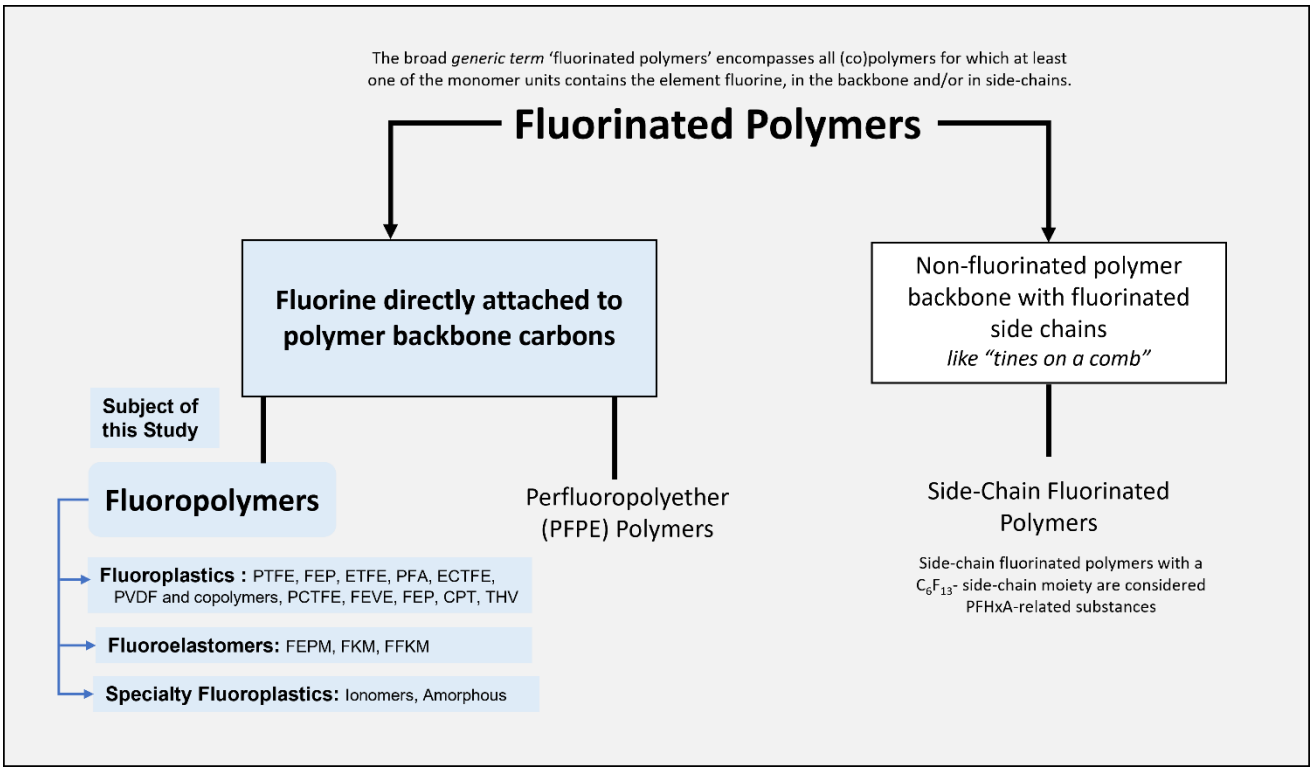


Figure 6.1

Fluoropolymers are very different in composition and structure as well as physical, chemical and biological properties versus Side-Chain Fluorinated Polymers (SCFPs).

Fluoropolymers

Fluoropolymers, such as polytetrafluoroethylene (PTFE), have a carbon atom backbone with fluorine atoms (F) bound to the polymer backbone carbon atoms. Fluoropolymers have molecular weights up to millions, meaning thousands of connected carbon atoms to which fluorine is bound. Imagine a string of pearls one hundred thousand pearls long, each pearl representing a carbon bearing fluorine.

Polytetrafluoroethylene (PTFE)

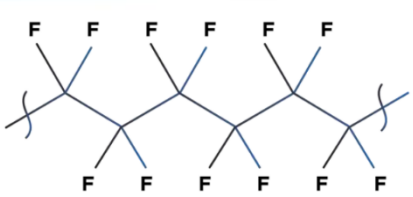


Figure 6.2

Fluoropolymers have material properties. The unique properties of fluoropolymers include durability, mechanical strength, inertness, thermal stability, and resistance to chemical, biological,

and physical degradation. Some can be classed as Polymers of Low Concern according to OECD criteria as they are chemically stable, biologically stable/inert, negligibly soluble in water, non-bioavailable, non-bioaccumulative; and non-toxic. (Henry et al. 2018, Buck et al. 2011).

Side-Chain Fluorinated Polymers

Side-Chain Fluorinated Polymers are a hydrocarbon polymer backbone with a polyfluoroalkyl side-chain connected to the backbone via functional group. The side-chain frequently contains a six-carbon perfluoroalkyl moiety as well as side-chains that have no fluorinated carbons.

The polymer has a comb structure where some of the tines (aka teeth) are a side-chain with the perfluoroalkyl moiety (imagine six pearls, using the analogy above) while other side chains contain hydrocarbon functionality, no fluorine.

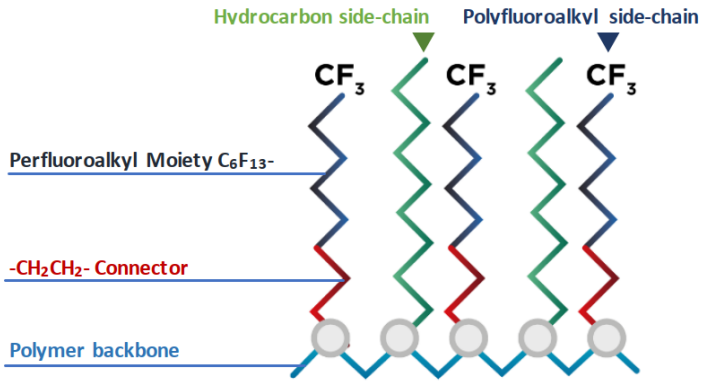


Figure 6.3

Side-chain fluorinated polymers have surface properties. They are polymer dispersions in water used as coatings applied to textiles, carpets, nonwovens and paper to provide water, soil, oil and stain resistance.

See Also:
https://fluoropolymers.plasticseurope.org/index.php/fluoropolymers/irreplaceable-uses-1/reports-policy-documents/policy-position-documents

7. Fluorinated Polymerization Aids (PA)

Why fluorinated polymerization aids (PA's) are necessary was briefly described in Henry et al (2018).

Some additional information is provided here to give added perspective.

Water, which has a high specific heat, is commonly used to control the highly exothermic and potentially explosive decomposition of TFE in a "water-cooled" polymerization reaction. Water is the most efficient way to ensure the reaction energy is controlled, therefore ensuring the safety of the process. Fluorinated polymerization aids (PA) stabilize growing polymer particles during emulsion polymerization. Fluorinated polymerization aids (PA) stabilize the process and enable the synthesis of high molecular weight polymers.

Suspension polymers, which do not use a PA, exhibit a different morphology than emulsion polymerization produced polymers. In addition, composition and microstructure of the polymers that are produced with these different processes are not comparable.

A PA is a surfactant and has a polar head and a non-polar head. In water, the PA forms spheres, or micelles, with the polar heads facing outwards and a core of non-polar heads inside stabilizing the fluorinated monomer (e.g., TFE). It is inside these spheres in these dissolved areas where the initiator/free radical/TFE can mix and the polymerization reaction proceeds.

8. Fluoropolymers are neither bioavailable nor bioaccumulative.

Fluoropolymers are neither bioavailable nor bioaccumulative. These solid materials cannot be absorbed through a cell membrane via passive or active transport and do not bind or interact with the cell surface showing that the PLC criteria are valid for fluoropolymers.

Factors affecting Bioavailability:

Fluoropolymers are 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 or groups accepting of hydrogen atoms.
- They are hydrophobic and lipophobic and have little or no hydrogen bond donating potential because they have few hydrogen bonds
- They are not structurally similar to steroids, peptides, natural compounds, etc.

Active Transport and Cell Surface Binding / Signaling

- Is dependent on shape, volume/size, rotational bonds, etc. and requires interaction with the cell surface. Fluoropolymers have none of the required properties to interact with the cell surface.
- Fluoropolymers do not “fit” into cell surface receptors to signal events within the cell. They are insoluble solids.
- The types of high molecular weight compounds that can be bioavailable through active transport or cell surface binding/signaling are “natural compounds”

9. Toxicity studies on Fluoropolymers are not technically possible

Whilst aquatic and mammalian toxicology studies may be desired to have for fluoropolymers, they are technically challenging for insoluble, solid, high MW polymers like fluoropolymers. OECD test guidelines spell this out in many cases.

This is reiterated 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.”

From REACH Annex VII
https://reachonline.eu/REACH/EN/REACH_EN/articleVII.html

9.1.1. Short-term toxicity testing on invertebrates (preferred species Daphnia)The registrant may consider long-term toxicity testing instead of short-term.	9.1.1. The study does not need to be conducted if: there are mitigating factors indicating that aquatic toxicity is unlikely to occur, for instance if the substance is highly insoluble in water or the substance is unlikely to cross biological membranes, or long-term aquatic toxicity study on invertebrates is available, or adequate information for environmental classification and labelling is available. The long-term aquatic toxicity study on Daphnia (Annex IX, section 9.1.5) shall be considered if the substance is poorly water soluble.
9.1.2.Growth inhibition study aquatic plants (algae preferred)	9.1.2. The study does not need to be conducted if there are mitigating factors indicating that aquatic toxicity is unlikely to occur for instance if the substance is highly insoluble in water or the substance is unlikely to cross biological membranes. |
9.1. Short-term toxicity testing on fish: the registrant may consider long-term toxicity testing instead of short-term.	9.1.3. The study does not need to be conducted if: there are mitigating factors indicating that aquatic toxicity is unlikely to occur, for instance if the substance is highly insoluble in water or the substance is unlikely to cross biological membranes, or long-term aquatic toxicity study on fish is available. Long-term aquatic toxicity testing as described in Annex IX shall be considered if the chemical safety assessment according to Annex I indicates the need to investigate further effects on aquatic organisms. The choice of the appropriate test(s) will depend on the results of the chemical safety assessment. The long-term aquatic toxicity study on fish (Annex IX, Section 9.1.6) shall be considered if the substance is poorly water soluble. |
9.1.4.Activated sludge respiration inhibition testing	9.1.4.The study does not need to be conducted if: there is no emission to a sewage treatment plant, or there are mitigating factors indicating that microbial toxicity is unlikely to occur, for instance the substance is highly insoluble in water, or the substance is found to be readily biodegradable and the applied test concentrations are in the range of concentrations that can be expected in the influent of a sewage treatment plant. The study may be replaced by a nitrification inhibition test if available data show that the substance is likely to be an inhibitor of microbial growth or function, in particular nitrifying bacteria.

10. Fluoropolymers – Global Market Perspectives

The commercial fluoropolymer global market sales cited in the 2016 Dams et al publication (Dams et al 2016; assumed to be 2015 data) was about 230,000 MT. Given the expected fluoropolymer market growth (ranging from approximately 5% to 7-8%), the 2015 data was projected to 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 was estimated to be approximately 330,000 MT in 2021. See Table 10.1 below 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 (projected). The sales volume of these four fluoropolymers is represented by the first 4 bars in waterfall Figure 10.1 below.

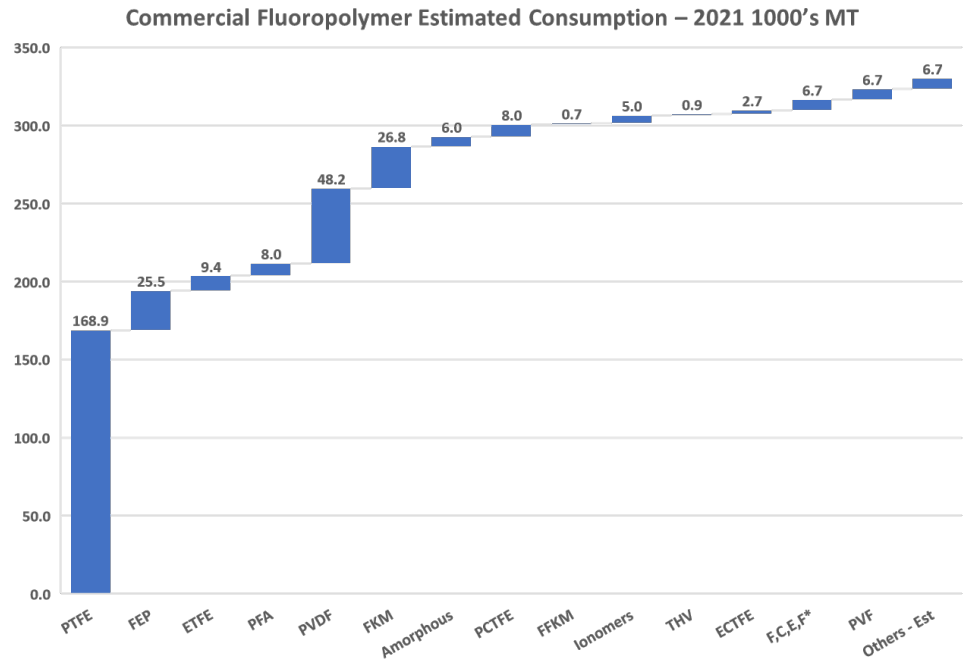
This study discusses 14 fluoropolymers representing an additional 32% of the global fluoropolymer market. Therefore, this study in combination with Henry et al. 2018, present PLC data from manufacturers of commercial fluoropolymers which represent approximately 96% of the global

commercial fluoropolymer market that meet the criteria to be considered polymers of low concern. 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. 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 shown in Figure 10.1 Other fluorinated polymers, perfluoropolyethers and side-chain fluorinated polymers are not addressed in this study.

Table 10.1 Fluoropolymer Global Market Data (Pro forma)

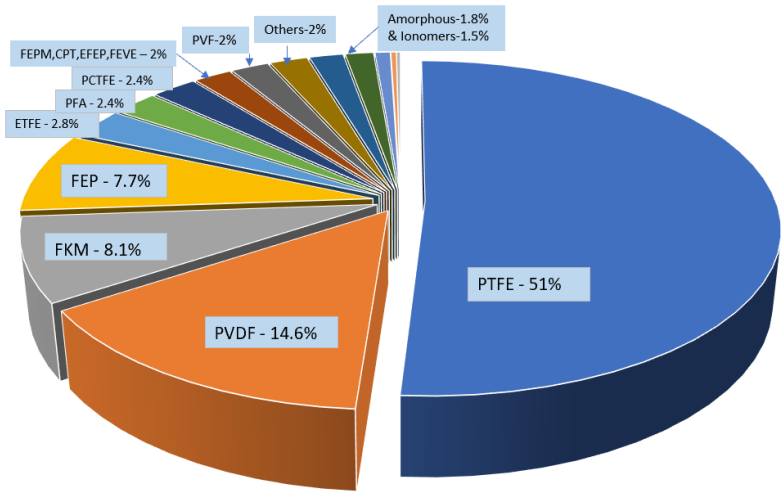
	Current, 1000's						
Fluoropolymer	MT-2021			Henry et al	FP II	PVF	Other No ID
PTFE	168.9	51.1%		64.1%			
FEP	25.5	7.7%					
ETFE	9.4	2.8%					
PFA	8.0	2.4%					
PVDF	48.2	14.6%			31.8%		
FKM	26.8	8.1%					
Amorphous	6.0	1.8%	Company				
PCTFE	8.0	2.4%					
FFKM	0.7	0.2%					
Ionomers	5.0	1.5%	Company				
THV	0.9	0.3%					
ECTFE	2.7	0.8%					
FEPM, CPT,EFEP,FEVE	6.7	2.0%	Estimates				
PVF	6.7	2.0%				2.0%	
Others -Est	6.7	2.0%	Estimates				2.0%
1000's MT - 2021	330.2						

Figure 10.1 Commercial Fluoropolymer Estimated Consumption (1000's MT)



***FEPM, CPT, EFEP, FEVE**

Figure 10.2 Commercial Fluoropolymers Estimated Global Volume (1000's MT)



11. Fluoropolymers – Socioeconomic Analyses

11.1 Socio-economic Analysis of the European Fluoropolymer Industry

A study comissioned by the Fluoropolymer Products Group of Plastics Europe.

https://fluoropolymers.plasticseurope.org/index.php/fluoropolymers/irreplaceable-uses-1/reports-policy-documents/socio-economy-analisis or

https://fluoropolymers.plasticseurope.org/application/files/7816/1167/4026/Final_SEA_Fluoropolymers_summary2017_3.pdf

Executive Summary from the Report

This independent report commissioned by AGC, Chemours, Daikin and 3M evaluated the socio-economic contribution to US society and economy of a group of plastics and elastomers known collectively as fluoropolymers, e.g. PTFE, FEP, FEPM, PFA, PVDF, FKM, FFKM, THV, ETFE and ECTFE. This industry differs from others in several ways. The manufacture and sale of fluoropolymers in their basic form generates economic and social effects from revenues, investment and jobs, but larger effects are generated by the downstream use of the fluoropolymers as they are incorporated into a wide range of products in several sectors. While the fluoropolymer content of final products may be tiny, they offer specific unique combinations of properties. These include: non-wetting, light weight, high performance dielectric properties, non-stick, fire resistant, temperature resistant, weather resistant and with near universal resistance to chemicals. Reflecting this, fluoropolymers provide specific functionality in a wide range of products and within complex systems. They improve

efficiency, durability and enable innovation while reducing business and consumer cost via extending lifetimes of products. Drawing on publicly available data, a survey of FluoroCouncil members and interviews with a selection of downstream users, the socio-economic analysis (SEA) evaluates effects in seven strategically important sectors.

11.2 Socio-economic Analysis US Fluoropolymer Industry

A study commissioned on behalf of FluoroCouncil is highlighted below.

https://fluoropolymerpartnership.com/fluoropolymer-facts/socioeconomic-importance/

The starting point of the US value chain, sales of fluoropolymers in their basic form, is a $2 billion industry and 85,000 tons of product was manufactured in 2018. The US industry is a net exporter of higher value product; the sales value of exports exceeds $1 billion, with imports of around $500 million. A highly innovative sector, some $150 million was invested in research and development (R&D) in 2018. This represented over 6% of revenues, well above the Organization for Economic Co-operation and Development (OECD) average and more than double the average US R&D investment rate. Indirectly, the industry is also estimated to have generated some $150 million in R&D spill over effects, a further $2.4 billion indirect and induced economic activity along with 15,000 direct and indirect US jobs. The location of the fluoropolymer industry in the US has an important role in allowing US-based customers to meet lead times for the various end user sectors. This is necessary in maintaining innovation and R&D, as companies are continually customizing products for their customers.

The value chain – sectors dependent on fluoropolymers

Fluoropolymers provide vital performance characteristics to products or production processes. Collectively this creates socio-economic value far beyond the direct impact created by the industry itself. While not all of these benefits can be easily quantified, the report analyzes this value in seven strategically important sectors:

Electronics:

The largest downstream sector by sales, fluoropolymers are critical to the semiconductor manufacturing process. Components of the semiconductor manufacturing process must withstand the aggressive etching chemicals while providing the required purity; any contamination severely affects yield. The US semiconductor industry is a $210 billion sector, employing 250,000 Americans. Semiconductors are used in millions of ever more powerful but smaller products. Fluoropolymers dielectric properties has enabled miniaturization of components and final products, alongside improved fire safety, high transmission speeds, ease of installation and reliability of wires, optical and data transmission cables. These last up to three times longer, enabling a wide range of information and communications technology (ICT) functionality, industrial, automotive, medical imaging and analysis;

Transportation:

Fluoropolymers are critical for the performance of key components in the automotive and aerospace industries, as they provide them with resistance against heat, cold, fire, smoke, aggressive fluids and fuels, humidity, vibrations and compression. They prolong the useful life of various components, protect corrosion, prevent leaks, improve safety and enable communication. In automobiles, fluoropolymers contribute to improved reliability, engine efficiency, weight reduction and emission control, improving fuel efficiency, reducing CO2, leaks and fugitive emissions. Alongside other technologies they have contributed to a 48% increase in fuel efficiency (based on average miles per gallon, 1980-2016) in US cars. This has been achieved alongside increases in average horsepower, while maintaining weight. A key element of fuel cell technology, they contribute toward further and faster fuel efficiency gains and emission reductions. In aerospace, for example Airbus A320 users experienced a 93% corrosion reduction in cargo bays and the US Army fleet of Apache helicopters benefited from avoided friction damage, from the use of one specific product;

Medical and first responder:

Fluoropolymers are used in surgically-implantable medical devices; increasing lifetime of implants, reducing the likelihood of infection and invasive surgery. They provide excellent performance and long lifetimes in equipment such as catheters, guide wires, filters and pumps. They reduce medical complications, replacements, cross-infections and clogging of medical equipment, contributing to the reduction/avoidance of pain and discomfort alongside the avoided treatment costs. At the same time, they enable advanced medical imaging (via electronic chips and semiconductors in X-ray, MRI, CT scan and echography) and protect firefighter safety (via water resistant, bodily fluids resistant, abrasion-resistant and insulated clothing);

Chemical and industrial processes:

Fluoropolymers enable a high level of efficiency and safety in various chemical and industrial manufacturing processes, helping them remain internationally competitive. Fluoropolymers contribute to corrosion and leaching prevention, fewer leaks, lower maintenance and prevention of emissions, particularly in applications involving aggressive chemical fluids. They are used in coatings, linings, piping, vessels, fluid-handling components, filters, vents and cable coatings. Corrosion costs the US economy over $250 billion per year, so even a nominal reduction in corrosion would result in avoided costs of some $2.5 billion per year to US industry;

Consumer products:

A $1.5 billion industry, fluoropolymer-coated cookware provides easy-clean, non-stick properties, saving time, water and energy. Products last longer and facilitate cooking with less added fat. Consumer survey data shows strong preference both for non-stick properties in cookware and for using less fat in cooking;

Energy:

Fluoropolymers have contributed to significant technical advances in solar power generation, production efficiencies in wind turbines and to the development of lithium ion batteries. The costs of solar photovoltaic (PV) cells have halved in recent years, with installed capacity enough to power 11.2 million American homes. Production efficiency increases of ETFE modules relative to glass provide a potential yearly saving of up to $4 billion for US PV module manufacturers. Fluoropolymers enable efficiency gains in wind turbine production. Installed capacity of both PV and wind energy is increasing quickly; a pre-requisite is unit cost reductions driven by efficiency gains. Fluoropolymers facilitate advanced energy storage and conversion technologies and are key components of lithium ion batteries; and

Building and construction:

Fluoropolymers provide durable, thermally stable, easy-to-clean, building materials which can both reduce building cooling costs and energy use, enabling novel “landmark” architectural designs. These include the Mercedes Benz Stadium, Atlanta, GA, and Denver Airport’s ETFE and PTFE fiberglass roofs.

What about alternatives?

Overall, while some alternatives might have a similar performance to fluoropolymers for a parameter or property, it is the combination of properties required for the applications that sets fluoropolymers apart from the alternatives. Implications of a transition could include lower performance, lower durability and reliability, and increased weight (with associated effects on fuel consumption and fuel efficiency). Some applications, like semiconductor manufacturing would be severely impaired, based on current technical knowledge. Economic implications include regression of advanced technologies and the reduced ability of the United States to attract high and medium technology manufacturing investment, efficiency losses, higher capital and maintenance costs. The diversity of fluoropolymer applications would pose major product qualification issues in addition to design implications. Environmental / health and safety implications include potential higher safety risks to medical patients and consumers and increases in emissions from technical regression.

12. Fluoropolymers – Risk Management Options Analysis (RMOA)

(FPG, 2021a) https://fluoropolymers.plasticseurope.org/index.php/fluoropolymers/irreplaceable-uses-1/reports-policy-documents/rmoa

Alternatives Section from RMOA Section 2.5 A few examples are provided here

Key market	Sector	Alternative/s	Example potential application	Overview of likely technical economic and environmental implications
Transport	Automotive	Stainless steel, aluminium, or copper	Fuel lines Protection for plastic fuel lines	Fuel lines made entirely of copper or stainless steel are available in the market. However at least some products are only suitable for relatively old cars (1980s and earlier). Plastic fuel lines covered with braided metal thread are also commercially available; indeed, some fuel hoses made of FPs are covered with braided metal. However, in applications where the use of metals may be technically feasible, they are heavier and have lower chemical resistance, with the associated maintenance and replacement costs this implies, in what are "hard to reach" parts, they would also lead to increased fuel use and reduced fuel efficiency.
		XLPE (cross-linked polyethylene), thermoplastic elastomers (TPE)	Hoses, cables, and wire solutions	Successful for applications in other sectors and in some automotive applications e.g., in cold air intake systems or control elements in car interiors. Although thermal resistance of XLPE and TPE is in the range of that for certain FPs such as standard ETFE, their chemical resistance does not reach the standards provided by FPs.
		Silicone rubbers	Gaskets, cables, or hoses	Silicone materials offer a range of properties that are suitable for other applications used in various applications in modern vehicles such as paint additives, air bag coatings, and radiator seals. Whilst they offer a range of properties suitable for these applications, they do not have the specific combination of properties required in FP applications.
		Mica-insulation (as above)	Mica-insulated sensor cables for oxygen and nitrogen sensors	This is a very specific application with particular requirements. It is likely that sensors would have to be placed in less demanding locations, since these cables are not able to resist the conditions at the optimum measurement point. This would result in less accurate measurements, which would in turn lead to higher emission levels and less efficient fuel consumption, as an accurate control of the air-fuel ratio is essential for fuel efficiency. Also, mica-insulated cables are heavier and more rigid and brittle.
		Polyetheretherketone (PEEK), polyether sulfone	Fuel hoses, lines, gaskets, seals, cables, wire insulation	They have similar temperature resistance. For example, PEEK is able to resist up to 260 °C. They are rigid, which may impact on design possibilities, and chemical resistance is lower. Also, electrical and data transmission properties are inferior.

Key market	Sector	Alternative/s	Example potential application	Overview of likely technical economic and environmental implications
Transport	Aerospace	Same as proposed for the automotive industry	As in the automotive industry	Many of the applications in the automotive industry are the same in the aerospace industry, with at least as demanding operating conditions, durability requirements, safety performance tests and approval systems. The sector has particularly strict quality testing and approval procedures, which would delay the appearance of alternatives in the market for the applications where FPs are used.
Renewable energy	-	Glass (Top sheets) UV-resistant PET or polyimide (Back sheets)	Top sheets / Back sheets in solar panels	Glass has been historically used and UV-resistant PET and polyimide are currently available in the market. Glass is brittle and fragile. As for UV-resistant PET and polyimide, evidence suggests that FP-based back sheets perform better in certain parameters such as adhesion between layers (especially those based on ECTFE).
Cookware	-	Ceramics	Coating for non-stick cookware	Ceramics is already in the market. Initial non-stick properties are acceptable but not as good as those of PTFE-coated cookware. Ceramic-coated cookware is eventually more expensive since it reportedly loses its non-stick properties considerably faster and has to be replaced more often.
Medical applications	-	PEEK	Tubes, catheters, and other hospital material	This alternative is commercially available. It is resistant to high temperatures and the products made of this alternative can be sterilised with autoclave. They are suitable solutions for disposable hospital goods. It is biocompatible but it is generally not suitable for uses where longer term (30+ day) contact with tissue or blood is required. As a result, they are inferior to FPs for solutions such as heart patches. Some publicly available evidence suggests that PEEK may eventually be suitable for long-term solutions but is currently comparatively expensive. The sector has particularly strict quality testing and approval procedures, which would delay the appearance of alternatives in the market for the applications where FPs are used.
	-	Polyurethane	Tubes and catheters	It is not suitable for steam sterilisation. Higher costs than current solutions. Concerns with clogging are highlighted by users.
Textiles and architecture	Architecture	Steel	Insulation materials, pipes, and tubes	It is heavier and more inflexible than FPs. It is not resistant to corrosion, leading to higher maintenance costs. It is not able to meet the design possibilities of FPs.

Key market	Sector	Alternative/s	Example potential application	Overview of likely technical economic and environmental implications
Textiles and architecture		Polycarbonate sheets	Membranes for architectural applications such as roofing	They are resistant to temperature and UV light and can withstand force. PVC/PES membranes for architectural applications are common. However, these are often coated with a protective layer (often made of PVDF, a FP) providing UV-resistance and weatherability. Without this coating, they offer lower performance due to not being resistant to denting nor certain chemicals.
	Leather production -	Silicon-based anti-soiling auxiliary	Manufacture of leather articles	Similar performance for anti-soiling properties with exception to resistance to coffee.
Renewable Energy	-	Pb (Lead acid) battery	Batteries	Lead batteries are around one third heavier than lithium-ion batteries in which FPs are used.
	-	High temperature fuel cells	Fuel Cells (stationary applications)	The key disadvantage, compared to PEM fuel cells is that they can only be used in stationary applications.

https://fluoropolymers.plasticseurope.org/index.php/fluoropolymers/irreplaceable-uses-1/reports-policy-documents/rmoa

SUPPLEMENTAL DATA

The RMOA Table of Contents is provided below:

58