

TECHNICAL REPORT:

Development of a non-fluorinated polymerisation aid for the manufacturing of PTFE (via emulsion polymerisation)

Final report

prepared for

Gujarat Fluorochemicals Limited

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Technical Report: Development of a non-fluorinated polymerisation aid for the manufacturing of PTFE (via emulsion polymerisation)

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List of abbreviations and acronyms

ASTM	American Society for Testing and Materials
CIC	Combustion Ion Chromatography
CLP	EU Regulation 1272/2008 on classification, labelling and packaging of substances and mixtures
CEH	Chemical Economics Handbook
DOC	Dissolved Organic Carbon
DSC	Differential scanning calorimetry Thermogram
EC50	Concentration at which 50% of its maximum response is observed
ECHA	European Chemicals Agency
EEA	European Economic Area
EOL	End Of Life
FPS	Fluoropolymers
FPA	Fluorinated Polymerisation Aid
FTIR	Fourier Transform Infrared Spectroscopy
HS-GC/MS	Headspace-gas Chromatography/Mass Spectrometry
GFL	Gujarat Fluorochemicals Limited
GHS	Globally Harmonised System of Classification and Labelling of Chemicals of the United Nations
HPLC	High Performance Liquid Chromatography
Kow	The n-octanol/water partition coefficient
Koc	Organic carbon-water partition coefficient
LC-MS/MS	Liquid Chromatography/Mass Spectrometry
LC50/LD50	Dose at which a substance is lethal for 50% of tested subjects
LOD	Limit Of Detection
LOQ	Limit Of Quantification
MDL	Method Detection Limit
NFPA	Non-fluorinated Polymerisation Aid
OECD	Organisation for Economic Co-operation and Development
PBT	Persistent, Bioaccumulative, and Toxic
PFAS	Per- and polyfluoroalkyl substances

PFCAs	Perfluoroalkyl carboxylic acids
PFOA	Perfluorooctanoic acid
PFOS	Perfluorooctane sulfonic acid
PFSAs	Perfluoroalkyl sulfonic acids
PLC	Polymer of Low Concern
PTFE	Polytetrafluoroethylene
PTV-GC/MS	Programmable Temperature Vaporizer injection to Gas Chromatography/Mass Spectrometry
REACH	EU Regulation 1907/2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals
RIVM	National Institute for Public Health and the Environment (Netherlands)
R&D	Research and Development
RL	Reporting Limit
RMO	Regulatory Management Option
RMOA	Regulatory Management Option Analysis
SCAS	Semi-Continuous Activated Sludge
SDA	Soap and Detergent Association
SDS	Safety Data Sheet
SSG	Standard Specific Gravimetry
SIM	Selected Ion Monitoring
TD-GC/MS	Thermal Desorption-Gas Chromatography/Mass spectrometry
TF	Total Fluorine
TFE	Tetrafluoroethylene
TGA	Thermogravimetric Analysis
TIF	Total Inorganic Fluorine
TOF	Total Organic Fluorine
US EPA	United States Environmental Protection Agency
US FDA	United States Food and Drug Administration.
XRD	X-Ray Diffraction Analysis

Executive summary

The manufacture of emulsion polytetrafluoroethylene (PTFE) using a non-fluorinated polymerisation aid is presented in this report, which implies the substitution of short-chained poly- and perfluoroalkyl substances (PFAS) as polymerisation aids. The different options to carry out the polymerisation reaction of PTFE are explained, with details on the role played by the surfactants or emulsifiers used as polymerisation aids during the process.

The hazard, toxicology and ecotoxicology profile of the non-fluorinated polymerisation aid is presented, along with its potential emissions, which results in overall reduced risks compared to the traditional use of PFAS in the process. Furthermore, different analytical tests have been performed on PTFE samples manufactured with the use of the non-fluorinated polymerisation aid. All the evidence collected suggests that those samples do not contain oligomers or fluorinated by-products. In addition, the polymer exhibits technical properties that point towards equivalent (or even improved) performance in the different applications in which PTFE is commercially used.

This is a significant step forward in the ambition to discontinue the use of PFAS in the manufacturing process of fluoropolymers, and it opens the door to further research that industry can develop in the future, with the aim to identify similar options to eliminate fluorinated polymerisation aids for the manufacture of other fluoropolymers.

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1. Introduction

Gujarat Fluorochemicals Limited (GFL) is an Indian company with over 30 years of expertise in fluorine chemistry. GFL is specialized in the manufacture of a wide range of chemicals involving fluorine, with domain expertise in fluoropolymers (FPs) and other fluorospecialties. With three manufacturing sites in India, GFL is a global company with strategic assets in other geographic areas. The company is an established worldwide player on FPs and it is active in all relevant markets for these products. GFL follows closely the scientific developments on these chemicals, including increased societal concerns and regulatory developments (GFL, 2022a).

Per- and polyfluoroalkyl substances (PFAS) have been at the core of regulatory discussions over the past years. In Europe, a key initiative was the announcement in 2020 by five Competent Authorities from different countries¹ of the intention to propose a restriction under the REACH Regulation² on the manufacture and use of PFAS in the European Economic Area (EEA). PFAS is a large family of chemicals that covers thousands of highly fluorinated synthetic substances. Based on their chemical and structural properties, PFAS can be grouped into non-polymer and polymer substances. Certain chemicals within the non-polymer PFAS group, such as short and long-chain per- and polyfluoroalkyl carboxylic acids³ (PFCAs) and per- and polyfluoroalkyl sulfonic acids⁴ (PFSAAs) have been recently highlighted by regulators and relevant stakeholders globally, due to concerns related to their toxicity for human health and for the environment, in combination with their potential to bioaccumulate, to be persistent, and/or mobile in the environment.

Due to their chemical structure, FPs belong to the PFAS polymer group. These substances are high molecular weight polymers with a chemical structure consisting of fluorine atoms directly attached to their carbon backbone. Their physiochemical properties are unique and completely different from the non-polymer substances mentioned earlier. Therefore, it is expected that the properties that raise concern related to short-chained PFAS would not be applicable to the case of FPs. Indeed, the main FPs used by industry are considered to meet the conditions of Polymers of Low Concern (PLC) (OECD, 2009) and are therefore considered to be of insignificant risk to human health and the environment. In order to demonstrate that FPs meet the PLC criteria, and that they are different from other classes of PFAS, a number of studies have been conducted on a selection of representative FP substances, including Polytetrafluoroethylene (PTFE). The results of those studies show the absence of acute or sub-chronic systemic toxicity, irritation, sensitization, local toxicity, *in vitro* and *in vivo* genotoxicity, among other properties (Henry *et al.*, 2018).

FPs are used in many industrial applications, related to sectors such as transport, manufacturing of chemicals, power, electronics, semiconductors, medical devices, or renewal

¹ The Netherlands, Germany, Sweden, Denmark, and Norway

² Regulation (EC) No 1907/2006 on the Registration, Evaluation, Authorisation and Restriction of Chemicals

³ Example: Perfluorooctanoic acid (PFOA)

⁴ Example: Perfluorooctane sulfonic acid (PFOS)

energy, for which they are currently regarded by industry as irreplaceable. Due to their unique combination of functionalities, which are critical to ensure optimal performance, no reliable alternatives to FPs are available. FPs have low flammability, neutral electric charge, and high resistance to degradation, in addition to outstanding thermal, chemical, photochemical, hydrolytic, oxidative and biological stability. They are practicably insoluble in water and are resistant to virtually any chemical. These properties render FPs as highly valuable products, particularly in situations that are extremely demanding in terms of purity (e.g., manufacture of semiconductors or use of medical devices) or protection against chemical attack (e.g., transport or chemical industries). Indeed, FPs are the material of choice for many essential uses to society in which other materials cannot provide the necessary properties that FPs offer (PlasticsEurope, 2018).

However, there are some concerns related to the use of other PFAS substances in the manufacturing process of FPs. Under certain conditions, the use of short-chain PFAS as processing or polymerisation aids (surfactants) is necessary to achieve the final FP substance. This may result in situations of exposure to and emissions of PFAS from the FP manufacturing process. In addition, residuals of these fluorinated polymerisation aids (FPAs) may be carried over with the final FP substance down the supply chain which may also result in additional PFAS emissions from FP products. The polymerisation reaction can also involve the generation of unintended fluorinated oligomers or low molecular weight polymers during the process.

All the above items of concern have been flagged by researchers (Lohmann *et al.*, 2020) and regulators. The FP industry is also committed to addressing these issues, and improvements in the FP manufacturing process continue to be investigated. Furthermore, the FP industry in Europe, via the Fluoropolymer Products Group (FPG) of Plastics Europe, recently commissioned a Regulatory Management Option Analysis (RMOA) on FPs. The objective of the RMOA was to evaluate the possible Regulatory Management Options (RMOs) that could be applicable to FPs, and to identify the most appropriate one in terms of different parameters, such as effectiveness and proportionality. As a conclusion of this RMOA (PlasticsEurope, 2022), the FP industry in Europe has established a commitment to make efforts to address the existing concerns related to the use of polymerisation FPA in the manufacture of FPs, and to work on minimizing emissions of low carbon chain fluorinated by-products.

In line with these objectives, GFL has developed the use of a non-fluorinated polymerisation aid (NFPA) for the manufacture of emulsion PTFE substituting the use of FPAs. This major step forward from GFL is the result of significant Research and Development (R&D) efforts undertaken by the company, and it demonstrates that in certain cases, it is possible for industry to provide solutions for substituting PFAS from the manufacturing process of FPs, resulting in reduced PFAS emissions and thus helping to achieve global environmental objectives, such as those covered in the European Green Deal⁵.

⁵ https://ec.europa.eu/info/strategy/priorities-2019-2024/european-green-deal_en

2. Description of the PTFE manufacturing process

As a polymer compound, the manufacture of PTFE involves the polymerisation of a monomer, Tetrafluoroethylene (TFE). Tetrafluoroethylene can be polymerised by means of two technologies, *suspension* and *dispersion (emulsion)*, to produce PTFE resins.

The *suspension* method yields granular polymers, which are processed as moulding powders. Homopolymers and modified polymers of PTFE are produced by this technique. PTFE polymerised via suspension is commonly used in the manufacture of seals, gaskets and valves, expansion joints, pipes, and electrical insulators that can be made by compression moulding or extrusion processing methods.

Dispersion (emulsion) polymerisation is the regime by which *fine powder* and *dispersion* PTFE products are manufactured. Fine powder resins (average particle diameter of about 500 µm) are fabricated by paste extrusion where a hydrocarbon is added to the powder as an extrusion aid, later removed prior to sintering. In the PTFE dispersion concentrate, the concentration of the product is about 60% and it can be directly applied on various surfaces for non-stick properties and durability.

Dispersion products are primarily used to produce thin parts like tapes, wire insulation, or thin tubes and consumed by coating methods and filled co-coagulation applications. PTFE dispersion polymerisation products can be also used to impregnate glass or metal coatings and can be applied in materials used in sectors such as construction, electrical and electronics, semiconductor, filtration systems, or food processing.

Homopolymers and modified polymers are also produced by dispersion polymerisation. The main difference between both processes is that suspension polymerisation does not require the use of polymerisation aids, while the emulsion process requires the use of such processing aids to favour the intimate mixing of the monomers to complete an efficient and safe reaction. These aids are typically FPAs belonging to the short-chained PFAS group of substances. While it is possible to perform the emulsion process of certain FPs without the use of FPAs, this has so far not been possible for the emulsion polymerisation of PTFE.

Another difference related to the output of both polymerisation processes is the particle size of the manufactured product, which has an impact on the properties of the polymer and potential applications further down the value chain. When the suspension polymerisation process is used, coarse PTFE particles are obtained (of few millimetres size); in contrast, PTFE nanometric particles are obtained via the emulsion process.

All three forms of PTFE are produced by batch polymerisation under elevated pressure in specially designed reactors. Polymerisation media is high purity water, which is virtually devoid of inorganic and organic impurities that impact the reaction by inhibition and

retardation of the free radical polymerisation. The surfactant of choice in these reactions is anionic and often a perfluorinated carboxylic ammonium salt. (Ebnesajjad, 2014).

An initiator solution is added to the reaction vessel, and then the TFE monomer is gradually charged, leading to the initiation of the polymerisation process of the monomer dissolved in the aqueous phase. Since PTFE is insoluble in water, the polymerised product is precipitated from water to form primary particles. If there is no dispersant in the water, the primary particles will aggregate into coarse particles, which is commonly known as suspension polymerisation. When a small amount of polymerisation aid is dissolved in the aqueous phase, the primary particles are protected, and the system is a temporarily stable dispersion, i.e., a dispersion polymerisation.

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3. Motivation to substitute the use of FPA in the PTFE emulsion manufacturing process

GFL is fully committed with the implementation of initiatives aimed at improving the sustainability of its processes worldwide. GFL puts in place procedures and governance mechanism in line with international standards, and collaborates with all stakeholders (e.g., customers, suppliers, employees, and business associates) to build a sustainable value chain. GFL aims at manufacturing products by environmentally sustainable processes fulfilling all the regulatory requirements, optimizing energy and water consumption, reducing carbon footprint and emissions to the environment, and ensuring adequate protection of human health and the planet.

To achieve these goals, GFL is continuously investing in R&D initiatives to improve product safety and to reduce the environmental impact of its processes. With a specific focus on the increased concern on the hazardous properties of PFAS, GFL has placed substantial efforts in improving the conditions related to the manufacture of FPs. As a result of such efforts, GFL has successfully replaced FPAs with a NFPA in an improved emulsion process for the manufacture of PTFE. This NFPA is an organic compound based on sulfonated hydrocarbon chemistry. The PTFE product obtained by this process has similar physiochemical properties, and even improved performance on certain parameters, compared to PTFE produced via the typical emulsion process using FPAs. This has been confirmed by technical analysis using specific tests on the final PTFE product, and by evaluation of properties of the alternative NFPA used, which are further described in this report. The evaluation performed on the properties of the NFPA and the resulting PTFE product fit with internal objectives set by GFL to address the concerns raised by the use of FPAs in the production of FPs, with a focus on emissions of PFAS during PTFE manufacturing process, as well as on the generation of free oligomers or unintended PFAS by-products during the polymerisation that may be carried over through the supply chain.

The global production of FPs is estimated at approximately 320,000 tonnes per year. Table 1 below shows information from sources related to total volume of the main substances in the FP family (IHS, 2019). This information is supplemented with additional knowledge on the FP market (CEH, 2016). PTFE stands out as the largest FP of interest in terms of volume, with more than 50% of the total production of this type of polymers. It is assumed that approximately 50% of the PTFE production globally is done via the emulsion process. Considering the different FPs that are produced without the need to use FPAs, it is anticipated that, by converting all the emulsion PTFE manufactured worldwide to the use of the NFPA, as developed by GFL, there is a potential to reduce the total FP production that would require the use of PFAS as polymerisation aids to less than 20%.

Table 1. Global production of FPs and use of FPA.

Fluoropolymers	Volume (tonnes)	% of total volume	Use of FPA	% volume that do not require use of FPA	% volume that do not require use of FPA
PTFE Total	169,759	53%			
PTFE Suspension	84,879.5	26.5%	N	26.5%	26.5%
PTFE Emulsion	84,879.5	26.5%	Y		26.5%
PVDF (Homopolymer + Copolymer)	51,248	16%	N	16%	16%
FEP	32,030	10%	Y		
PVF	6,406	2%	Y		
PFA	3,203	1%	Y		
ETFE	3,203	1%	Y		
FKM	35,000	10.9%			
FKM Copolymer	25,000	7.8%	N	7.8%	7.8%
FKM Terpolymer ⁶	10,000	3.1%	Y/N	1.6%	1.6%
THV	800	0.3%	Y		
ECTFE (Copolymer + Terpolymer)	2,200	0.3%	N	0.3%	0.3%
PCTFE	8,600	2.7%	N	2.7%	2.7%
Others	7,851	2.5%			
TOTAL	320,300			54.8%	81.3%

It is worth noting that all activities related to the manufacture of PTFE⁷ developed by GFL take place at the production sites located in India. While this implies exclusively the need to comply with national legislation on human health and environmental protection during the different steps of the manufacturing process (e.g., direct handling of the selected NFPA, environmental emissions), GFL takes a serious commitment to observe the highest environmental and safety standards globally, and therefore intends to ensure best practices worldwide and down its value chain.

In terms of expected consumption of the selected NFPA for the coming years, GFL anticipates that this could be approximately 25 tonnes per year, assuming 100% aqueous PTFE and PTFE fine powder conversion based on existing capacity. It is to be noted that an additional technological advantage of PTFE manufacturing process with the use of selected NFPA is, in

⁶ Assuming 50% of FKM Terpolymer does not require the use of FPA

⁷ INOFLON^R is the brand name used by GFL for its PTFE products

addition to not using FPA, that consumption of polymerisation aid per unit of PTFE production is reduced by at least 60% or 70%.

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4. Profile of the NFPA used

The main properties of the NFPA used by GFL in the innovative emulsion polymerisation for the manufacture of PTFE related to health and safety will be described in this section. This includes information on the hazard classification, toxicological and ecotoxicological profile. The main source of information is the Safety Data Sheet (SDS) made available by the supplier of the NFPA, as well as open literature sources, such as the European Chemicals Agency (ECHA) dissemination website of registered substances under REACH.

4.1. Hazard classification

According to the SDS made available by the supplier, the NFPA is classified as follows:

- GHS hazard classification:
 - Serious eye damage category 1 (H318)
 - Aspiration hazard category 2 (H305)
 - Short-term (acute) aquatic hazard category 1 (H400)
 - Long-term (chronic) aquatic hazard category 1 (H410)
 - GHS Pictograms: GHS05 (corrosive), GHS08 (health hazard), GHS09 (environmental hazard)
- CLP hazard classification:
 - Serious eye damage category 1 (H318)
 - Short-term (acute) aquatic hazard category 1 (H400)
 - Long-term (chronic) aquatic hazard category 1 (H410)
 - GHS Pictograms: GHS05 (corrosive), GHS09 (environmental hazard)

It is worth noting that, although the NFPA is a substance that has been classified as hazardous, the classification of PTFE manufactured with the NFPA is not impacted because the concentration of NFPA in the final product (< 0.1% w/w) is below the generic concentration limits applicable to each hazard category.

At GFL production sites, handling of NFPA is done with automated process and minimum intervention by human workforce resulting in low occupational hazard.

4.2. Toxicological profile

Information on the NFPA related to the main toxicological endpoints is displayed in Table 2. This is consistent with the classification information and the different regulatory schemes evaluated (GHS⁸, CLP⁹) mentioned in Section 4.1.

Table 2. Summary of the main toxicological data for the NFPA.

Acute oral toxicity	> 5000 mg/kg; Very low toxicity if swallowed
Acute inhalation toxicity	> 2000 mg/kg; Prolonged contact unlikely to result in absorption in harmful amount
Acute dermal toxicity	Not determined; No adverse impact anticipated
Skin corrosion/irritation	Brief contact is essentially non-irritating to skin.
Eye damage/irritation	May cause severe irritation with corneal injury which may result in permanent impairment of vision, even blindness. Chemical burns may occur.
Sensitization	Did not cause allergic skin reactions when tested in guinea pigs; no relevant data found for respiratory irritation
Specific Target Organ Systemic Toxicity (Single Exposure)	Not classified
Specific Target Organ Systemic Toxicity (Repeated Exposure)	In animals, effects have been reported on the following organs: kidney, liver
Carcinogenicity	Did not cause cancer in laboratory animals.
Teratogenicity	Did not cause birth defects or any other foetal effects in laboratory animals.
Reproductive toxicity	In animal studies, did not interfere with reproduction.
Mutagenicity	<i>In vitro</i> genetic toxicity studies were negative. Animal (<i>in vivo</i>) genetic toxicity studies were negative.
Aspiration hazard	Aspiration into the lungs may occur during ingestion or vomiting, causing lung damage or even death due to chemical pneumonia.

⁸ United Nations Globally Harmonised System for Classification and Labelling of Chemicals

⁹ Regulation (EC) No 1272/2008 on the Classification, Labelling and Packaging of Substances and Mixtures

4.3. Ecotoxicological profile

As mentioned in Section 4.1, the substance is classified as hazardous to the environment. Ecotoxicological parameters for the justification of such classification are shown in Table 3.

Table 3. Summary of the main ecotoxicological data for the NFPA.

LC50 (96hr) – Fish	< 1 mg/L; very toxic to aquatic organisms
EC50 (48hr) – Aquatic invertebrate	13.9 mg/L
EC50 (72hr) - Algae	Not available

One of the main concerns related to some PFAS is that they are considered to be PBT substances. Being this a critical element in the evaluation of the validity of an alternative polymerisation aid, and in order to avoid regrettable substitution (understood as the replacement of a hazardous substance by another one resulting in an equivalent level of risk or concern), technical data on these parameters of the NFPA used are needed. The information provided by the supplier of the NFPA is shown in Table 4.

Table 4. Summary of the evaluation of PBT properties of the NFPA.

Persistence and degradability	Not readily biodegradable (OECD 301D guideline); Inherently biodegradable (OECD 302B guideline, Zahn-Wellens procedure)
Bioaccumulation	Log Kow: <1.82 (OECD TEST GUIDELINE 117); Low potential to Bioaccumulate
Mobility in soil (active ingredient)	Log Koc: ≥ 4.54 ; ≤ 4.81 ; Low Mobility in Soil (According to EPA Soil Mobility Classification criteria & REACH Dossier)
Mobility in water (active ingredient)	Water solubility > 1,000 g/L; Log Koc > 4

Biodegradability of the NFPA has been evaluated in various screening studies, and it can be concluded that this substance is not readily biodegradable (OECD301D) but inherently biodegradable (OECD302B). Biodegradability tests details are summarized as follows:

- according to the semi-continuous activated sludge (SCAS) test specified by the Soap and Detergent Association's (SDA) Subcommittee on Biodegradation Test Methods,

greater than 90% reduction were achieved in methylene blue active allowing classification of these products as biodegradable under the SCAS test conditions;

- according to the OECD 301D closed bottle study, 0 - 6% biodegradation was observed that means that NFPA is considered as not readily biodegradable (ECHA, 2019);
- according to the OECD 302B guideline Zahn-Wellens procedure, 54% dissolved organic carbon (DOC) removal was achieved and the NFPA could be classified as inherently biodegradable.

Moreover, the NFPA is biodegradable in river water and sediment as well as in soil, primary degradation occurring at a faster speed (half-life ranging from 2.2 to 180 days) while ultimate degradation (mineralization) occurring at a much slower speed (ECHA, 2019).

Regarding bioaccumulation, the NFPA is expected to have low bioaccumulation potential because of its high solubility in water (> 1,000 g/L) and low octanol-water partition coefficient ($\log K_{ow} < 1.82$). This substance is a solid substance with negligible vapor pressure and highly soluble (dispersible) in water. (ECHA, 2019). On the other hand, it is also expected to have low mobility in soil due to relatively high soil adsorption coefficients. Volatilization of the substance is not expected to be an important environmental fate process since it is a sodium salt and is not volatile. Therefore, it is not expected to be present in the vapor phase nor in the atmosphere. When introduced into soil compartment, this substance will mainly reside in the soil compartment. When released into water, this compound will be distributed between the water and sediment compartments. (ECHA, 2019).

5. Emissions from PTFE emulsion manufacturing process with use of NFPA

GFL has assessed the potential emissions to the environment that could be generated by using the NFPA during the manufacturing process of PTFE. In the production of PTFE aqueous dispersions, the only possible source of NFPA discharge to the environment is through the effluent water. In the case of PTFE powder production, the NFPA can be released to the air and to the effluent water. In PTFE powder manufacturing process, all drying ovens are connected to air scrubbing systems in order to treat all outgas in water. The water is previously treated to be discharged to the water effluent stream. At GFL production sites, all the effluent water streams are equipped with activated carbon bed systems for absorption of undesired organic impurities. Spent carbon is incinerated at high temperature ($> 600^{\circ}\text{C}$) to completely destroy organic impurities at a government authorized incineration facility.

GFL has tested the absorption behaviour of the NFPA internally at its laboratory using different absorbent types. These consist of ion exchange resins based on different functional groups and activated carbon, and the conclusion is that the most effective one is activated carbon. For testing, 350 ppm standard solution of the NFPA in water was used, and the released concentration was measured. Results are shown in Table 5.

Table 5. Summary of absorbent options for emissions related to the use of the NFPA.

Absorbent type	Detected concentration (ppm)
OH based resin	6
Mixed bed resin with sulphonic acid and tertiary amine groups	5
Non-ionic polymeric adsorbent - Styrene divinylbenzene copolymer	8
Activated carbon	Not detected

Based on the findings described above and the method already in use at GFL, the absorption of the NFPA through activated carbon bed is considered to be an efficient way to remove any residual content of the substance. Activated carbon thus consumed should be incinerated at high temperature ($> 600^{\circ}\text{C}$).

With all control measures in place, the NFPA content in the final effluent discharge stream is not detected up to 500 ppb level in High Performance Liquid Chromatography (HPLC), which corresponds to the known Method Detection Limit (MDL).

6. Purity of emulsion PTFE manufactured with the use of NFPA

GFL has tested the PTFE manufactured with NFPA in the emulsion polymerisation process, in order to evaluate the content of free oligomers, unreacted monomers or unintended PFAS that may have been generated during the manufacturing process. Different batches of PTFE were produced and tested under different analytical methods. Results were compared with samples of PTFE manufactured with the use of FPA (HFPO-DA). Some of these studies were commissioned to Intertek in the Netherlands, a well reputed and experienced global laboratory.

6.1. Oligomer analysis

The purpose of the analysis is to determine any presence of oligomers to verify that PTFE manufactured with the NFPA complies with the PLC requirement established in the OECD guidelines of < 1% oligomer (OECD, 2009).

6.1.1. Spectrometry techniques

Several PTFE samples were analysed by means of three spectrometry techniques:

- headspace-gas chromatography/mass spectrometry semi-quantitative analysis (HS-GC/MS);
- programmable temperature vaporizer injection to gas chromatography/mass spectrometry semi-quantitative analysis (PTV-GC/MS) (Tsuge Shin, 2011);
- thermal desorption-gas chromatography/mass spectrometry semi-quantitative analysis (TD-GC/MS).

In all cases, a Selected Ion Monitoring (SIM) with mass over charge (m/z) values of 50, 81, 100, 131 and 150 (Intertek, 2021a) was performed on the HS-GC/MS chromatogram to detect PTFE oligomers. These m/z values are characteristic for PTFE polymers and their oligomers.

The results, which are summarised in Table 6, indicate that oligomers were not detected in any analysis (Intertek, 2021a).

Table 6. Summary of oligomer analysis by spectrometry techniques

Batch reference ¹⁰	Test method	Results
INOFLON AD9300EX ¹¹ T50A9321FH	HS-GC/MS	No PTFE oligomers detected
INOFLON AD9300EX T44A9321FH	HS-GC/MS	No PTFE oligomers detected
INOFLON AD9200EX ¹² T12A9221FH	HS-GC/MS	No PTFE oligomers detected
INOFLON AD9300EX T50A9321FH	PTV-GC/MS	No PTFE oligomers detected
INOFLON AD9300EX T44A9321FH	PTV-GC/MS	No PTFE oligomers detected
INOFLON AD9200EX T12A9221FH	PTV-GC/MS	No PTFE oligomers detected
INOFLON FP7040EX ¹³ G0804212DE	TD-GC/MS	No PTFE oligomers detected
INOFLON GN7040 G1704212BR	TD-GC/MS	No PTFE oligomers detected

6.1.2. Thermogravimetric Analysis

Samples of PTFE manufactured with the use of the NFPA (INOFLON FP7040EX) and with FPA (INOFLON GN 7040) were analysed by Thermogravimetric Analysis (TGA). The test results (Intertek, 2021a) can be seen in Figures 1 and 2. It can be concluded that there is no significant gravimetric loss after the heating stage and isothermal analysis at 350 °C for 1 hour for any of the samples that were analysed.

In summary, the results obtained from the TGA analysis suggest that there is no presence of oligomers in the products.

¹⁰ Batch references with 'EX' termination refer to PTFE samples manufactured with the NFPA; references with 'GN' indication refer to PTFE samples manufactured with the FPA

¹¹ AD9300: Homopolymer PTFE aqueous dispersion

¹² AD9200: Modified PTFE aqueous dispersion

¹³ FP7040: PTFE fine powder

Figure 1. TGA analysis of INOFLON FP7040EX (use of NFPA); weight variation vs time.

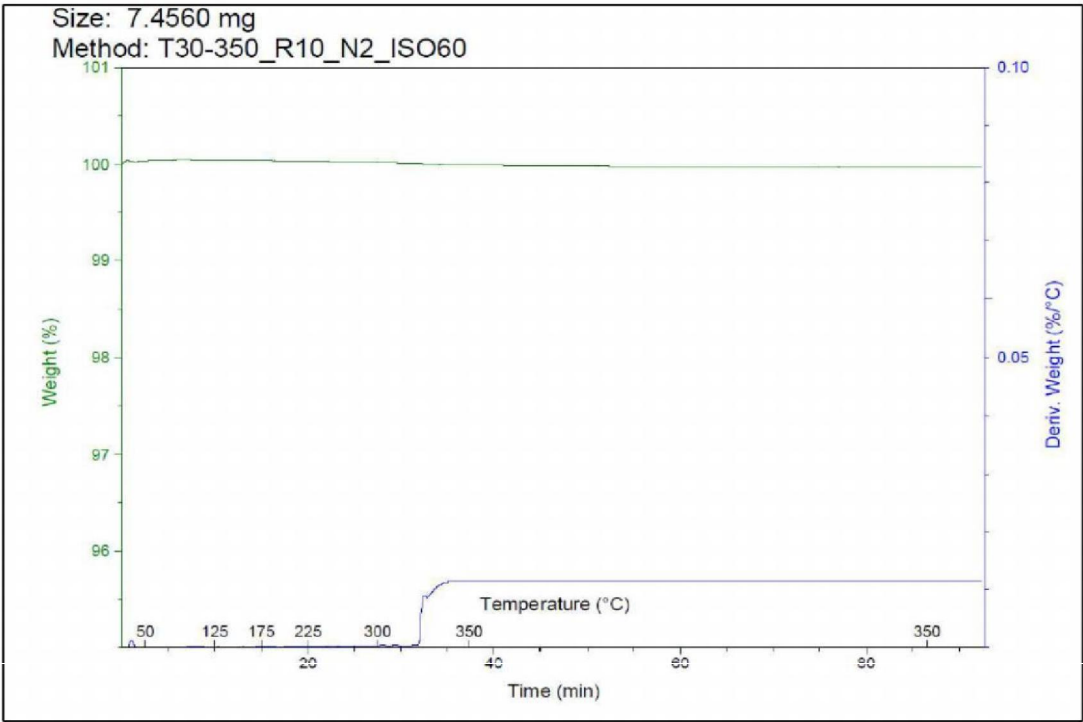
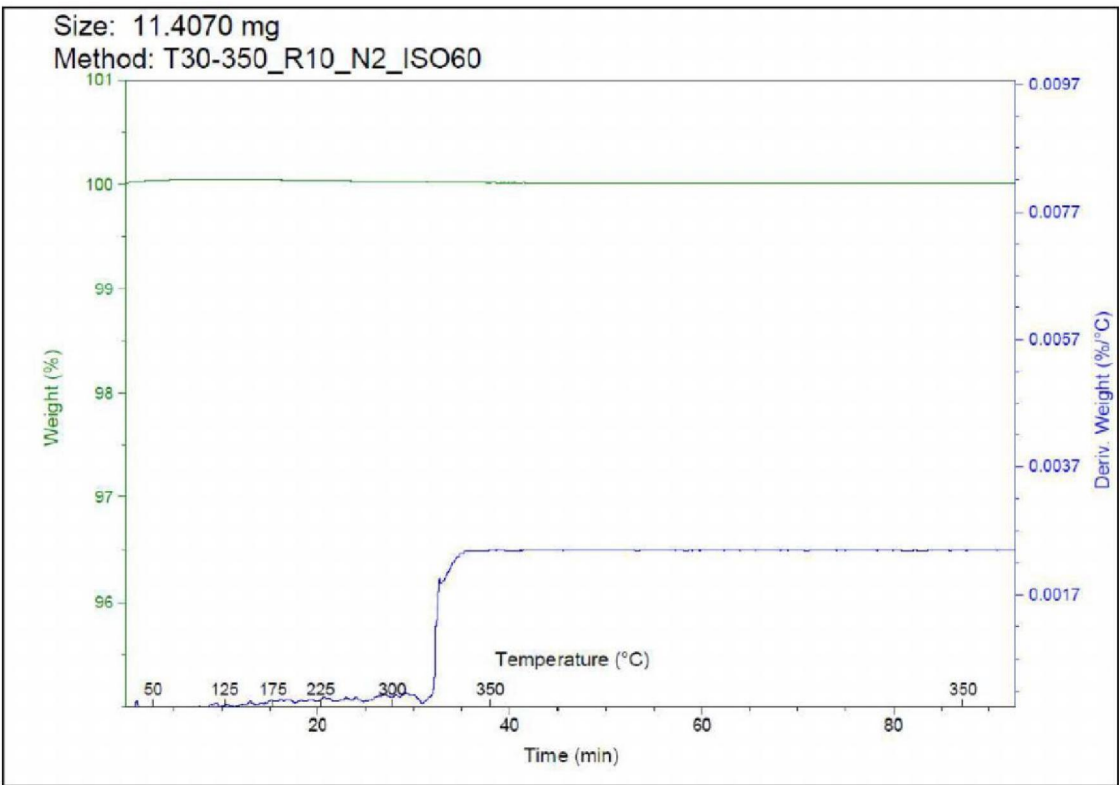


Figure 2. TGA analysis of INOFLON GN 7040 (use of FPA); weight variation vs time.



6.1.3. X-Ray Diffraction Analysis

X-Ray Diffraction Analysis (XRD) was performed on PTFE samples manufactured with both the NFPA (INOFLON FP7040EX) and FPA (INOFLON GN 7040). The results obtained in this analysis (Intertek, 2021a) show that the signals of the two samples are fully overlapped and both diffractograms are nearly identical, which means that the identity of the analysed substances is the same. The sample signals match with the PTFE reference pattern as can be seen in Figures 3 and 4. XRD analysis indicates the crystalline structure of FPA based grades and NFPA based grades is similar, and there is no indication of smaller crystalline structures (low molecular weight fractions) observed in NFPA based grades in comparison to FPA grades.

Figure 3. XRD analysis of sample INOFLON FP7040EX.

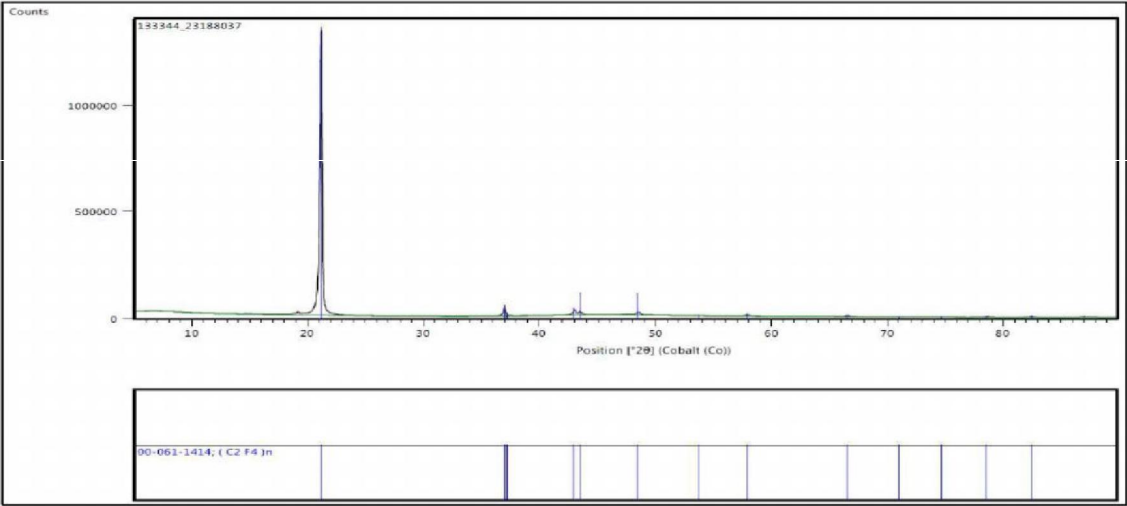
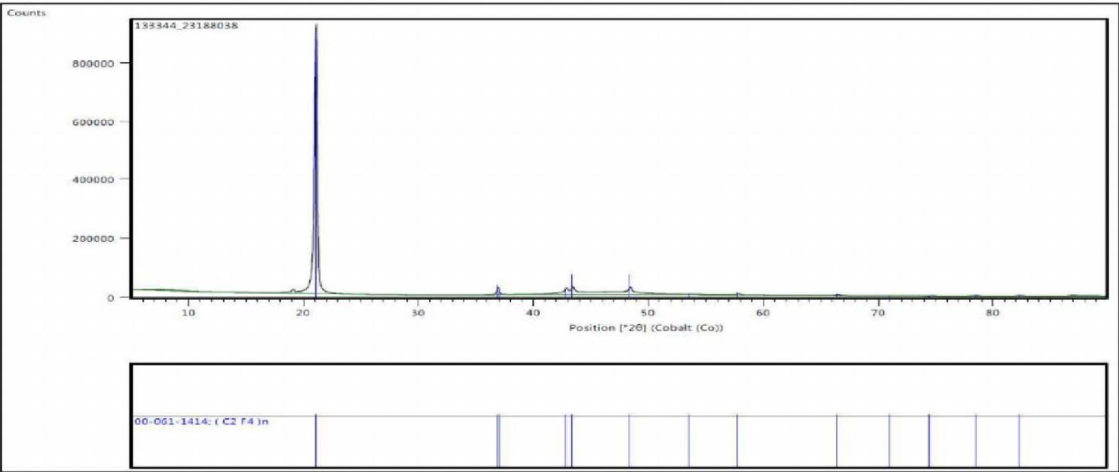


Figure 4. XRD analysis of sample INOFLON GN 7040.



6.1.4. Fourier Transform Infrared Spectroscopy analysis

A comparative Fourier Transform Infrared Spectroscopy (FTIR) analysis of samples INOFLON FP7040EX (NFPA based) and INOFLON GN 7040 (FPA based) was performed, in order to determine the identity of the substances (Intertek, 2021a). As it can be observed in Figure 5, the molecular structure of both grades is similar, since both infrared fingerprints are overlapped. Moreover, it can be also observed that all infrared bands can be assigned to the CF_2 vibrations, and no other functional groups were detected, therefore it can be argued that in both cases the chemical reaction has been completed, and thus no by-products nor unreacted raw materials are present in the final PTFE samples produced. A reference spectrum of PTFE is shown in Figure 6 for comparison.

Figure 5. FTIR analysis of samples INOFLON FP7040EX and INOFLON GN 7040.

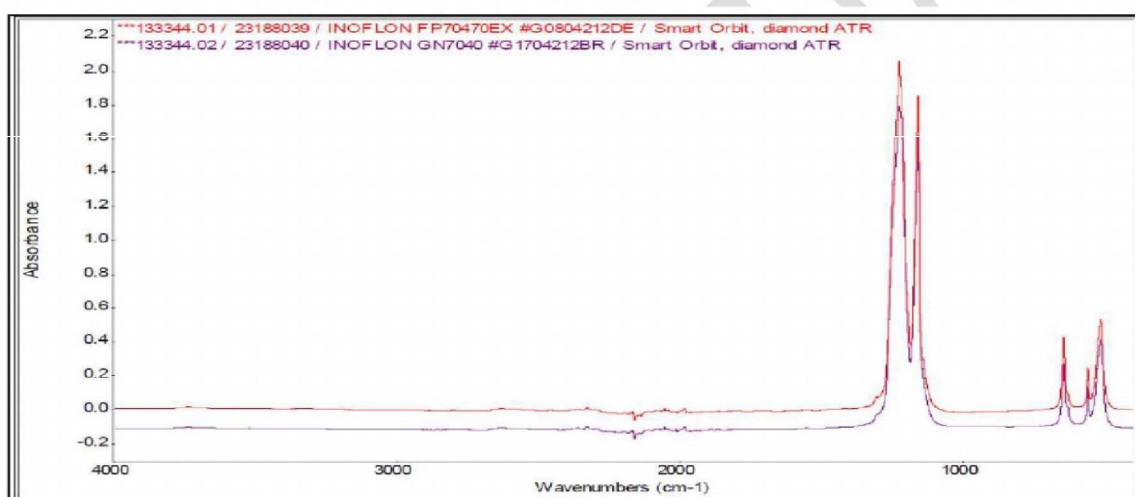
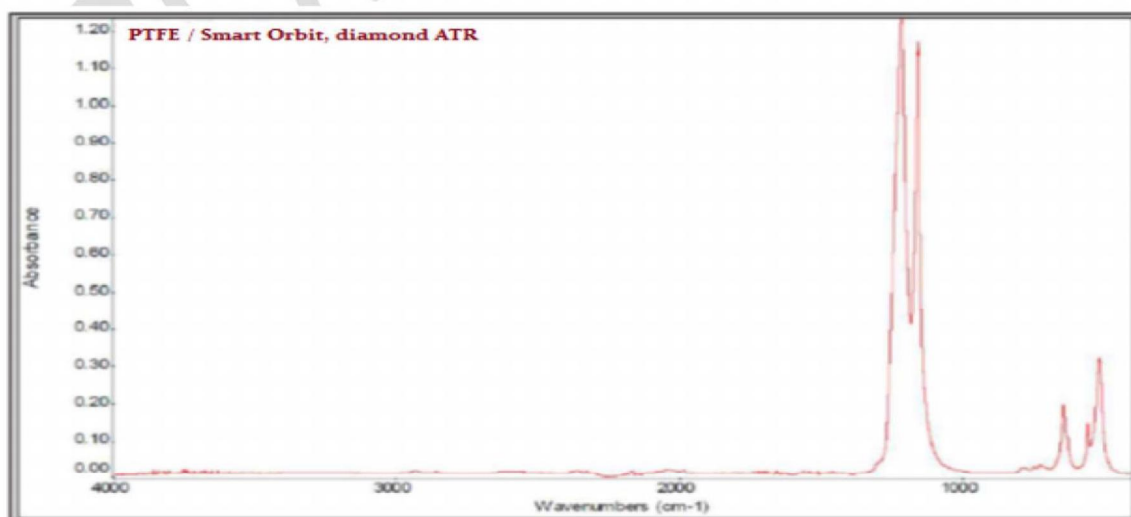


Figure 6. FTIR reference spectrum of PTFE.



6.1.5. Differential Scanning Calorimetry

Table 7 presents the values obtained from Differential Scanning Calorimetry (DSC) tests on PTFE samples manufactured using NFPA and FPA (GFL, 2021a). Relevant values for fusion and crystallization points are similar, which suggests that products are equivalent, and no relevant oligomers are present. DSC thermogram for both samples can be seen on Figures 7 and 8.

Table 7. Main temperature and enthalpy parameters obtained from DSC analysis for PTFE samples manufactured with NFPA and FPA.

	1st fusion		2nd fusion		Crystallization	
	Melting point (°C)	Enthalpy (J/g)	Melting point (°C)	Enthalpy (J/g)	Crystallization point (°C)	Enthalpy (J/g)
NFPA based - batch G0804212DE	339.85	65.00	326.93	17.02	315.66	22.52
FPA based - batch G1704212BR	343.65	69.00	326.37	20.56	314.64	25.41

Figure 7. DSC thermogram for PTFE manufactured with the use of NFPA.

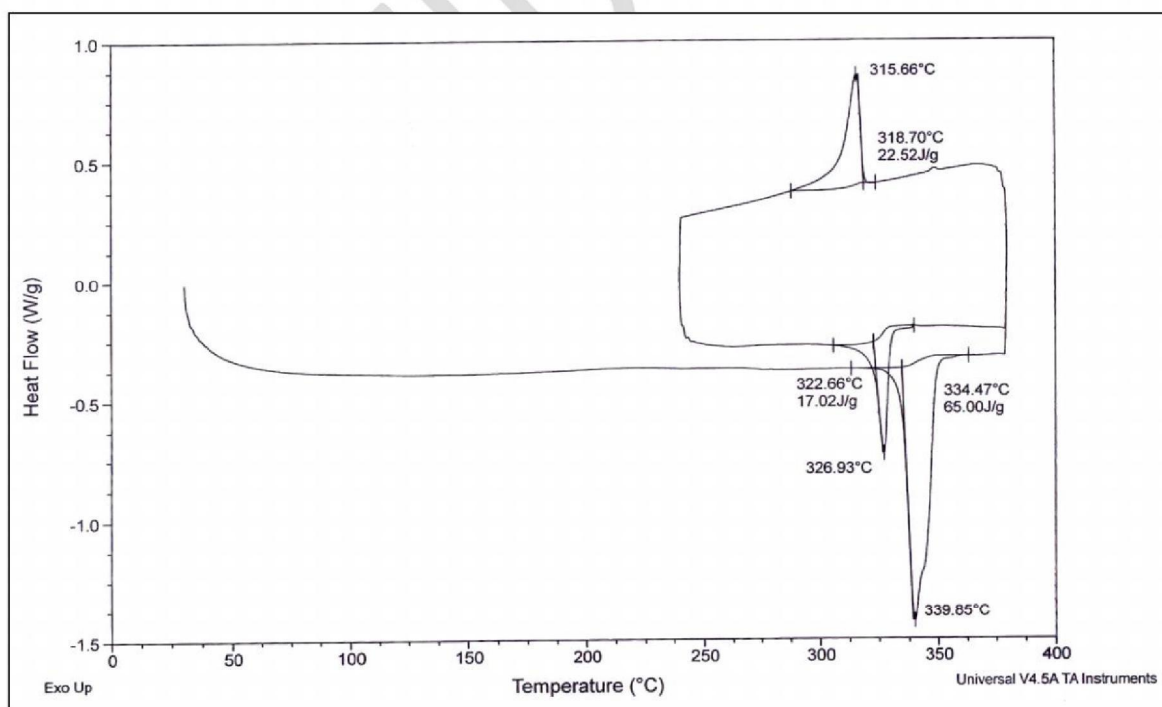
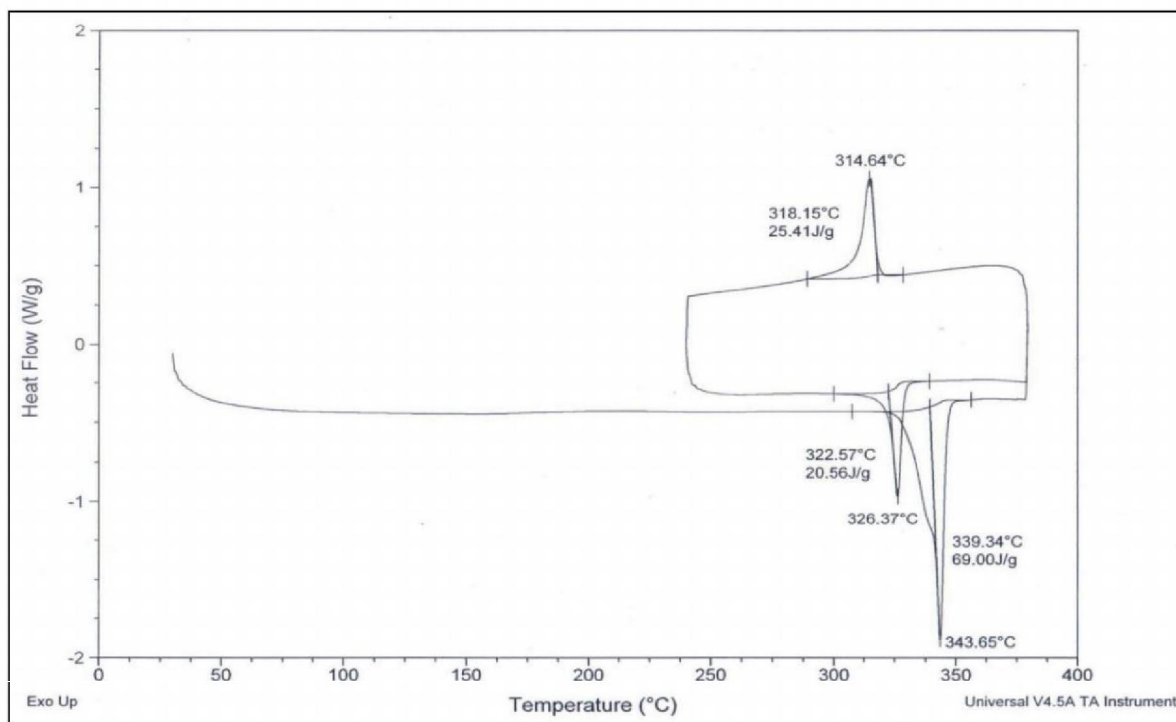


Figure 8. DSC thermogram for PTFE manufactured with the use of FPA.



6.2. PFAS analysis

The potential presence of unintended PFAS in the PTFE produced with the use of NFPA as a polymerisation aid was tested by means of Liquid Chromatography/Mass Spectrometry (LC-MS/MS). The test was run according to US EPA method 537.1 (GFL, 2022c). The samples were prepared by solid phase extraction (SPE).

The results of this analysis are shown on Table 8. No known targeted PFAS were observed in the tested material, except for Hexafluoropropylene Oxide Dimer Acid (HFPO-DA) at trace level. This can be explained, since the manufacturing process is run at the same reactor in which PTFE was previously manufactured using HFPO-DA. Indeed, under the conditions of manufacture of PTFE, HFPO-DA is not expected to be a chemical that could be produced as a by-product of the manufacturing process. After stabilization and elimination of HFPO-DA, only traces of this substance were identified at very low level (below 10 ppb). It needs to be highlighted that such a low concentration of HFPO-DA cannot be regarded as playing any role in the successful manufacture of PTFE with the NFPA; indeed, approximately 15 kg of HFPO-DA are required for one batch of emulsion PTFE of around 800-1,200 kg, which is significantly lower than the concentration in the order of few ppb detected in the analysis.

The low concentration value of HFPO-DA detected in batches manufactured with the NFPA is expected to further decrease (until not detectable levels) over time. While, at present, it is not

possible to establish a clear timeline by when levels of HFPO-DA may be brought to undetectable levels, it is anticipated that this will result in the course of the coming months.

It is worth noting that under the current set-up that GFL uses for the manufacture of PTFE, it is not possible to run the polymerisation process of PTFE at a different reactor. Ultimately, it is the goal of GFL to completely stop the use of FPA for the manufacture of PTFE, which will mean that all grades of PTFE manufactured by GFL will be equivalent in composition, regardless of the equipment in which they are produced.

It is also relevant to highlight that at present time, GFL estimates that approximately 45 different PFAS can be detected via LC-MS/MS. The results displayed in Table 8 cover 45 compounds that match the PFAS definition. GFL will continue to expand the list of PFAS to be analysed from PTFE samples manufactured with the NFPA, in a continued effort to completely demonstrate absence of any PFAS from the product. Still, if none of the substances listed in Table 8 has been identified (except for HFPO-DA), it is reasonable to expect that indeed no PFAS are generated during the manufacturing process.

Some progress has been recently made related to the PFAS determination. In February 2022, the UK Environment Agency published the results of a survey launched to collect information from different laboratories (Sims *et al.*, 2022), in relation to the specific PFAS they are currently analysing in the environment (e.g., vertebrates, invertebrates, plants, soil, sediment, groundwater, drinking water). Information included, the analytical techniques used, details on sample preparation, and Limits of Detection (LOD).

The main conclusion from the report was that currently, around 130 PFAS are being determined by the laboratories that participated in the survey. The most common PFAS analysed are PFCAs and PFSA.

Regarding the information on LODs, they have been reported for a few PFAS only, most of them were covered by the European Drinking Water Directive¹⁴. The information on LODs is not considered representative enough due to the large number of existing PFAS (in the range of thousands), therefore further research will be needed in the coming years on this topic (Sims *et al.*, 2022).

¹⁴ Directive (EU) 2020/2184 of the European Parliament and of the Council of 16 December 2020 on the quality of water intended for human consumption

Table 8. Summary of analysis¹⁵ of PFAS in PTFE samples manufactured with NFPA.

Compound Name	Abbreviation	CAS No.	MDL	RL	INOFLOX 9300EX - Batch 012E9322BH	INOFLOX 9300EX - Batch 011E9322BH
Perfluorobutanoic acid	PFBA	375-22-4	0.25	0.75	ND	ND
Perfluoro-3-methoxypropanoic acid	PFMPA	377-73-1	0.25	0.75	ND	ND
Perfluoropentanoic acid	PFPeA	2706-90-3	0.25	0.75	ND	ND
Perfluoro-4-methoxybutanoic acid	PFMBA	863090-89-5	0.25	0.75	ND	ND
Hexafluoropropylene Oxide Dimer Acid	HFPO-DA	13252-13-6	0.3	1.0	3.1	3.5
Nonafluoro-3,6-dioxaheptanoic acid	NFDHA	151772-58-6	0.5	1.5	ND	ND
Perfluoro-1-butanefulfonic acid	PFBS	375-73-5	0.3	1.0	ND	ND
Perfluorohexanoic acid	PFHxA	307-24-4	0.5	1.5	ND	ND
Perfluoro(2-ethoxyethane) sulfonic acid	PFEESA	113507-82-7	0.5	1.5	ND	ND
1H,1H,2H,2H-Perfluorohexane sulfonic acid	4:2 FTS	757124-72-4	0.5	1.5	ND	ND
Perfluoro-1-pentanesulfonic acid	PFPeS	2706-91-4	0.3	1.0	ND	ND
Perfluoroheptanoic acid	PFHpA	375-85-9	0.3	1.0	ND	ND
2-perfluorohexyl ethanoic acid	6:2 FHET	53826-12-3	1.0	3.0	ND	ND
4,8-Dioxa-3H-perfluorononanoic acid	ADONA	919005-14-4	0.3	1.0	ND	ND
Perfluoro-1 -hexanesulfonic acid	PFHxS	355-46-4	0.3	1.0	ND	ND
Perfluorooctanoic acid	PFOA	335-67-1	0.3	1.0	ND	ND
1H,1H,2H,2H -Perfluorooctane sulfonic acid	6:2 FTS	27619-97-2	0.5	1.5	ND	ND
Perfluoro-1-heptanesulfonic acid	PFHpS	375-92-8	0.3	1.0	ND	ND
Perfluorononanoic acid	PFNA	375-95-1	0.3	1.0	ND	ND
2-perfluorooctyl ethanoic acid	8:2 FOET	27854-31-5	1.0	3.0	ND	ND
Perfluoro-1-octanesulfonamide	FOSA-I	754-91-6	0.3	1.0	ND	ND
Perfluoro-1-octanesulfonic acid	PFOS	1763-23-1	0.3	1.0	ND	ND
N-Methylperfluorooctanesulfonamide	N-MeFOSA	31506-32-8	0.5	1.5	ND	ND
Perfluorodecanoic acid	PFDA	335-76-2	0.3	1.0	ND	ND

¹⁵ All units are µg/l

Table 8 (continued). Summary of analysis of PFAS in PTFE samples manufactured with NFPA.

Compound Name	Abbreviation	CAS No.	MDL	RL	NOFLOX 9300EX - Batch 012E9322BH	NOFLOX 9300EX - Batch 011E9322BH
N-ethyl perfluorooctanesulfonamidoacetic acid	N-EtFOSAA	2991-50-6	0.5	1.5	ND	ND
N-ethylperfluorooctanesulfonamide	N-EtFOSA	4151-50-2	0.5	1.5	ND	ND
1H,1H,2H,2H -Perfluorodecane sulfonic acid	8:2 FTS	39108-34-4	0.5	1.5	ND	ND
9-Chlorohexadecafluoro-3-oxanonane- 1-sulfonic acid	9Cl-PF3ONS	756426-58-1	0.3	1.0	ND	ND
Perfluoro-1-nonanesulfonic acid	PFNS	68259-12-1	0.3	1.0	ND	ND
2-(N-methylperfluoro-1- octanesulfonamido)-ethanol	N-MeFOSE	24448-09-7	1	3	ND	ND
Perfluoroundecanoic acid	PFUnDA	2058-94-8	0.3	1	ND	ND
N-methyl perfluorooctanesulfonamidoacetic acid	N-MeFOSAA	2355-31-9	0.5	1.5	ND	ND
2-(N-ethylperfluoro-1- octanesulfonamido)-ethanol	N-EtFOSE	1691-99-2	1	3	ND	ND
Perfluoro-1-decanesulfonic acid	PFDS	335-77-3	0.3	1	ND	ND
Perfluorododecanoic acid	PFDoDA	307-55-1	0.5	1.5	ND	ND
1H,1H,2H,2H-perfluorododecane sulfonate (10:2)	10:2 FTS	120226-60-0	0.5	1.5	ND	ND
11-Chloroeicosafluoro-3-oxaundecane- 1-sulfonic acid	11Cl-PF3OUdS	763051-92-9	0.3	1	ND	ND
perfluoro-1-undecanesulfonic acid	PFUnDS	441296-91-9	0.3	1	ND	ND
Perfluorotridecanoic acid	PFTriDA	72629-94-8	0.3	1	ND	ND
Perfluorododecane sulfonic acid	PFDoS	79780-39-5	0.3	1	ND	ND
Perfluorotetradecanoic acid	PFTeDA	376-06-7	0.3	1	ND	ND
perfluoro-1-tridecanesulfonic acid	PFTTrDS	174675-49-1	0.3	1	ND	ND

Table 8 (continued). Summary of analysis of PFAS in PTFE samples manufactured with NFPA.

Compound Name	Abbreviation	CAS No.	MDL	RL	NOFLON 9300EX - Batch 012E9322BH	NOFLON 9300EX - Batch 011E9322BH
Perfluoro-n-hexadecanoic acid	PFHxDA	67905-19-5	0.3	1	ND	ND
Perfluoro-n-octadecanoic acid	PFODA	16517-11-6	0.5	1.5	ND	ND
Sodium bis(1H,1H,2H,2Hperfluorodecyl) phosphate	8:2diPAP	678-41-1	0.3	1	ND	ND

6.3. Total Organic Fluorine content

In addition to demonstrating that the final PTFE product does not contain free PFAS, it is very important to confirm that there are no unintended PFAS emissions to water. In order to do this, water samples were analysed for Total Fluorine (TF) and Total Inorganic Fluorine (TIF) content by bomb combustion ion chromatography (CIC) according to ASTM D7359M. Water samples were prepared by coagulating latex and filtering coagulated water through 100 nanometre filter. The Total Organic Fluorine (TOF) content was calculated by subtraction of TIF from TF.

TOF analysis of water samples from coagulated latex showed no organic impurities and tested organic fluorine value was zero. This indicates that no fluorine-based product is being generated by side reactions.

All possible environmental regulation will come over water samples only to detect presence of overall PFAS (non-targeted) by TOF. Direct use of FP samples for TOF is not appropriate as FP itself interfere with TOF results. Table 9 shows the main results from the TOF analysis (Intertek, 2021b) for samples of PTFE manufactured with NFPA and with FPA as a polymerisation aids.

Table 9. TOF evaluation of PTFE samples manufactured with NFPA and FPA.

Sample name	Total Fluorine content (mg/kg)	Total Inorganic Fluorine (mg/kg)	Total Organic Fluorine (mg/kg)
Coagulated water from AD9300 batch 121021Q2J1 (FPA)	260	<0.1	260
Coagulated water from AD9300EX batch T06A9321JH (NFPA)	31	31	<1
Coagulated water from AD9300EX batch T43A9321FH (NFPA)	31	31	<1

In conclusion, based on the different analytical studies conducted by GFL, it can be established that no oligomers or unintended PFAS are created during the manufacturing process of PTFE with the use of the NFPA. It is to be noted that the PTFE manufactured by GFL with the use of NFPA can also be regarded as being of high quality, as demonstrated by the comparative analysis performed. Indeed, no oligomers or unintended PFAS (other than HFPO-DA itself, as a consequence of remaining product in the process reactor) are found in the batches that were tested with the use of the NFPA. The comparative analysis performed allows to conclude that PTFE manufactured with the NFPA is of equal quality in this respect, while it allows to discontinue the use of FPA.

7. Technical performance of emulsion PTFE manufactured with the use of NFPA

GFL has commissioned analytical studies to demonstrate that, by using the NFPA in the emulsion polymerisation process of PTFE, all the required physiochemical properties of the final polymer are met. Properties from EX grades (based on the NFPA) show comparable results, or even improved ones, in a selection of critical properties when compared to grades based on FPA. Detailed comparison of properties can be seen throughout this section.

Comparison has been established between samples from dispersion grades (Table 10) and powder grades (Table 11). As it can be seen from the results obtained, higher values of stability and critical cracking thickness have been achieved with PTFE dispersion grades (both homopolymers and modified polymers) using the NFPA, which suggests an improved performance over grades manufactured with FPA. It is also interesting to note that Standard Specific Gravity (SSG) values and melting points measured indicate the formation of high molecular weight PTFE, which is a desired outcome. In relation to PTFE fine powder grades, data displayed on Table 11 related to SSG and melting point indicates that PTFE obtained with the NFPA is a high molecular product as required for its industrial applications. Values of Thermal instability index are also meeting the mandatory critical requirements of <50 units as per US FDA requirements. (GFL, 2021b).

Table 10. Comparison of basic properties of PTFE samples (dispersion grades) manufactured with NFPA (EX) and with FPA.

Property	Unit	Homopolymer		Fully modified		Partially modified	
		AD9300	AD9300EX	AD9200	AD9200EX	AD9400 ¹⁶	AD9400EX
Latex Particle Size	nm	225	250	225	240	220	250
Viscosity	cps	22	23	20	19	20	19
Shear Stability ¹⁷	min	21	25	22	30	25	30
Zeta Potential	mV	-58	-60	-56	-65	-56	-65
Critical cracking thickness	µm	15	20	15	25	14	25
SSG ¹⁸	-	2.19	2.18	2.2	2.19	2.2	2.18
Melting Point	°C	339	340	337	337	339	338
Thermal Instability Index	-	<50	<50	<50	<50	<50	<50

¹⁶ AD9400: Partially modified PTFE aqueous dispersion

¹⁷ Achieved higher values of stability and critical cracking thickness with NFPA PTFE dispersion

¹⁸ SSG value and Melting points indicate formation of high molecular weight PTFE

Table 11. Comparison of basic properties of PTFE samples (powder grades manufactured with NFPA (FP7040EX) and with FPA (GN7040).

Property	Unit	GN7040	FP7040EX
Average particle size	µm	500	535
Bulk density	cps	500	500
SSG	-	2.170	2.170
Extrusion pressure (RR 400:1)	MPa	35	35
Tensile strength	MPa	>30	>30
Elongation at break	%	>300	>300
Melting point	°C	344	340
Thermal Instability Index	-	<50	<50

8. Efforts made by GFL in the field of patent information

To ensure free of patent availability of its newly established production method for obtaining high quality PTFE by emulsion polymerisation with using NFPA in replacement of FPA, GFL performed intensive search activities to find and assess existing patents. These efforts also included involving several patent specialists, including independent patent attorneys' firms from India, UK, EU & USA. The new process involving the use of NFPA was confirmed not conflicting with any of the existing patents that were found and assessed.

Particularly, GFL identified documents that were published decades ago and that describe a process methodology for producing emulsion PTFE involving NFPA that was found suitable for the process established by GFL. GFL hence based its new production method on the principles of methodology that has been publicly available for a long time with selecting the specific organic compound based on sulfonated hydrocarbon chemistry as NFPA of choice that was found to enable an emulsion polymerisation process substituting the use of PFAS as FPA for production of high-quality grade PTFE dispersions and fine powders. For this particular and novel use of an organic compound based on sulfonated hydrocarbon chemistry as NFPA in PTFE emulsion polymerisation, GFL filed patent applications which are internationally pending with patent protection for India having already been granted.

9. Conclusions

Gujarat Fluorochemicals has successfully developed the use of a non-fluorinated polymerisation aid to manufacture PTFE via the emulsion polymerisation process. The new method uses a non-fluorinated polymerisation aid (organic compound based on sulfonated hydrocarbon chemistry) of overall lower risk than the typical fluorinated polymerisation aids used in some fluoropolymer manufacturing processes. Most importantly, the non-fluorinated polymerisation aid does not exhibit properties such as Persistent, Bioaccumulative, Toxic or Mobile, nor very Persistent, very Bioaccumulative or very Mobile.

The scientific information generated by Gujarat Fluorochemicals indicates that the polymer manufactured with the use of non-fluorinated polymerisation aid performs equally as the original product from a technical perspective, even with improved properties in certain parameters. Furthermore, data collected via different analytical techniques suggests that the use of non-fluorinated polymerisation aid does not lead to the generation of oligomers or other fluorinated by-products, and thus the polymer manufactured with the non-fluorinated polymerisation aid can still be regarded as a Polymer of Low Concern. Therefore, it is expected that emissions of PFAS during manufacture and use of PTFE will not occur with PTFE manufactured with non-fluorinated polymerisation aid.

It is anticipated that PTFE manufactured using non-fluorinated polymerisation aid could have a major impact in the efforts by industry to minimise (or, wherever possible, to eliminate) the use of fluorinated polymerisation aid. Based on available data on worldwide manufacture of fluoropolymers, and assuming that all the manufacture of PTFE via the emulsion polymerisation route could be turned to the use of non-fluorinated polymerisation aid, this would result in a significant reduction of the use of PFAS by industry, which could fall to below 20% of the overall fluoropolymer production globally.

This major step forward from Gujarat Fluorochemicals is the result of significant R&D efforts undertaken by the company, resulting from their commitment to the improvement of the manufacturing process of fluoropolymers. While this achievement is so far limited to the manufacture of PTFE, the use of non-fluorinated processing aid opens the possibility to new projects that may lead to similar results for other fluoropolymers that, as of today, still require the use of fluorinated polymerisation aids for their manufacture. In any case, this development proves that industry is willing to take steps towards addressing concerns related to the use of PFAS in their processes, and that it is possible to progress into safer and cleaner manufacturing processes for fluoropolymers.

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