The elegant roof of the Dyneon PTFE-coated glass fiber fabric emphasizes the features to the court of honor of the German Federal Chancellor's Office at Berlin. PTFE accounts for the largest portion of the fluoropolymers consumed (© 3M, photo: Werner Huthmacher)

Fluoropolymers

Social Megatrends Give Fluoropolymers a Boost

The importance of fluoropolymers will continue to increase in the coming years. With an average global growth rate of around 4.5 %, fluorothermoplastics in particular will be the driving force in new applications. Megatrends are leading to an increase in the demand for fluoropolymers. At the end of their life cycle, the plastics can now be chemically recycled on a large scale using the Up-Cycling process.

The most important source of raw materials for all fluoropolymers is fluorspar (CaF_2). The material was temporarily scarce in the years 2009 and 2010, but is now being mined mineral again in many places in the world. The supply for the future is thus secured. Nevertheless, it should be considered that other industries use this resource in addition to the fluoropolymer industry. These include in particular the manufacturers of refrigerants for air-conditioning units in vehicles and buildings, the foaming agent for the manufacture of insulating plastic foam or the fire extinguishing agents which, especially in aviation applications, cannot do without the highly effective fluorine compounds.

Following the value added chain, the well-known monomers such as tetrafluoroethylene (TFE), hexafluoropropylene (HFP) or vinylidene fluoride (VDF) are initially synthesized from fluorspar before being processed into the raw material fluoropolymer by means of polymerisation. Changes in legal regulations governing environmental protection and the protection of the earth's atmosphere, safety in traffic and aviation, CO_2 emissions and the building industry can lead

to a decisive redirection of the synthesis paths and thus possibly to shortages in individual areas. An important lesson from the very recent past: where individual value added chains are less profitable, they remain undersupplied when resources are scarce or if there are peaks in demand.

PTFE Is still the Most Important Representative

Around 270,000 t of fluoropolymers were consumed in 2015 (**Fig. 1**). The portion of those accounted for by polytetrafluoroethylene (PTFE) was 52 % (140,000 t) (**Title figure**). This is followed by the fluorothermoplastics, of which polyvinylidene fluoride (PVDF) is the most important representative with regard to the production volume with 15 % (41,000 t). Fluorinated ethylene-propylene (FEP) follows in third place with 8 % (22,500 t) in front of ethylene-tetrafluoroethylene copolymer (ETFE) with 3 % (8400 t). The broadly diversified product group of fluoroelastomers (FKM), which includes both the so-called bipolymers and the terpolymers, forms the third pillar alongside the PTFE types and the fluorothermoplastics with a total of 12 % (31,000 t).

Bipolymer fluoroelastomers are those representatives that are used in particular at lower temperatures due to their reduced fluorine content, while the terpolymers are brought closer to the property profile of PTFE through the additional incorporation of tetrafluoroethylene. They are characterized in particular by their high resistance to media. As opposed to PTFE and the fluorothermoplastics, fluoroelastomers require a chemical crosslinking after molding, as a result of which the components retain their final shape and the material obtains its actual property spectrum.

The era of thermoplastically processable fluoroelastomers has not yet begun on a technical scale. It remains to be seen how long it will take for the development engineers to succeed in transferring the positive development of thermoplastic elastomers to the fluoroelastomer area.

Construction Sector Tips the Scales

PTFE represents the largest fluoropolymer segment in both standard and modified form in Europe, too (**Fig. 2**). At 48 % the proportion in comparison with worldwide consumption is somewhat lower, which is mainly attributable to the rapid growth of the fluoroelastomers and that of PVDF. Fluoroelastomers are being used in more and more applications in the automotive and aviation sectors in particular, while PVDF represents the fastest growing fluoropolymer worldwide and is used as insulating material in electrical and electronic applications and as a coating in the construction industry. FEP accounts for only about 4 % in Europe, while its proportion worldwide is nearly double that at 8 %. The reason for that is the lack of a "Plenum Wire" market segment in Europe, i. e., the insulation of LAN cables in buildings using FEP.

Although FKM and fluorothermoplastics are the fastest growing, the PTFE and modified PTFE product segment still »

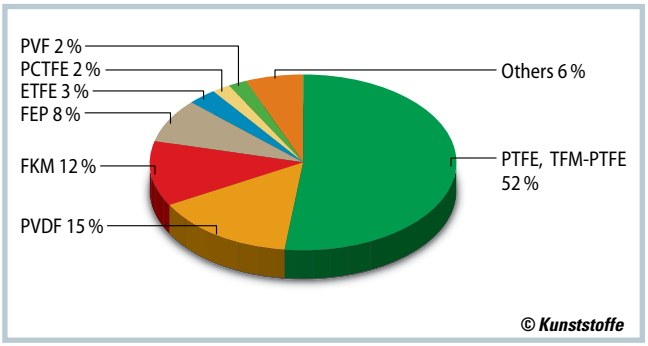

Fig. 1. PTFE was the most processed fluoropolymer in 2015 with 140,000 t (52 %). Overall 268,700 t of fluorpolymers were consumed last year (source: Dyneon GmbH extrapolated based on CEH report 2013)

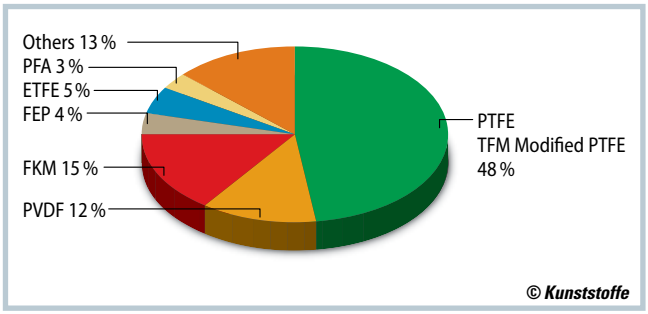

Fig. 2. The lack of a plenum wire application for FEP in Europe is the reason why it is under-represented. The rapid growth of PVDF and the fluoroelastomers has resulted in the share of PTFE dropping to < 50 % in Europe in comparison with global consumption (source: Dyneon GmbH extrapolated based on CEH report 2013)

covers the largest area of applications. The reason for this is that 3M Advanced Materials has succeeded in expanding the property profile of PTFE towards fluorothermoplastics with the development of modified PTFE, 3M Dyneon TFM Modified PTFE. Applications for which perfluoroalkoxy (PFA) is preferably used in other regions are implemented in Europe with second-generation PTFE. These include in particular applications in the chemical processing industry in the aggressive chemicals segment, where high chemical resistance is required in conjunction with a high barrier effect. The additional advantages of the low cold flow are put to use not only in unfilled TFM Modified PTFE, but especially in many compounds that are used above all for the sealing of plants and fittings.

The different methods of construction in Europe in comparison with the US and other regions of the world influences the regionally differing demand for FEP in a significant way. Since construction in Europe is essentially of the solid construction type, in which the insulation materials for electrical cables are permanently integrated in the wall, these can be made of standard plastics such as PVC. Conversely, the lightweight construction method in the USA and the industrial construction method with cable ducts in suspended ceiling construction necessitate cable insulation that meets the high fire protection requirements. For that reason the plenum wire market has developed in the USA into the largest single market for fluorothermoplastics.

Megatrend	Industry, Markets	Trends, new challenges	Innovative applications of fluoropolymers
Limited resources	Chemistry	Production processes preserving resources	Up-cycling of end-of-life products
			All-fluoropolymer reactor design for enhanced yield of reaction
		Extension of plant lifetime	Corrosion protection with fluoropolymers (reactor-, mounting- and pipelining)
	Energy	Fluctuating plant utilization for compensation of varying wind and solar energy	Improved corrosion protection provided by fluorpolymer lining in the region of flue gas ducts and cleaning modules
		Cables being resistant to seawater	Fluoropolymer insulation
	Architecture	Saving energy, enhanced lifetime	Optimized membrane construction for buildings
Digitization	Data transfer, data storage	Smaller design and improved performance of high-frequency components	Fully fluorinated fluoropolymers providing better insulation with thinner insulation layers at higher frequencies, also combined with lightweight construction; printed circuit boards for high frequency technology
	Industry 4.0	Electronic steering, operating and communication of machines	Nonflamable indoor high frequency (LAN) cables
Change of climate and technology	Automotive	CO_2-reduction (Euro Six Norm)	Fuel hoses with permeation barrier
		Reduced consumption of gasoline	More sensors in exhaust gas flow
		E-Mobility	Batteries of new technology, bipolar stack design using fluoropolymer components
	Chemistry	Reduction of plant emissions (TA Luft)	Permeation-reduced gaskets; all-fluoropolymer system solutions to eliminate the need for 'leaking' gaskets
Aging population	Pharmacy	Increasing demand for medical devices	Components for dialysis devices
		Person related medication through biotechnology	Packaging and medication of drugs in liquid state
	Medicine	Endoscopic surgery	Surgery equipment made from fluoropolymers, resistant to sterilisation processes
	Consumer goods	Cook- and bakeware for the growing population in the emerging regions of the world, e.g., BRIC states	Non-stick coatings for rice cookers, frying pans and bakeware

Table 1. Megatrends are giving rise to new challenges and applications that can be solved through system solutions using fluoropolymers (source: Dyneon)

With that exception the applications for fluorothermoplastics in Europe and the other regions of the global market are very similar.

New Applications and Processes Enable the Growth

Taking into account demographic changes, but also against the backdrop of continuously new applications for fluoropolymers, experts expect continuous worldwide growth in fluoropolymer materials from 2016 to 2020. For Europe an annual growth of 2.2 % is expected for the largest product group, PTFE, while above-average growth of 3.0 % is predicted for the fluorothermoplastics sector, which is smaller in terms of volume. The use of fluoroelastomers will also increase, but only at the average rate of all three product groups of about 2.5 % (**Fig. 3**). The decisive factor here will be whether there is a breakthrough in the direction of thermoplastically processable fluoroelastomers in the period under consideration. This innovation leap could give the FKM segment new growth impetus.

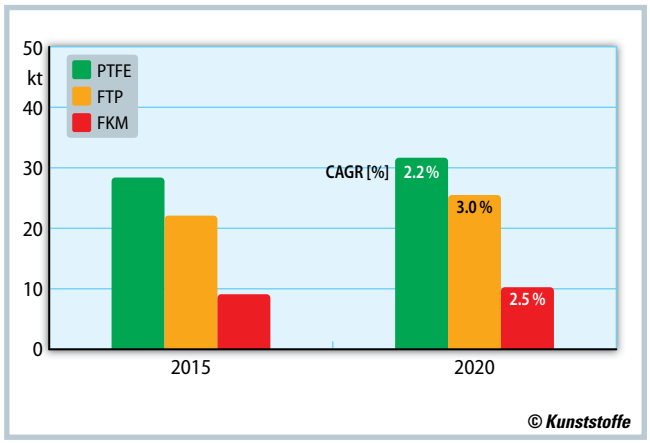

Fig. 3. Continuous, calculable growth (CAGR: compound annual growth rate) for all three product groups of the fluoropolymers PTFE, FTP and FKM (source: Dyneon GmbH extrapolated based on CEH report 2013)

The new additive processing methods for thermoplastics and thermosets such as stereo lithography (SLA), selective laser sintering (SLS), fused deposition modelling (FDM), 3D printing or the polyjet process are being examined for their usability with fluoropolymers, but currently play no part in the application, process and market shares.

PTFE Occupies a Special Position in Europe

With over 40 % of the market volume, the chemical industry is the main purchaser of PTFE products in Europe (**Fig. 4**). This is mainly due to the universal chemical »

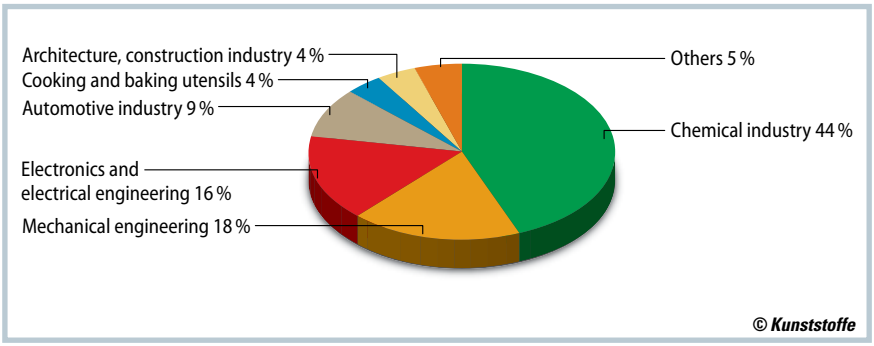

Fig. 4. The chemical industry, mechanical engineering, electronics and the automotive industry are the main purchasers of PTFE in Europe (source: Dyneon GmbH extrapolated based on IHS Chemical Estimates)

resistance of PTFE and modified PTFE. These materials are thus very well suited for use as corrosion protection of chemical plants. The dominant position of chemical plant construction in Europe, through which "World Scale Plants" are also fitted out, especially in China, Saudi Arabia, India or other countries in the Asian region, is certainly one of the main reasons for the special position of PTFE in Europe. In the semiconductor industry, where exclusion of metal ions is demanded in addition to corrosion protection, plants and fittings in full PTFE or TFM Modified PTFE versions are used. These mainly include pumps, valves or pipelines.

In second place with a market share of 18 % is general mechanical engineering (mainly the food and pharmaceutical industries), followed in third place with 16 % by applications in electrical engineering/electronics. Whereas seals in the form of PTFE compounds account for the bulk of applications in general mechanical engineering, unfilled TFM Modified PTFE is preferably used in food machinery and pharma technology due to the existence of all necessary approvals and resistance to aggressive cleaning chemicals. There are many different uses of PTFE applications in electrical engineering/electronics. The reasons for that are the good insulating properties and the low attenuation of high frequencies in comparison with other insulating materials.

Megatrends Generate New Applications

How growth develops will also depend on the degree to which fluoropolymers can be integrated in the solutions to our current challenges, i.e., the so-called megatrends. The limited availability of resources, the global digitisation, the climate change and the increasingly aging population are giving rise to new challenges that can only be solved with joint efforts (**Table 1**).

The complexity of the interrelationships can be shown by the example of the increased need for corrosion protection of conventionally-fired power plants. The compensation of the strongly fluctuating regenerative wind and solar energy in the power grids by conventional power plants necessitates continuous adaptation of the utilisation of these power plants, which are designed to cover the base load. As a result the operating conditions in the exhaust gas cleaning area are significantly changed and the frequent alternation between dry and wet operation leads to premature wear of the plants through corrosion. The short-term conservation during a temporary plant standstill, e. g., at the weekend, is a further unsolved challenge. The wet-dry alternating conditions are mastered by the consistent conversion to all-fluoropolymer modules, especially in heat exchangers and for the corrosion protection of the flue gas duct system using fluoropolymer films. In addition, conservation can be dispensed with in the case of short-term shut-downs.

Up-Cycling – Closing the Loop

For the first time in industrial polymer recycling, Dyneon has developed a method on a pilot scale with which fully-fluorinated fluoropolymers can be reused after the end of their life-cycle: the Up-Cycling process. Plant operation began in 2015 and enables the splitting of both end-of-life products and processing waste back into the monomers in a chemical recycling process. Following cleaning by distillation, the monomers can then be polymerized again.

As opposed to mechanical recycling processes, no deterioration in the polymer properties need be accepted with chemical cleaning. The new products from the Up-Cycling process do not differ in any way from the original products. Therefore this cyclic process can be applied any number of times. The environmental relief achievable through the recovery of the monomer tetrafluoroethylene (TFE) is enormous on account of the complexity of the TFE manufacturing process: The Up-Cycling of 1,000 t of TFE saves resource extraction in the amount of 6000 t and the environment is spared by more than 25,000 t of by-products.

Summary

Fluoropolymers have found a permanent place in industry and the products of our daily life. They have now established themselves in many applications. For that reason growth will continue in the coming years in all three product areas: PTFE, fluorothermoplastics and fluoroelastomers. If we are successful in developing new, important applications for fluoropolymers, especially for megatrends such as the finiteness of resources, digitization, climate and technology change, electromobility and the aging population, then the growth will be given additional impuls as a result. ■

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