Comments on PFAS Restriction Proposal (ETFE)

On behalf of Juhua Technology Center Co., Ltd., we 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 products exported to EU. We support the ambitious attempts of EU to reduce the risks caused by toxic and harmful substances, and 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 limit over 10000 kinds of organic fluorine compounds (PFAS).

Perfluorinated 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) defines 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 a perfluoromethyl (-CF3) or a perfluoromethyl (-CF2), except for a few exceptions that have been pointed out. 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 with a broad scope. It is impossible to effectively and scientifically evaluate and regulate the entire compound. This broad definition does not consider the specific and distinct characteristics of different individual PFAS, and therefore it is not suitable for the purpuses of regulatory risk management.

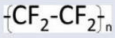
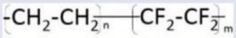
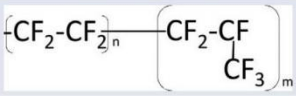
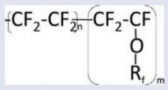
Ethylene tetrafluoroethylene copolymer (ETFE) is one of the main products of Juhua Group Technology Center. It is essential for use in wind energy (film, coating and cable), building film, etc., and currently there are no substitutes that meet the performance requirements and available in the market. Therefore, we advocate that ETFE should be exempted from the regulation management and control. The relevant detailed discussion, physical property comparison data and citations are as follows.

1. ETFE has no toxicity and bioaccumulation

ETFE is a high molecular weight polymer with thermal, chemical, photochemical, hydrolysis, oxidation and biological stability. Its residual monomer and oligomer content can be ignored with almost no leachable materials. It has the characteristics of being insoluble in water, not flowing (without long-distance migration), and as its molecular weight exceeds far over 100000 Da, it cannot penetrate the cell membrane,so it has no bioaccumulation nor toxicity. It does not release any toxic byproducts and oligomers under conventional use, so it does not meet PBT standard[1].

Four fluoropolymers including ETFE are evaluated based on the Polymer of Low Concern (PLC) standard defined by OECD, and the results are summarized in Table 1. ETFE meets the conditions specified in 13 PLC standards[14-16]: polymer composition, molecular weight, low polymer content, charge, low molecular weight leachable matter content, water/lipid solubility, reactive functional groups, functional group equivalent, particle size, polymer stability, thermal stability, abiotic stability and biological stability. In addition, ETFE is insoluble in water and therefore does not have the long-distance transfer; it cannot penetrate the cell membrane with no bioaccumulation; high thermal, chemical and biological stability, durability; and it is not considered a substance of high concern (SVHC). Although ETFE has durability, it lacks degradability under normal usage conditions and at the end of its lifespan, making such special polymers completely inert and harmless to human health or the environment, which are not classified as hazardous chemicals. In fact, based on the best available scientific test technology, Food and Drug Administration (FDA) has not found any evidence to show the ETFE found in the samples may have human health problems[1].

□1 □□□□□ PLC □□[14]

Assessment criteria[a]	Fluoropolymers PTFE CAS 9002-84-0	ETFE CAS 25038-71-5, 68258-85-5	FEP CAS 25067-11-2	PFA CAS 26655-00-5, 31784-04-0
Structure				
Polymer composition (must have C, H, Si, S, F, Cl, Br, or I covalently bound to C)	Yes	Yes	Yes	Yes
Molecular weight	389 000–8 900 000[bc]	—	—	—
(M_n > 1000 Da and oligomer content < 1%)	520 000–45 000 000[bd]	530 000–1 200 000[ef]	241 000–575 000[eg]	200 000–450 000[eh]
Molecular weight distribution MW ÷ number average M_n (M_n and heterogeneity of MW distribution indicate if majority are >1000 or <1000 Da, which could penetrate the cell)	2.3[i]	1.4–2.7[f]	1.55–2.09[g]	1.7[j]
Wt % oligomer (see Figure 2) (<5% for <1000 Da oligomers, <2% for <500 Da oligomers)	Negligible	Negligible	Negligible	Negligible
Ionic character (cationic polymers associated with aquatic toxicity; polycationic with adverse human health effect)	Neutral	Neutral	Neutral	Neutral
RFGs[k] (some highly reactive functional groups associated with adverse human health and ecotoxicology effects, e.g., acrylates, isocyanates, anhydrides, aziridines)	<1 (see section *Reactive functional groups and RFG ratio to MW*)	<1 (see section *Reactive functional groups and RFG ratio to MW*)	<1 (see section *Reactive functional groups and RFG ratio to MW*)	<1 (see section *Reactive functional groups and RFG ratio to MW*)
FGEW[k] (typical value) (the lower the FGEW, the more reactive the polymer and the higher the potential for health and environmental impact)	$>10^5$–10^7	$>10^5$–10^6	$>10^5$	$>10^5$
Low molecular weight leachables (MW < 1000 Da able to enter cell)	<1 ppm	No active leachables by USP class VI[l] (121 °C)	No active leachables by USP class VI[l] (121 °C)	No active leachables by USP class VI[l] (121 °C)
Residual monomers (monomers have lower MW than polymers; typically more hazardous than polymers)	<1 ppm	<50 ppb	<50 ppb	<50 ppb
Ratio of residual monomers to molecular weight (typical value) (more low MW monomer content per mole increases bioavailability and hazard potential)	$\sim10^{-13}$ to 10^{-15}	$\sim10^{-13}$ to 10^{-14}	$\sim10^{-13}$	$\sim 10^{-13}$
Structural similarities to RFG of concern (increases potential risk of adverse effects)	None	None	None	None
Reference standard see also ISO 1133 (ISO 2011), ISO 12086 (ISO 2006)	ASTM D 4894 (ASTM 2015a), D 4895 (ASTM 2015b)	ASTM D 2116 (ASTM 2016a)	ASTM D 3159 (ASTM 2015c)	ASTM D 3307 (ASTM 2016b)

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

Note: ASTM American Society for Testing and Materials; CAS Chemical Abstracts Service; Dalton; ETFE ethylene tetrafluoroethylene copolymer; FEP fluorinated ethylene-propylene; FGEW functional group equivalent weight; ISO International Organization for Standardization; MMAD median mass aerodynamic diameter; OECD Organization for Economic Cooperation and Development; PFA perfluoroalkoxy; PFPE perfluoropolyether; PLC polymer of low concern; PTFE polytetrafluoroethylene; PVDF polyvinylidene fluoride; PVF polyvinyl-fluoride; RFG reactive functional groups; USEPA United States Environmental Protection Agency; USP United States Pharmacopoeia.

In the “VI level” test of USP<88>, 2 g plastic (such as FEP, ETFE or PFA) is extracted from the following solutions at 121 ℃: 1) 0.9% sodium chloride solution; 2) sesame oil, NF; 3) alcohol physiological saline and d) polyethylene glycol. Acute systemic toxicity and intradermal reactivity tests are carried out with these extracts. The muscle implantation test is conducted with plastics. These three tests indicate that the release concentration of any leachable substance will not have these adverse effects, and will not result in a quantitative concentration of leachable substances. (Refer to USP 2018).

The following substances are not covered in this paper: perfluoropolyether, side chain fluorinated polymers, fluoroelastomers, polyvinylidene fluoride and polyvinylidene fluoride.

Additionally, in,regards of toxicity, German Ministry of Environment (UBA) has proposed a test of 5 parts involving the data of whether the substance has carcinogenicity, germ cell mutagenicity or reproductive toxicity; whether these is any other evidence of chronic toxicity; and whether there is evidence indicating an impact on or through breastfeeding, as well as the adverse effect level derived. Toxicological studies on ETFE have shown that ETFE does not possess bioavailability or bioaccumulation: acute and subchronic systemic toxicity, stimulation, sensitization, implantation local toxicity, cytotoxicity, in vitro and in vivo genetic toxicity, hemolysis, complement activation and thrombosis[14].

2. ETFE has its irreplaceability

The fluoropolymer industry in Europe has evaluated the contributions made by fluoropolymer (FP) manufacturers in terms of income, investment and employment, while many more significant benefits are created along the value chain through the use of FP in various key applications. These high value-added polymers must be separated from traditional PFAS,which are crucial for daily life[1].

ETFE is an important high value-added fluorinated polymer which possesses the heat resistance, chemical resistance, electrical insulation properties of polytetrafluoroethylene (PTFE) resin, as well as the thermoplastic processing properties of Fluorinated ethylene propylene (FEP). Additionally, radiation resistance and mechanical properties are significantly improved due to introduction of ethylene, various mechanical properties have achieved a good balance: extremely strong tear resistance, high tensile strength, medium hardness, excellent impact resistance and long expansion and contraction life. Tensile strength of ETFE can reach 50MPa, close to twice that of PTFE. Compared with PTFE, ETFE can greatly improve its processing performance and exhibits outstanding adhesion to metal surfaces. It can be processed into fluoroplastic tight lining equipment that can withstand negative pressure. Moreover, ETFE has high thermal stability and reaches B1 and DIN4102 fire rating standards. When it is used in ventilation systems and structures, it has a higher fire safety risk compared to other polymers. Due to its excellent flame retardant and anti-corrosion properties, it has become the selected anti-corrosion lining material for smoke exhaust pipes to control fire spread by FM Global.

Additionally, the durability under harsh conditions makes ETFE play an irreplaceable role in fields such as electronic information, chemical anti-corrosion, functional architecture, military industry and aerospace. ETFE foil/membrane (100% PFAS) commonly used in the building roofs and exterior walls can be fully recycled, with a service life of more than 40 years, which can meet the long-term application needs. Composite building films (polyester/polyvinyl chloride with TiO2 surface coating and organic silicon coated glass fiber fabric) can be regarded as a substitute for fluoropolymer (ePTFE, PVDF or ETFE) foil/film building films to some extent, but the service life of fluoropolymer building films is much longer than that of alternative composite films, and their quality is lighter, more energy-saving and environmentally friendly (with a transmittance of up to 95%, which can effectively use natural light). Additionally, glass fiber fabrics are not flexible.In many cases they cannot be directly used for the same purpose as perfluoropolymer membranes (other design schemes are required), while organic silicon coated glass fiber fabrics have poor soil/dirt resistance[17].

Application of ETFE involves health, safety, performance and operation of the society, and its substitutes should be evaluated based on standards such as performance, availability, resource efficiency, waste generation, cost, stability and lifespan. At present, the substitutes mentioned in the proposal that exist in the market cannot be the complete replacement. Therefore, we think that ETFE should be exempted from regulatory management and control, additionaly, it is necessary to find various solutions for recycling, reuse, circular economy and life cycle analysis.

3. ETFE can be recovered and recycled

In recent years, FP manufacturers have realized the potentially negative impact of PFAS polymerization additives currently used to replace PFOA, and regulatory authorities are driving the industry to rapidly shift towards sustainable technologies, with a focus on developing the technologies for effective degradation, recovery and reuse of PFAS compounds[1]. FP manufacturers typically formulate the scheme based on two strategies:

i) Improve the process for eliminating fluoride by-products (such as low molecular weight oligomers, residual reactants and other volatile compounds) by improving the emission reduction techniques in FP manufacturing and recovery of PFAS surfactant. Since 1990s, these processes have reduced the emissions of fluorinated surfactants by 99%[2], and it has increased it to 99.99% by the recent research[3]. There is much literature on the control and treatment of PFAS emissions in industrial processes[4], and many studies are still under way[5]. For example, unfilled PTFE waste can be reused in plunger extrusion applications after cleaning[6] and grinding, or decomposed into low molar mass PTFE through heating, which is mixed with other materials in the form of micropowders for reuse[7]. For example, perfluorosulfonic acid is degraded through photochemical methods, such as UV photolysis of aqueous solutions containing sensitizers such as sulfites and iodine ions [9]. This mechanism begins with the generation of hydrated electrons through UV photolysis of added sensitizers, followed by reductively elimination of fluoride ions in PFASs[10]. In addition, hydrothermal treatment methods are also studied to effectively degrade these compounds. High temperature and high pressure alkaline water continuously can defluorinate various PFASs, and the final products are fluoride and carbonate ions[11]. The specific method is to completely defluorinate FP (including PVDF, as well as copolymers of VDF and TFE as a perfluorosulfonic acid membrane) into F-ions through superheated water (or “pressurized”). (with hot water of at approximately 100-300℃). This type of water is considered environmentally friendly 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]. The carbon content decomposes into CO_2 in the gas phase, while HCO_{3-} is generated into the reaction solution. In the presence of Ca $(OH)_2$, the released fluoride anions lead to the formation of “artificial fluorite” (CaF_2), which is the source of fluorine chemical processes. FP mineralization will help to form an effective fluorine element loop.

ii) Produce high molar mass FP without fluorinated polymerization additives (FPA), without any by-products, which meet PLC standard. In fact, significant progress has been made in the past decade, and some FP manufacturers have been using NFPA (or surfactants) to improve their production. Technology overview over the past decade based on NFPA has emphasized that the entire industry (such as 3M, AGC, Arkema, Chemours, Daikin, GFL and Solvay) has taken significant innovation and tried to claim the patents for such NFPA technologies when submitting multiple application. In fact, in 2022, multiple FP manufacturers announced the cessation of the use of FPA in their manufacturing[8]. Therefore, FP production without any FPA should be exempted from all the uses in all industries, including consumer applications, as they do not pose risks to the environment, as well as to the health of mammals and humans. Recently, the main issues have been solved, including the use of NFPA and the control of PFAS emissions exceeding 99% related to appropriate emission reduction technologies in FP industrial production[8]. Therefore, FP produced using NFPA technology has been successufl commercially, which further promote the industry to work harder in this direction. Their applications involve the health, safety, performance and operation of the society. 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, based on: (1) production of FP in the presence/absence of such surfactants (by reducing the process to obtain PFAS concentrations below 25 ppb), (2) essential use standards (safety, performance and health aspects), (3) process improvement, and (4) alternative schemes.

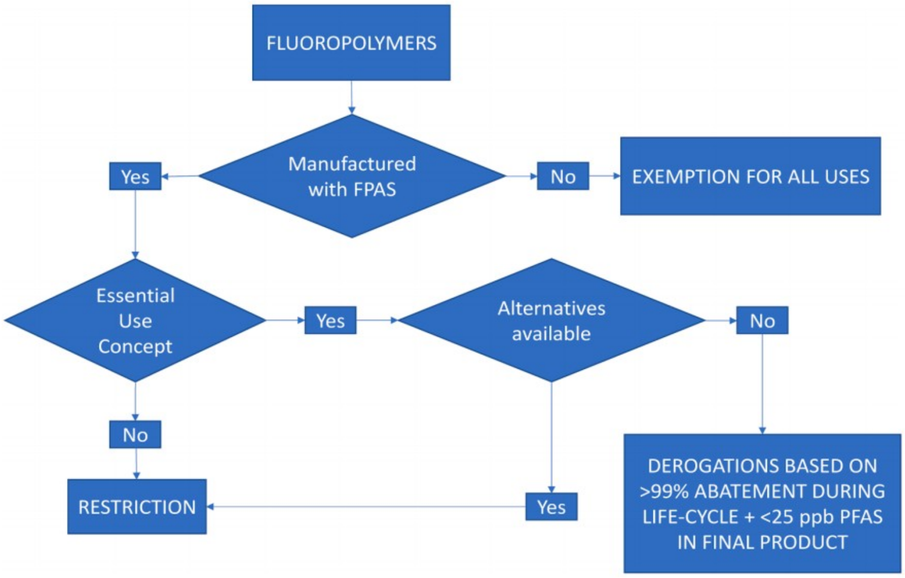

Figure 1. Regulatory Decision Tree for Fluoropolymers[8]

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