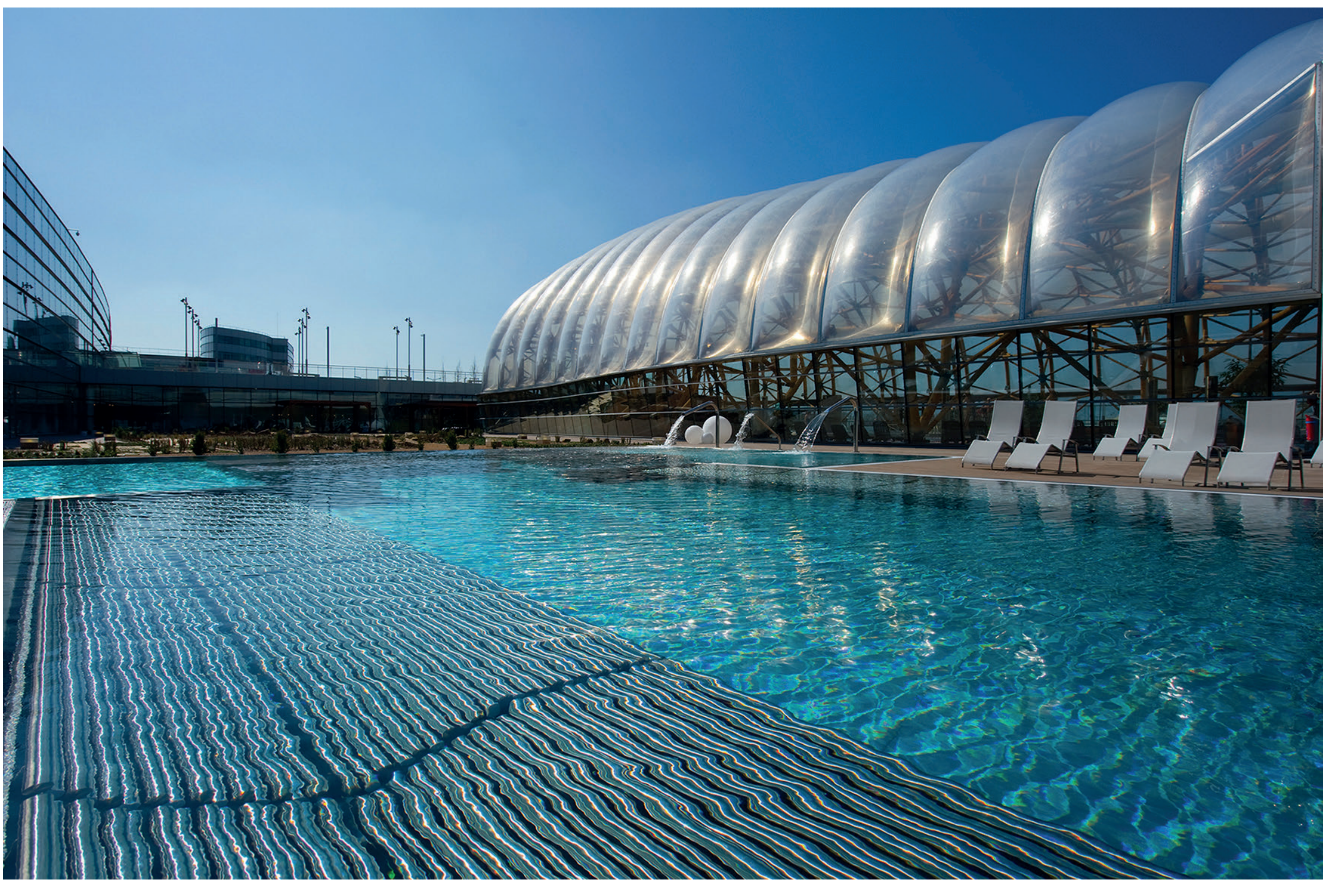
An Impact Way beyond its Small Market Share

Fluoroplastics Improve the Durability and Chemical Resistance of Products

Although fluoroplastics only make up a very small part of the overall plastics market, they are an indispensable component of many applications. These materials play a central role in today's megatrends of digitalization, clean-energy generation and modern mobility concepts.

In fluoroplastics, the hydrogen atoms of the main carbon chains are completely or partially replaced by fluorine atoms. Because these carbon-to-fluorine bonds are very stable, fluoroplastics exhibit a special combination of features, such as almost universal chemical resistance, suitable for very low to very high temperatures, inherent resistance to UV, and weather, fire and abrasion resistance. They also have a low refractive index as well as excellent electrical properties such as a strong insulating effect and low dielectric loss factor. Fluoroplastics further exhibit low surface energy, resulting in a correspondingly very low wettability and adhesion, a low friction coefficient and excellent tribological properties.

An estimated 380,000 t of fluoroplastics will be consumed around the world this year [1]. Although they only make up an exceedingly small proportion of the total volume of plastics – around 0.1 %– they have become an integral part



The roof of the Vitam leisure center in Neydens, France, is made from ETFE film. A wooden structure supports the 53 ETFE cushions with a total surface area of 4300 m^2 © AGC Chemicals

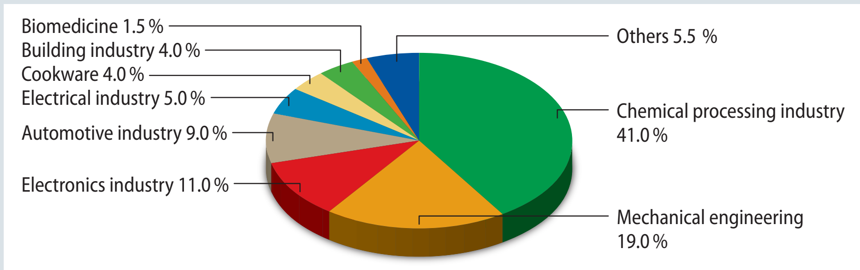


Fig. 1. Consumption of PTFE in 2019 in Western Europe by industry Source: [2]; graphic: © Hanser

of many applications thanks to their special properties. Areas of application range from consumer products such as cookware, kitchen utensils or garden implements (non-stick coatings) through mechanical, automotive and aviation engineering (seals, sliding elements, sensors, hydraulic and fuel lines), the chemical and pharmaceutical industry as well as process technology (linings, hoses, coatings) right through to electrical and electronic engineering (cable sheathing, dielectrics, substrates for printed circuits). Additionally, fluoroplastics are used as breathable membranes in the textile industry and are used as linings and membranes for roof structures and cladding in the construction sector.

33,800 t of polytetrafluorethylene (PTFE) were consumed in Western Europe in 2018. Thus, this fluoroplastic took pole position ahead of polyvinylidene fluoride (PVDF) at 10,800 t, fluoroethylene propylene (FEP) at 2600 t, perfluoroalkoxy (PFA) at 1500 t and ethylene-tetrafluoroethylene (ETFE) at 1200 t. The largest consumer of PTFE was the chemical processing industry at 41 %, followed by mechanical engineering and the electrical and electronics industry (**Fig. 1**) [2]. In the chemical processing industry, PTFE is mainly used for applications including corrosion-resistant linings for pipes and vessels (**Fig. 2**). The material is particularly well-suited to these applications thanks to its high chemical and temperature resistance and its excellent non-stick properties.

Modern flue gas desulphurisation systems in fossil-fuel power stations and waste incinerators deploy heat-exchanger systems to increase their efficiency. PTFE-based heat-exchanger tubes withstand the attack of highly corrosive substances that are released when flue gases cool to temperatures far below the acid dew point. A good example of this application is the AlWaFlon tubes by Wallstein Ingenieur GmbH, Recklinghausen, Germany. They feature an exceptionally high usage temperature of up to 260 °C and a similarly high Vicat softening point of 130 to 140 °C, combined with both a high flexural fatigue strength and stress cracking resistance.

High Performance Applications

Expanded PTFE (ePTFE) is a form of this fluoroplastic that has undergone a special process and was discovered by Robert and Bill Gore in 1969. Expanding causes orientation and stretching of the PTFE molecular fibers, lending the material high strength and creep resistance. Because of these special properties, ePTFE is used in a wide range of high-performance applications. Typical examples are breathable membranes in leisure clothing and workwear, seals for chemical plants, ventilation membranes for electronic components and batteries, wire and cable sheathing, and also filter membranes. It is also suitable as a substrate for ion exchange membranes.

The largest customer for PVDF in 2018 was the chemical industry, which bought up 60 % of the material. Because of its outstanding resistance to high temperatures and pressures, aggressive chemicals and mechanical stresses, it is primarily used for pipe and tank linings, fittings, valves, filters and heat exchangers. Lithium-ion batteries that are used in modern mobile phones, tablets and electric tools are a promising growth market for PVDF. The field of electrical mobility is seeing a similar sharp increase in demand for powerful, lightweight and cost-efficient batteries for hybrid and electric vehicles. PVDF is used as an electrode binder and separator coating in these batteries. Manufacturers such as Sol- »

The Author

Claus-Peter Keller is Sales & New Business Manager for Fluoropolymers at AGC Chemicals Europe in Amsterdam, Netherlands; claus-peter.keller@agcce.com

Service

References & Digital Version

- You can find the list of references and a PDF file of the article at *www.kunststoffe-international.com/2020-9*

German Version

- Read the German version of the article in our magazine *Kunststoffe* or at *www.kunststoffe.de*

Fig. 2. Fluoroplastics are often used as chemical- and temperature-resistant tank linings for the chemical, pharmaceutical and semi-conductor industry © Rudolf Gutbrod GmbH

vay, Brussels, Belgium, and Arkema, Colombes, France, have been constantly expanding their product range in this sector over recent years. Electrode binders enable excellent dispersion of the active materials and conductive additives to an electrode and allow adhesion to the current collector. Newer variants feature enhanced adhesion and mechanical stability and can be worked more easily and quickly, enabling more powerful and longer lasting lithium-ion batteries with a high energy density to be manufactured at lower costs.

More Light Permeable than Glass, PE and PC

Because of its high resistance to numerous aggressive chemicals, ETFE is suitable for vessel linings and also as a material for valves, fittings and hoses in the chemical and pharmaceutical industry. ETFE membranes are used for roof structures and building claddings in the architectural sector thanks to their low net weight and high transparency. AGC Chemicals Europe, based in Thornton-Cleveleys, United Kingdom, and part of the Tokyo-based Japanese AGC Group, is the world's largest manufacturer of this material. The product range marketed under the name Fluon includes grades that can be worked in the molten state as well as powders and films. Fluon ETFE films are used in many applications in modern-day architecture. They are inherently flame-retardant, offer long-term resistance to weather and environmental influences, have an outstanding thermal insulating effect and are lighter than glass.

AGC Chemicals markets special ETFE films for use in greenhouses under the F-Clean brand (**Fig. 3**). They are more permeable to daylight and ultraviolet light than glass, polyethylene (PE) or polycarbonate (PC), meaning that the full spectrum of sunlight can permeate the interior of the greenhouse. This enables increased plant growth with reduced use of fertilizers, higher yields and a better quality of produce. These films have a very long service life because they are free from plasticizers that can diffuse out over time, causing brittleness.

Increasing rates of digitalization and the advent of 5G technology place high demands on the materials used. PTFE and FEP are among the group of materials that are frequently used in applications for transmitting high-frequency signals over long distances without additional boosting. Both types are fully fluorinated and thus have an exceedingly low dielectric constant of 2.1 and minimal attenuation. Copper-clad laminates (CCL; **Fig. 4**) are frequently used in the antenna technology of 5G transmitters and receivers as well as in cable technology. These multi-layer composites consist of a PTFE-coated glass cloth on to which a fluoropolymer film made from PTFE, modified PTFE or FEP is applied. A conducting copper foil completes the assembly. The different layers are combined with one another by means of a hot laminating process performed in special multi-daylight presses.

Fig. 3. ETFE greenhouse films are long-lasting and can promote plant growth. The greenhouse in the picture has a surface area of 5000 m^2 and has been covered with a single-layer F-Clean film © AGC Chemicals

CCL Improve Signal Transmission

The roughness of the copper foil has a direct effect on the attenuation properties and thus the quality of the signal transmission. Functionalized fluoropolymers are new innovations on the market. These are modified by the introduction of reactive groups along the polymer chain in order to produce specific properties, such as reactivity and compatibility with other materials. Under its Fluon+ Adhesive brand, AGC Chemicals offers a range of ETFE and PFA grades that have been modified with adhesive groups. For example, PFA Fluon+ EA-2000 combines a very low dielectric constant, a low dielectric loss factor and high temperature and chemical resistance with adhesive properties, enabling combination with other materials in a single-stage process without the need for surface treatment or the application of an additional adhesive layer. This enables copper foils with a very low roughness and thus good signal transmission properties to be used in the manufacture of CCLs. **Figure 5** shows the schematic composition of a multi-layer CCL.

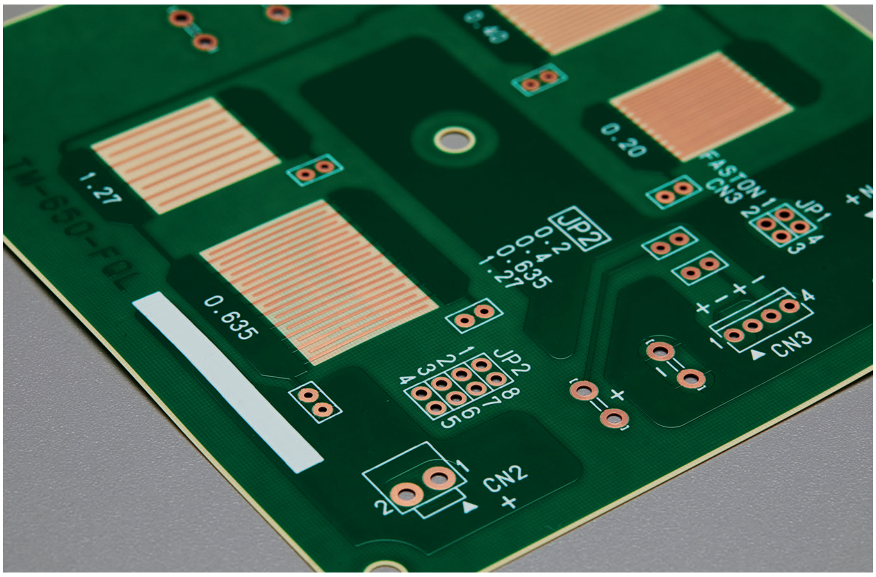


Fig. 4. Copper-clad laminates (CCL) are some of the most interesting applications of fluoroplastics. They are used above all in the antenna technology of 5G transmission and receiver stations and cable technology © AGC Chemicals

Fluoropolymers-Based Composites

In the field of composites, functionalized fluoropolymers offer chemical reactivity and improved compatibility with other materials. Ideal uses for the reactive fluoropolymers of the Fluon+ ETFE family from AGC Chemicals include material combinations, polymer blends or as part of composite and sandwich structures. As a result, thermoplastic composites with specific fluoropolymer properties that exhibit excellent fiber-matrix adhesion and thus excellent mechanical qualities to be manufactured, for instance.

Fluorochemicals, and to an extent also fluoropolymers, have come under fire due to the amount of time they remain in the environment. The manufacturers of fluoroplastics are therefore working on improving the sustainability of their products. For example, AGC Chemicals, the U.S. chemical company Chemours and the Bavarian plastic manufacturer Dyneon stopped using perfluorooctanoic acid (PFOA) as a wetting agent in the emulsion polymerization of fluoropolymers years ago as part of a voluntary undertaking. PFOA is very long-lasting and bioaccumulative, meaning that it can become concentrated in the bodies of animals and humans. It has come under fire both for this reason and also due to its potential harmful effects on human health.

However, this is not the only source of PFOA. Because of its beneficial properties, PTFE is frequently used as an additive in the form of a micropowder in paints and lacquers, thermoplastic and duroplastic polymers, elastomers and lubricants. It helps increase the longevity of products and reduces friction and wear and thus also energy consumption. In the typical manufacturing process of this micropowder, radiation is used to transform macromolecules with a high molecular weight into molecules with shorter chains, i.e. into PTFE with a low molecular weight. This can also give rise to small quantities of PFOA, which can also be traced in end products.

In 2017, the European Union passed Regulation EU 2017/1000 to amend Schedule XVII of the REACH Regulation. Accordingly, there has been a maximum limit of 0.025 mg/kg for the ratio of PFOA in many products since 4 July 2020. For PTFE micropowders and the products produced from them, however, Regulation EU 2019/1021 permits a transitional period of a maximum of two years under certain circumstances, provided the threshold value of 1 mg/kg PFOA and its salts is not exceeded. For that reason, all manufacturers of such PTFE additives operating in Europe have gone to great lengths over recent years to convert their production methods accordingly and comply with statutory provisions. ■

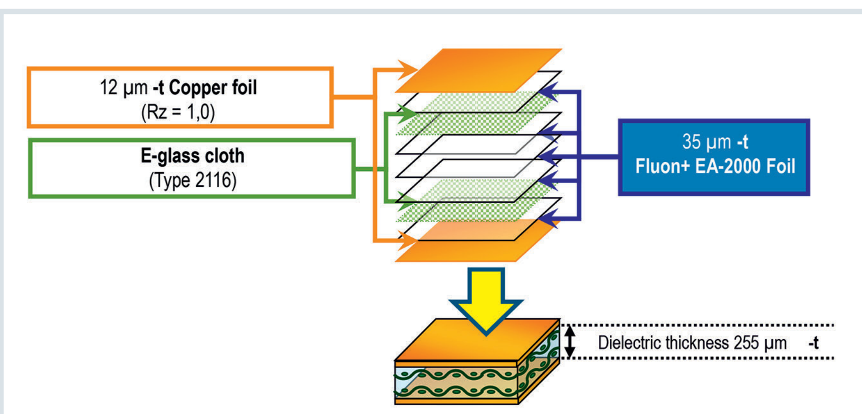


Fig. 5. Schematic composition of a multi-layer CCL for 5G technology: the multi-layer composite systems consist of a PTFE-coated glass cloth, a fluoropolymer film made from PTFE, modified PTFE or FEP and a conductible copper film © AGC Chemicals