

Opinions on PFSA (Perfluorosulfonic Acid Resin) Regulations

We, on behalf of Juhua Technology Center Co., Ltd., would like to express our greetings to the five countries proposing the ECHA and PFAS management and control draft. Our company has always made unremitting efforts to comply with domestic and international regulations, and continuously make strict self review on the compliance of the products exported to EU. We would support the ambitious attempt of EU to reduce the risks caused by toxic and harmful substances, and would take sincere practical measures to meet the requirements of EU chemical regulations, including REACH. However, we believe that the PFAS restrictions proposed by five European countries are an excessive measure as they restrict more than 10000 kinds of organic fluorine compounds (PFAS).

Perfluoroalkyl and polyfluoroalkyl substances (PFAS) are a large group of highly fluorinated compounds with different properties, which have been widely used in various industrial and consumer applications since 1950s. Organization for Economic Cooperation and Development (OECD) has defined PFAS as a fluorinated substance that contains at least one perfluoromethyl or methylene carbon atom (without any H/Cl/Br/I atom) in its structure, including at least one perfluoromethyl ($-CF_3$) or one perfluoromethylene ($-CF_2$), except for a few exceptions put forward. It covers over 10000 substances with different physical, chemical, and biological properties: polymers and non polymers; solids, liquids and gases; persistent and non persistent substances; highly active and inert substances; flowing and insoluble (non flowing) substances; and (ecologically) toxic and non-toxic chemicals. PFAS has a broad definition and is too broad to effectively and scientifically evaluate and regulate the entire compound. This broad definition does not consider the specific and different characteristics of different individual PFAS, and therefore is not suitable for the purposes of regulatory risk management.

Perfluorinated sulfonic acid resin (PFSA) is a key material in new energy fields such as fuel cells and flow battery, and currently there are no substitutes in the market that meet performance requirements and are widely available. Therefore, we advocate that

perfluorinated sulfonic acid resin should be exempt from legal control and obtain permanent exemptions.

1. Non toxicity and bioaccumulation of perfluorinated sulfonic acid resin (PFSA)

Per- and polyfluoroalkyl substances (PFAS) are divided into two main categories, non polymers and polymers. Non polymer category includes perfluoroalkyl and polyfluoroalkyl surfactants with different functional groups, such as perfluoroalkyl sulfonic acid and perfluoroalkyl carboxylic acid. Two notorious compounds, perfluorooctane sulfonic acid (PFOS) and perfluorooctane carboxylic acid (PFOA), belong to these two kinds of surfactants, which are widely present in the environment and biota (including humans), making them a focus of attention for the researchers and regulatory agencies.

Polymer categories of PFAS include fluorinated polymers, perfluoropolyether (PFPE) polymers, and side chain fluorinated polymers. Fluorinated polymers (FPs), as high molecular weight polymers, have the characteristics of thermal, chemical, photochemical, hydrolysis, oxidation and biological stability, which make them highly stable in the environment. Their residual monomer and oligomer content can be ignored, with little or no leachable substances. They have the characteristics of being insoluble in water, non flowing (without long-distance migration), and due to its molecular weight far exceeding 100000 Da, they cannot penetrate the cell membrane. Therefore, from the perspective of the environment and human health, it has no bioaccumulation and toxicity, and does not release any toxic byproducts and oligomers under conventional use, thus not meeting the PBT standard^[1].

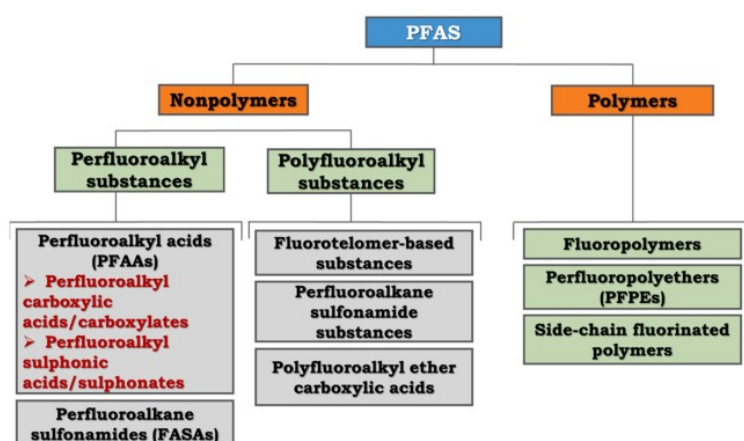


Figure 1. PFAS Classification Summary ^[1]

2. Perfluorinated sulfonic acid resin (PFSA) has irreplaceable properties

Perfluorinated sulfonic acid ion exchange membrane is a solid-state polymer electrolyte with excellent proton conductivity, heat resistance, mechanical properties, electrochemical properties and chemical stability, which can be used in harsh conditions such as strong acid, strong alkali and strong oxidant media. Perfluorinated sulfonic acid proton exchange membrane is a dense membrane with ion selective permeation, which was first applied in seawater desalination and basic industry chlor alkali industry. In recent years, with the development of new energy technologies such as fuel cells and flow battery, proton exchange membranes have become key materials in the field of new energy, widely used in fields such as electrolysis water for hydrogen production, fuel cells and all vanadium flow battery.

Based on the key roles played in hydrogen production through electrolysis water, fuel cells and flow battery, proton exchange membranes need to possess high proton conductivity, good chemical and physical stability, moderate water absorption, good mechanical strength, low size change rate, low gas permeability, ion transfer ability with high selection, as well as high mechanical strength, good processability and appropriate cost performance. Due to its mature technology and excellent performance, perfluorosulfonic acid proton exchange membrane is currently the most widely used proton exchange membrane system. Although the grafting of proton exchange groups in the side chain structure of non perfluorinated proton exchange membranes can improve proton conductivity, their stability is poor with short lifespan, and their performance at room temperature is inferior to that of perfluorinated sulfonic acid ion exchange membranes. Although the fluorinated proton exchange membrane under development has low cost with high mechanical strength, it has poor chemical and thermal stability and low proton conductivity. Both types of proton exchange membranes cannot meet the application requirements of hydrogen preparation with electrolysis water, fuel cells and flow battery.

Chart: Proton Exchange Classification

Type	Perfluorosulfonic acid proton exchange membrane	Non perfluorinated proton exchange membrane	Fluorinated proton exchange membrane	Composite membrane
Structure	Consisting of a carbon nitrogen main chain and an ether branch chain with sulfonic acid groups	Fluorocarbon based, carbon chloride compounds, or aromatic side chains	Hydrocarbon groups, usually containing proton conducting groups	Composite membrane composed of modified materials and perfluorosulfonic acid resin
Advantage	High mechanical strength, good chemical stability, high conductivity, high current density at low temperatures, and low proton conduction resistance	Low cost, grafting of proton exchange groups in the side chain structure can improve proton conductivity	Low cost, low link pollution, high mechanical strength	Improved mechanical performance, improved water transmission and distribution within the membrane, and reduced internal resistance of proton exchange membranes
Disadvantage	The increase in temperature leads to poor proton conductivity, which is	Short lifespan and poor stability: performance at room temperature	Poor chemical and thermal stability; Low proton	High technical requirements for preparation

	prone to chemical degradation and high cost at high temperatures	is inferior to perfluorosulfonic acid proton membranes	conductivity	
--	--	--	--------------	--

Figure 2□Classification of Proton Exchange Membranes Existing and Under Development in the Market

According to the calculations, demand for proton exchange membranes in the four fields of hydrogen production from electrolyzed water, hydrogen fuel cells, vanadium flow batteries and iron chromium flow batteries will reach 867000, 1691000, 3147000 and 16702000 m² square meters totally from 2023 to 2026, the market size is expected to reach 25 billion yuan by 2026.

In summary, there is a high demand for perfluorinated sulfonic acid proton exchange membranes in the market, and currently there are no substitutes in the market that meet various performance requirements for new energy applications. Therefore, we propose that perfluorinated sulfonic acid resins should be kept away from legal regulations and receive permanent exemptions.

3. Perfluorinated sulfonic acid resin (PFSA) can be recycled and converted for utilization

In recent years, FPs manufacturers have realized the potentially negative effects of PFAS polymerization additives currently used as substitutes for PFOA. Supervision from various regulatory authorities are helping the industry quickly turn towards sustainable technologies, with a focus on developing technologies for effective degradation, recovery and reuse of PFAS compounds. FP manufacturers typically develop the scheme according to the following two strategies:

(1) Improve the process for eliminating fluoride by-products (such as low molecular weight oligomers, residual reactants and other volatile compounds) by improving the technology of emission reduction in FPs manufacturing and PFAS surfactant recovery. Since 1990s, these processes have reduced the emissions of fluorinated surfactants by 99%^[2], and recent research has increased it to 99.99%^[3]. There are lots of literature on

PFAS emissions and control and treatment during the industrial processes^[4], and there are still many studies under way^[5]. For example, unfilled PTFE waste can be reused in the plunger extrusion applications after cleaning^[6] and grinding, or decomposed into low molar mass PTFE through heating and mixed with other materials in the form of micropowders for reuse^[7]. Such as photochemical methods, for example, perfluorosulfonic acid is degraded through UV photolysis of aqueous solutions containing sensitizers of such as sulfites and iodine ions^[9]. This mechanism begins with the generation of hydrated electrons through UV photolysis of added sensitizers, followed by reductive elimination of fluoride ions in PFASs^[10]. In addition, hydrothermal treatment methods were also studied to effectively degrade these compounds. Alkaline water under high temperature and high pressure can continuously defluorinate various PFASs to get the final products of fluoride and carbonate ions^[11]. The specific method is to completely defluorinate FPs (including PVDF as well as copolymers of VDF and TFE as perfluorosulfonic acid membranes) into F-ions through superheated water (or "pressurized"). (Hot water at approximately 100-300°C). This type of water is considered harmless to the environment in waste management as it can convert hazardous chemicals into harmless products or generate value-added compounds^[12]. This process can also be carried out in the presence of potassium permanganate as an oxidation reactant or alkaline reagent (NaOH or KOH)^[13]. Carbon content decomposes into CO₂ in the gas phase and produces HCO₃⁻ in the reaction solution. In the presence of Ca (OH)₂, the released fluoride anions lead to formation of "artificial fluorite" (CaF₂), which is the source of fluorine chemical processes. Mineralization of FPs helps to form an effective fluorine element loop.

(2) Produce high molar mass FP without fluorinated polymerization additives (FPA), without any by-products and in compliance with PLC standards. In fact, significant progress has been made in the past decade, NFPA (or surfactants) has been used by with some FP manufacturers to improve their production. The technology overview based on NFPA over the past decade emphasizes that the entire industry (such as 3M, AGC, Arkema, Chemours, Daikin, Gujarat Fluorochemicals and Solvay) has made

significant innovations and tried to claim to have the patents for such NFPA technologies when submitting multiple applications. In fact, in 2022, many FP manufacturers announced the cessation of FPA use in their manufacturing^[8].

Therefore, FP produced without any FPA should be exempted to be used in all industries, including consumer applications, as they do not pose any risks to the environment, as well as to the health of mammals and humans.

Recently, the main issues have been addressed, including the use of NFPA and the control of >99% PFAS emissions related to appropriate emission reduction technologies in FP industrial production. Therefore, FP produced by NFPA technology has achieved commercial success and which stimulates the industry to work harder in this direction. Their applications involve the health, safety, performance and operation of the society^[1]. We believe that the legislative process should focus on the use and emissions of FPA. In this regard, the following regulatory decision tree^[8] (Figure 1) can be proposed, which is based on (1) production of FP in the presence/absence of such surfactants (reducing the process to obtain PFAS concentrations less than 25 ppb), (2) essential use standards (safety, performance and health aspects), (3) process improvement, and (4) alternative solutions.

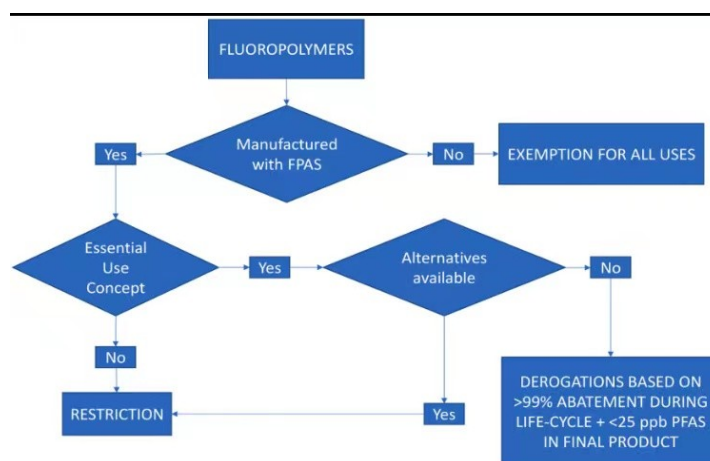


Figure 2. Regulatory Decision Tree for Fluoropolymers^[8]

References

- [1] B. Ameduri, Fluoropolymers: A special class of per and polyfluoroalkyl substances (PFASs) essential for our daily life, *Journal of Fluorine Chemistry*, 267, (2023) 110117
- [2] Fluoropolymer Products Group of Plastics Europe, Risk Management Options Analysis,

RMOA, (2021) <https://fluoropolymers.plasticseurope.org/index.php/fluoropolymers/irreplaceable-uses-1/reports-policy-documents/rmoa> (accessed on June 2022)

[3] R. DiStefano, T. Feliciano, R.A. Mimna, A.M. Redding, J. Mattis, Thermal construction of PFAS during full scale activation of PFAS laden granular activated carbon, *Mediation* 32 (2022) 231-238

[4] J. Liu, S.M. Avenda ~ No, Microbial degradation of polyfluoroalkyl chemicals in the environment: a review, *Environment Int.* 61 (2013) 98-114

[5] B. Trang, X. - S. XUE, M. ATEIA, K. N. HOUK, W.R. DICHTEL, Low performance mineralization of perfluorocarboxylic acids, *Science* 377 (2020) 839-845

[6] S. Ebnesajjad, *Introduction to Fluoropolymers: Materials, Technology, and Applications*, Elsevier, Amsterdam, (2013) 63-89, chapter 6

[7] B. Ameuri, H. Hori, G. Moeller, H. Mukue, K. Otoi, A. Tai, Recycling and end of life assessment of fluoropolymers: recent developments, challenges and future trends *chem, Soc. Rev.* (2023) under revision

[8] B. Ameduri, J. Sales, M. Schlipf, Developments in fluoropolymer manufacturing technology to remove PFAS as polymerization aids, submitted to *Intern, Chem Regul Rev* (2023)

[9] Z. Liu, Z. Chen, J.Gao, Y.Men, C.Gu, J.Liu. Accelerated degradation of perfluorosulfonates and perfluorocarboxylates by UV/sulfur+iodine: reaction mechanisms and system efficiencies *Environment Sci Technol* 56 (6), (2022) 3699 – 3709

[10] B.D. Fennell, S.P. Mezyk, G. McKay. Critical review of UV advanced reduction processes for the treatment of chemical pollutants in water *ACS Environment* 8 (2), (2022) 178-205

[11] S. Hao, Y. J. Choi, B. Wu, C.P. Higgins, R. Deeb, T.J. Strathmann. Hydrothermal alkaline treatment for construction of per and polyfluoroalkyl supplements in acute film forming foam *Environment Sci Technol* 55 (5), (2021) 3283-3295

[12] B and H. Hori, R. Honma, Composition of Fluoropolymers by their mineralization in subcritical water, in: S Fomin (Ed.), *Opportunities of Fluoropolymers*; Ameduri, Elsevier, Amsterdam, (2020) 03-331

[13] J. Hamamura, R. Honma, H. Hori, A. Manseri, B. Ameduri, Efficient fluoride recovery from poly (vinylidene fluoride), poly (vinylidene fluoride co hexafluoropropylene) copolymer and poly (ethylene co tetrafluoroethylene) copolymer using superheated water with alkaline reagent *Europe, Polymer J.* 182 (2023), 111724