Thanks to fluoropolymers, smartphones are waterproof and even work in the shower or after half an hour in the pool.
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Regulation

Replaceable or not

Finding alternatives for thermally and chemically resistant fluoropolymers: This is what companies in Europe are currently facing, as the European Union (EU) plans to restrict per- and polyfluoroalkyl substances (PFAS). Which compounds are suitable, and what are the problems?

In March 2023, the European Chemical Agency (Echa) submitted a proposal to restrict or ban the use of perfluorinated and polyfluorinated alkyl substances (PFAS). Fluoropolymers contain CF_2 or CF_3 groups. Comprising of 38 representatives, they form a small subgroup of PFAS. They are classified as polymers of low concern (PLC) – meaning they pose little risk to human health and the environment. Many countries, such as the USA, Canada, Great Britain, Denmark, France, China, and Japan, therefore want to exclude fluoropolymers from the ECHA proposal. Nevertheless, companies in the EU are researching alternatives to polytetrafluoroethylene (PTFE) and other fluoropolymers.

Properties of flouropolymeres

Plastics can be categorized according to their maximum permissible continuous service temperature: Up to 90 °C, they are referred to as commodity plastics, up to 140 °C as engineering plastics, and at even higher temperatures as high-performance plastics (Figure 1).

After 20,000 hours at their continuous service temperature, the plastics retain more than half of their properties, for example mechanical ones such as tear strength and elongation at break. All fluoropolymers are high-performance plastics. Fluoroelastomers are amorphous; PTFE, modified PTFE, and Fluorothermoplastics (FTP) are semi-crystalline. When searching for alternatives, it is also important to consider the binding strength: With a binding energy of 439 $kJ \cdot mol^{-1}$, the chemical bond between carbon and fluorine is the strongest organic bond. Its decomposition is energetically unfavourable. This is why PTFE, for example, is non-flammable. The fluorine atoms shield the carbon backbone of the PTFE molecules; chemical attacks at the weak points – the carbon-carbon bonds – are impossible (Figure 2). The carbon-fluorine bond is highly polar; the electronegativities of carbon and fluorine

Chemist Michael Schlipf earned his doctorate in polyamide manufacturing processes. Since 2013, he has been working on developing fluoropolymer products and applications, as well as processing methods for the insoluble, non-melting substance polytetrafluoroethylene. Today, he heads the company FPS (Fluorocarbon Polymer Solutions) that he founded in 2012. Since 1985, he has also been a university lecturer for plastics in mechanical engineering. Schlipf is the fluoropolymer group's chairman in the plastics association pro-K and a member of the Economic Council (a political networking platform).

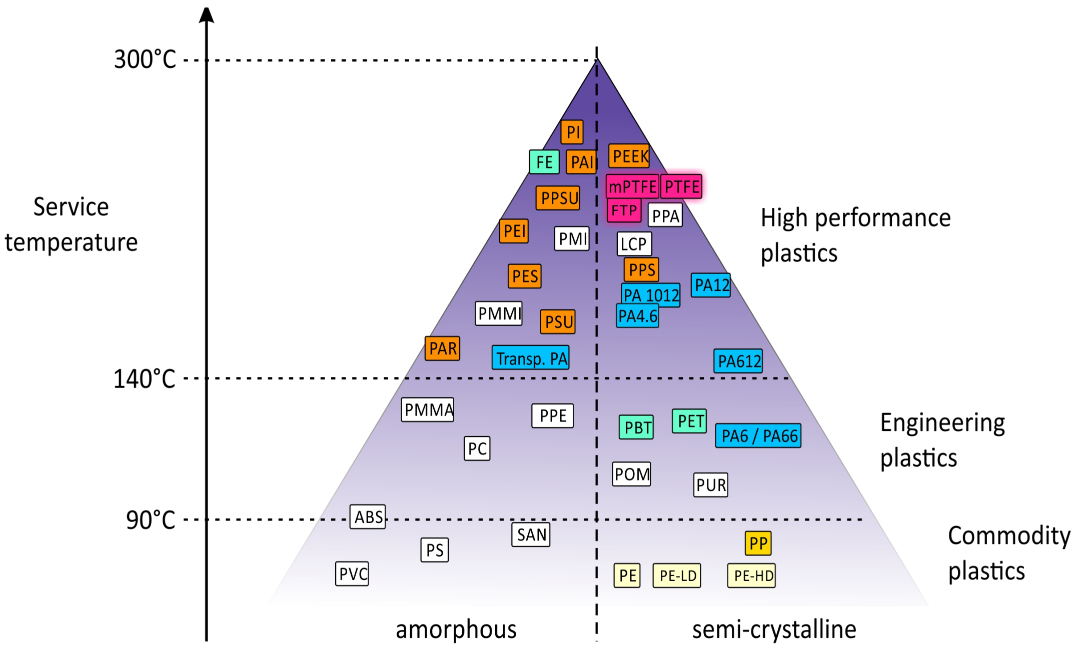

Fig 1. Plastics classified according to their continuous service temperature: All fluoropolymers are classified as high-performance plastics. Yellow: polypropylene; light yellow: polyethylene; blue: polyamides; magenta: polyesters; ochre: high-performance plastics with aromatic backbones; green: fluoropolymers; white: all other plastics.
Image: M. Schlipf, FPS

are 2.5 and 4.0. However, the PTFE molecule is nonpolar due to its helical structure and symmetry. Polymers with C_8 perfluoro side chains, for example, are both water- and oil-repellent. The fluorine shield is missing at the ends of the polymer chains. However, PTFE has only one end group per million carbon atoms on average.

Only when the end group concentration increases by a factor of 100 – to at least 100 end groups per million carbon atoms – do they affect the reactivity. This is the case for thermoplastic perfluoroalkoxy polymers (PFA). Here, the end groups must be post-fluorinated to stabilize them. Otherwise, end groups can be split off during processing at high temperatures (approximately 340 °C), resulting in the formation of hydrofluoric acid (HF). HF corrodes parts of the processing machine and thus contaminates PFA – disqualifying it for chip production in the semiconductor industry.

Controlling temperature resistance

The hydrocarbon fraction (CH_2 chains) and functional groups that link the polymer chains determine where polymers are located in the plastics spectrum (Figure 1). Standard plastics, such as polyethylene or PVC, consist of aliphatic hydrocarbon chains. Weak van der Waals forces between the chains stabilize the polymer network. Therefore, standard plastics can only be used up to temperatures of around 90 °C.

In engineering plastics, ionic interactions or hydrogen bonds strengthen the cohesion of neighbouring molecules, enabling continuous service temperatures up to approximately 140 °C. The polyamides PA6, PA66, and PA1014, for example, belong to the category of engineering plastics.

Operating temperatures of up to 300 °C cannot be achieved with polymers based on aliphatic hydrocarbons, as they would decompose. Several properties of high-performance plastics improve their stability: mesomerism, multi-strandedness as in ladder polymers, or functional groups such as imide or ether ketone groups. Due to the C–F bond's high binding energy, fluoropolymers also belong to the high-performance plastics.

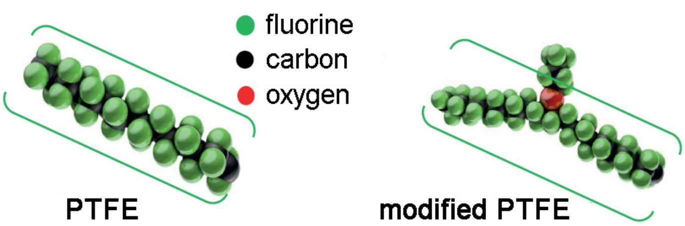

Fig. 2. Polytetrafluoroethylene (PTFE) and modified PTFE.
Image: M. Schlipf, FPS

Materials	Temperature (°C)	Water	Acid	Lye	Oils and fat	Fuels	Ozone	Aliphatic hydrocarbons	Aromatic hydrocarbons	Chlorinated hydrocarbons
PTFE	–190 bis 250	✓	✓	✓	✓	✓	✓	✓	✓	✓
EPDM	–30 bis 140	✓	✓	✓	✗	✗	(✓)	✗	✗	✗

Tab. 1. Resistance of polytetrafluoroethylene (PTFE) and ethylene propylene diene rubber (EPDM) materials used as pump diaphragms. Green checkmarks: suitable for the medium; red crosses: unsuitable. Source: Lit. 1)

Alternative materials

Ethylene propylene diene rubber (EPDM) could be an alternative to PTFE materials in chemical plants, such as pumps, valves, taps, or other fittings. It is already being used for dynamically stressed parts such as pump diaphragms.

If it can also be used for seals remains unclear. A comparison with PTFE (Table 1) shows that EPDM is not resistant to more than half of the media used in chemical plants – and is therefore not or only partially suitable for most applications. Various diaphragm materials were tested in double diaphragm pumps to determine the maximum possible load cycle until diaphragm rupture.[1)]

Similar results may be expected from a test using the 13 criteria established by the Organization for Economic Co-operation and Development (OECD) to classify safe products (products of low concern, PLC).[2)] These criteria include the stability against physical, chemical, or biological influences, electrical charge, and solubility.

Fluoropolymers meet all 13 criteria of the OECD materials classification. How to explain this?

The aliphatic fraction of EPDM is similarly resistant to those of polyethylene (PE) and polypropylene (PP). At 140 °C, the continuous service temperature of EPDM is higher than that of PE and PP (90 °C) because the material is chemically crosslinked to form an elastomer via diene monomers.[3)] However, EPDM does not reach the resistance of PTFE because EPDM is not mesomerically stabilized by its hydrocarbon backbone and the binding energy of the C–H bond, at 414 kJ · mol^{-1}, is lower than that of the C–F bond.

Natural rubber (NR), Perbunan (NBR), Therban (HNBR), Viton (FKM), Hypalon (CSM), or silicone (VQM) could also be considered as alternatives to PTFE. These elastomers are used in mechanical and automotive engineering or in chemical plants, for example, as membranes in sensors or pumps. They are indeed suitable for specific media. However, none of these materials is an all-rounder.

Switching to alternative materials bears costs for plant operators:

PTFE-based seals are suitable for almost all applications. The same seals can be used for all parts of a plant, even if it is a multi-purpose plant. Present PTFE alternatives are less universal. Therefore, different seals are necessary – which carries the risk of mix-up.

Required seal changes, for example, when changing to different products, result in additional effort and reduce plant availability.

New developments

In Germany and other European countries, many companies have invested time, money, and labour over the past two years to find answers to questions arising from Echa's approach to restrict PFAS. In addition, the submissions during the public discussion of the PFAS restriction proposal were extremely bureaucratic.

Companies had to select potential alternatives, develop them from scratch, process them, and test them. During this time, resources for new developments were no longer available; innovation gaps emerged. New developments in fluoropolymers did almost not exist.

Other regions of the world, such as China, differentiate between polymeric and non-polymeric PFAS in their regulations. The fluoropolymer market is therefore growing globally. Applications in e-mobility, semiconductor production, aerospace, computed tomography (CT), surgery, and 5G data transmission benefit from the high-performance capabilities of fluoropolymers. China, for example, developed batteries for electric vehicles which increase the driving range and dry electrodes to operate them safely. Both inventions would not have been possible without fluoropolymers.

Fluorpolymers also help making smartphones waterproof. Biaxially stretched fluoropolymer membranes, produced by a stretching process in the longitudinal and transverse directions, protect the openings required for microphone and speaker. These membranes prevent water from penetrating but allow sound waves to pass.

Another example is a PTFE membrane developed by the company FPS in 2024, which can achieve up to five times more pump strokes than previous products. Test runs were stopped after having reached several million strokes in order not to hinder market launch. The membrane can be used in the chemical process or semiconductor industry, food production, or paint shops to extend maintenance intervals and reduce the carbon footprint through longer operating times.

Comment

The PFAS regulatory approach deviates from the EU specifications: The proposal is not substance-related or risk-based. Instead, entire groups of substances are to be regulated, most of which are not yet classified – their risk potential is not yet known. Such an approach is not covered by the European legal framework. A general ban carries the danger of being disproportionate and ignoring the balance of risk and benefit.

The reasons given by those responsible for the substance group regulation are: large projected PFAS emissions of 75,000 tons in 2020[4] and the risk of regrettable solutions. These regrettable solutions are substances with similar properties that are used in industry after a substance has been banned. Although these alternatives are not banned, they usually have a similar solubility, mobility, and bioaccumulation due to their similarity to the regulated substance and could therefore also pose a risk in the future. Regulators were frustrated in the near past when industry responded to regulatory bans by introducing alternative solutions. This has often happened with PFAS in the last 25 years.

Following the ban on perfluorooctanoic acid (PFOA), an emulsifier used in the production of fluoropolymers, the chemical industry introduced alternatives such as Adona and GenX, which are fluorine-containing substances with shorter CF_2 chains than PFOA, and other perfluoroalkylcarboxylic acids as replacements. As polymerization aids, they are separated from the polymer after polymerization, recovered, recycled, and reused. In the past, this resulted in the release of small amounts of PFOA (a few hundred kilograms relative to the projected emissions of 75,000 tons of PFAS per year); today, there are improved processes with almost zero emissions.

However, there would have been a better solution than the ban: limiting PFOA release during polymerization. This could be achieved through closed water cycles, for example. PFOA still has advantages compared to all alternative emulsifiers introduced in the meantime: It can be used in smaller quantities and is the most easily recyclable one.

Fluoropolymers can also be produced without fluorinated emulsifiers, for example, in a suspension process or with non-fluorinated polymerization aids (NFPAs). The latter are less-suitable for fully fluorinated polymers, but suitable for producing partially fluorinated ones. Only fluorine-free emulsifiers are nowadays used for this purpose – a success in the ongoing PFAS restriction process.

Even though the EU‘s PFAS restriction process is still in its technical phase under the leadership of Echa, there are already effects on Europe‘s resilience as an industrial location: Companies postpone investments or invest outside of Europe. One example is the relocation of antibiotic production to India which increases Germany‘s dependence on imports of vital medicines from abroad. Although medicines with CF_2 or CF_3 structural elements are classified as PFAS, they are exempted from the restriction. However, they can no longer be manufactured under the PFAS regulation as before, since their synthesis requires PFAS, which are not classified as medicines and are therefore prohibited.

One might get the impression that the regulatory authorities have exceeded their capabilities with a general PFAS ban that simultaneously covers more than 14,000 mostly unknown, highly diverse substances. This approach also deviates from the prescribed substance-specific, risk-based approach. 5,642 submissions (in the form of an assessment of the regulatory proposal structured by twelve Echa-specified questions) were received during the public discussion of the PFAS regulatory process. The most comprehensive EU restriction procedure to date, with approximately 800 submissions, lasted five years. Based on this experience, the technical phase of the process for PFAS is not expected to end before 2030.

A political decision by the EU Commission and Parliament is therefore urgently needed soon to prevent damage to Europe as an industrial location: The general approach to regulate PFAS must be stopped and replaced by a differentiated approach. A suitable approach, already used in non-European regions, distinguishes between polymeric and non-polymeric PFAS. In any case, the criteria should help protect the environment and living beings while simultaneously enabling Europe to preserve and expand its industry. After all, standards for safety, environmental protection, and health protection are high in Europe. A getaway of the chemical and pharmaceutical industries to Europe carries the risk of increasing global environmental pollution. ■

1) *Firma Gottlob Dietz – Elastomerteile,* Werkstoffauswahl – kein Problem!, *2024*
2) *S. H. Korzeniowski, R. C. Buck, R. M. Newkold, A. E. Kassmi, E. Laganis et al.,* Integr Environ. Assess. Manag. *2023, 19, 326*, doi: *10.1002/ieam.4646*
3) *C. E. Mortimer, U. Müller,* Chemie: Das Basiswissen der Chemie in Schwerpunkten, *1973, Georg Thieme Verlag, Stuttgart*
4) *F. Averbeck, Vortrag: BioPRO BW – Regulatorik Nachgefragt: Bedeutung von PFAS in der Gesundheitsindustrie; 19.9.2024*

AT A GLANCE

Fluoropolymers are classified as PFAS and are resistant to temperatures above 140°C and almost all media such as acids, alkalis, oil, and solvents.

They are used in e-mobility, semiconductor production, aerospace, pharmaceuticals, and chemical plants, for example as fittings and seals.

Existing alternatives to fluoropolymers are less durable and less versatile.

Fluoropolymers should not be regulated in a general approach, but rather in a differentiated one based on their risk potential.