Permanent Protection against Corrosion

Lining of Pipes, Columns and Vessels with Polytetrafluoroethylene

For permanent protection against corrosion, the chemical industry relies on the property profile of fully-fluorinated fluoroplastics such as polytetrafluoroethylene (PTFE). These resist a wide range of aggressive media at process temperatures exceeding 100 °C. In combination with an economical processing technique like paste extrusion, pipelines, hoses and compensators as well as columns and vessels can be protected in this way against corrosion.

Column lined with PTFE
(figures: SGL Group)

In the chemical and pharmaceutical industries the corrosion protection of metal based equipment has a decisive effect on the total operating costs and makes a substantial contribution to plant safety. In comparison with the possible alternatives, the combination of the high strength of the metals with the almost unlimited chemical and temperature resistance of fully-fluorinated fluoropolymers, in particular PTFE, permits an unbeatable price/performance ratio for universal usage in highly corrosive applications. Chemical companies regularly check the actual performance of corrosion protection systems. In comprehensive series of tests they compare different materials and processing methods with regard to their property profiles and economic efficiency. On completion of the latest examinations, a large German manufacturer of special chemicals has committed itself to the two high-performance materials 3M Dyneon PTFE and 3M Dyneon TFM Modified PTFE (referred to below as TFM) from Dyneon GmbH, part of 3M Advanced Materials Division in Neuss, Germany.

Advantages at a Glance

PTFE and TFM belong to the group of perfluorinated fluoropolymers and are supplemented with regard to their range of applications by the thermoplastically processable 3M Dyneon Fluoroplastic PFA. All three materials are characterized by an almost universal chemical resistance. Although PTFE and TFM are also thermoplastics in terms of their chemical structure, they can only be processed into end products using special pressing or extrusion processes with a subsequent sintering process due to their very high melt viscosity. TFM, a modified second generation PTFE, differs from classic PTFE through the additional chemical modifier perfluoropropylvinylether (PPVE). Its molecular weight is about five times lower than that of standard PTFE. As a result, the viscosity of its polymer melt is significantly reduced and the TFM particles fuse more easily into a dense, low-void polymer microstructure.

The void content, which is already low in PTFE, is reduced further by a factor of two by the easier particle fusion due to the reduced melt viscosity. This improves the barrier effect of TFM and lowers the permeation rate. This in turn can increase the protection against corrosion, especially at high process temperatures.

The so-called Stretch Void Index (SVI) according to ISO12086 or ASTM D4895 enables an indication of the void content. It is a measure of the tendency to form additional voids when stretching the material and thus indicates how well and completely the coalescence of the particles and the sintering process have eliminated the smallest voids. Apart from the barrier effect already mentioned, a low void content is also important during thermoforming. In particular in the flange area or of pipe nozzles it is necessary to flare the lining material, whereby it is subjected to occasionally strong stretching processes leading to enlargement of the voids. A low SVI of the PTFE gives the user the security that the original material density is also retained in the flange region. Modified PTFE offers additional safety here (**Table 1**).

Fig. 1. Extruder head for the manufacture of a paste-extruded pipe made of PTFE

Beyond the advantages already mentioned, TFM has become established in the chemical-pharmaceutical processing industry as the first-choice material at high temperatures and under mechanical loads above all due to its considerably reduced deformation under load as well as its favorable reset behavior in case of load changes. The material is increasingly used in corrosion protection due to the combination of a wide service temperature range (from -200 to +260 °C) and nearly universal chemical resistance (**Table 2**). The profile is topped by unique non-stick, electrically insulating and sliding properties.

Property	Test method	Dyneon PTFE	Dyneon TFM
Specific gravity*) [g/cm³]	DIN EN ISO 12086	2.15….2.18	2.15….2.18
Tensile strength at room temperature [MPa]	DIN EN ISO 527-3	34…..42	35….47
Elongation at break at room temperature [%]	DIN EN ISO 527-3	370…. 470	400….625
Poisson ratio [-]	DIN EN ISO 527-3	≈ 0.4	≈ 0.4
Tensile modulus at room temperature [MPa]	DIN EN ISO 527-3	600	630
Stretch Void Index (SVI)	ASTM D 4894	300	60
Shear modulus [MPa]	DIN EN ISO 527-3	550….440	630….504
Deformation under load [%] Load 15 N/mm² at 23°C after 100 h and 24 h recovery = permanent deformation	Similar to ASTM D 621, cylinder 10x10mm	17 11	9….10 4….4.5
Ball indentation hardness [MPa]	DIN ISO 2039 Part 1, plate 4 mm	26	28
Shore hardness D	DIN EN ISO 868	56	59
Contact angle with water [°]	Intern	126	126

*) Comparative sample, determined at S-PTFE-types

Table 1. Comparison of the properties of standard and modified PTFE (TFM)

Medium	Temperature [°C]	Unit	Dyneon PTFE	Dyneon TFM
SO_2	23	cm³/m² x d x bar	360	210
HCl	54	cm³/m² x d x bar	640	460
Cl_2	54	cm³/m² x d x bar	320	160
He	23	cm³/m² x d x bar	3,900	2,600
O_2	23	cm³/m² x d x bar	320	180

Table 2. Permeation of different media through standard and modified PTFE (TFM)

Compact Microstructure with High Barrier Effect

The outstanding properties of PTFE liners and special constructions, which are manufactured using paste extrusion technology, are their homogeneous, compact microstructure with a high barrier effect against aggressive chemicals, combined with a very smooth surface. This is due to the special features of the processing method: firstly, the so-called E-PTFE existing in agglomerate form (E-PTFE: manufactured according to the emulsion polymerization method) is lubricated with a naphtha derivative, whereby the surface of the agglomerates and the primary grains, of which the agglomerates are composed, is wetted. Through this process step, macroscopically also known as “pasting”, the PTFE powder can then be extruded at room temperature by means of a piston extruder, as a result of which profiles, in particular pipes (**Fig. 1**), hoses and tubes as well as strands can be manufactured. The shear forces at the extruder die break down the PTFE agglomerates to the primary grains, which then form a longitudinally oriented, dense ball packing in the extrudate. After the extrusion step, the naphtha »

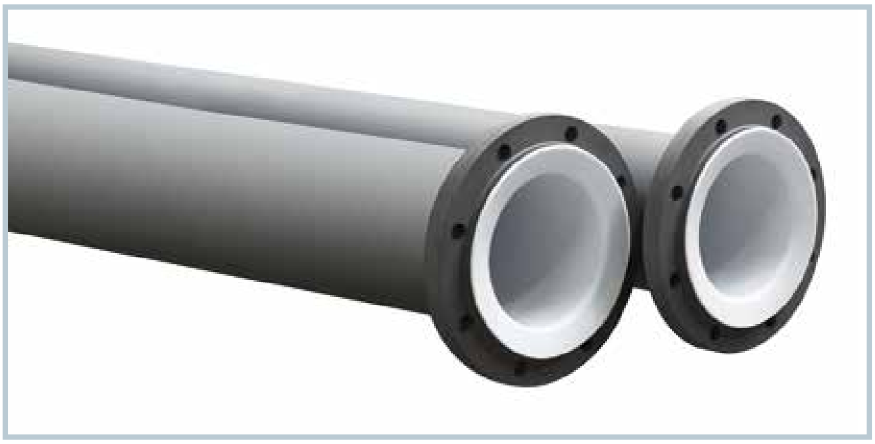

Fig. 2. Pipe lined with PTFE

derivative is completely removed by means of a drying process.

The extruded product obtains its final strength in the following sintering step. A further special feature of E-PTFE is its extremely small primary grains: with a diameter of only about 250 nm they form a very large internal contact surface area – the ideal conditions for perfect coalescence to form a homogeneous, compact polymer microstructure with an extremely smooth surface. Free from externally applied pressure, the particles coalesce practically exclusively under the effect of the so-called Laplace pressure, generated by the particle coalescence. In the case of modified PTFE, which exhibits even better particle coalescence due to the reduced molecular weight, a polymer microstructure that very closely resembles that of the thermoplastically processable Dyneon PFA is obtained through the paste extrusion process. Latest permeation measurements at Dr. Schnabel GmbH, Limburg, Germany, an SGL Group company, with helium on practically-relevant wall thicknesses of 4 mm indicate an over 50 % lower gas permeation of Dyneon PTFE, manufactured by paste extrusion, compared with frequently used RAM extrudates. The only limitation of the paste extrusion process is that it is restricted to the manufacture of relatively simple geometries.

Tight Fit of Loose Liner

When lining steel pipes, the sintered PTFE lining pipes are drawn into the steel pipe after pre-calibration. Thanks to the memory effect of PTFE they reset radially and in this way lie tightly against the inside of the steel pipes to be lined. The variable formation of gaps between PTFE inliner and steel pipe, a possible source of corrosion, is safely avoided. The material is flared at the flange areas and the pipes can be connected to each other without further processing steps (**Fig. 2**). The flared liner serves at the same time as a seal between the flanges. Additional gaskets are not required between components lined with PTFE. Using this method, pipe diameters can be manufactured today with seamless PTFE liners up to a nominal width of 600 mm.

In recent examinations by a chemical company, Dyneon PTFE and Dyneon TFM came out on top in a direct comparison as the most suitable high-performance materials. TFM is used at higher temperatures due to its improved permeation properties. Paste extrusion is thereby the ideal manufacturing method for the lining of long steel pipes. Unlike isostatic pressing methods, processors can manu

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Fig. 3. PTFE expansion joint compensates movements in pipe systems made of different materials

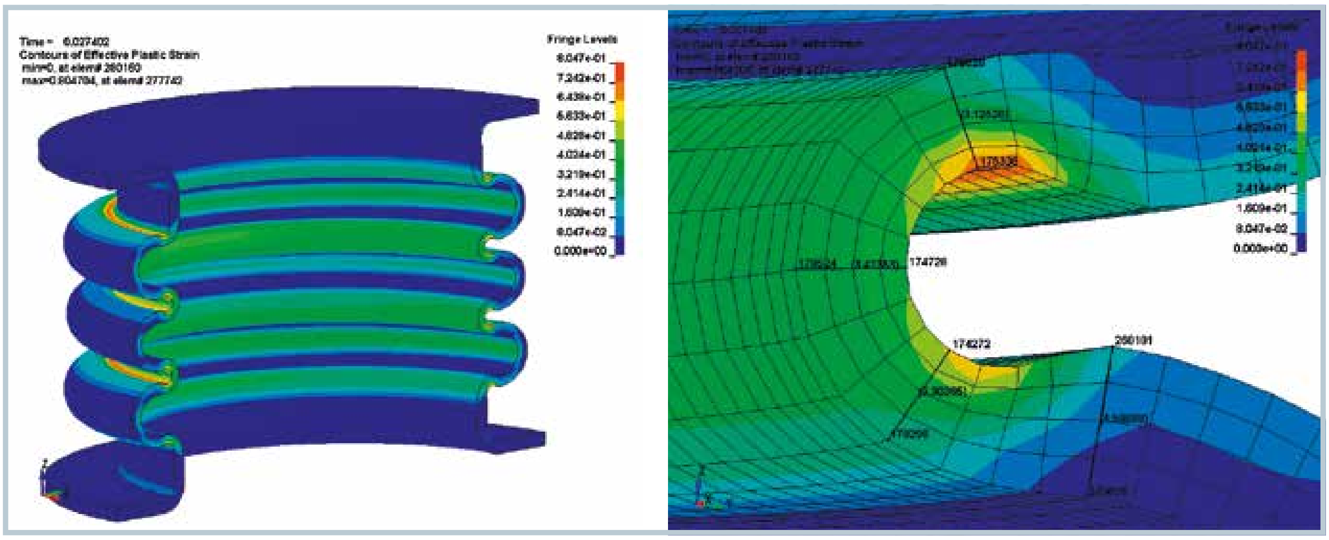

Fig. 4. FEM simulation of the maximum operating pressure of PTFE expansion joints before plastic deformation

facture longer pipe liners in a single work step and thus reduce the number of flange connections.

Liners for Special Cases

Paste-extruded liner segments can be connected with each other for dimensions where seamless linings are not available anymore. Depending on the type of PTFE, different welding methods are used at Dr. Schnabel GmbH for liner thicknesses of up to 8 mm. In this way reactors, columns or vessels even with various nozzles can be securely lined and protected against corrosion (**Title figure**). Welding seam lengths of 4,000 mm are possible with Dyneon TFM. Today, they allow column section lengths of up to 3,500 mm and thus cost advantages due to the lower number of flange connections. Despite the low permeation rate of the paste-extruded liners, some media such as hydrogen chloride (HCl) or hydrogen fluoride (HF) can "move" through the liner. Loose liners offer the advantage that the permeate can escape in a controlled manner via special venting systems. High plant availability and process reliability can thus be secured, as has been shown by Dr. Schnabel GmbH's many years of experience with Polyfluron in columns and vessels, including their internals.

PTFE expansion joints serve the compensation of thermal expansion in pipelines made of the most diverse materials (**Fig. 3**). Owing to their large adjustment range they are also suitable in particular for use in plastic or glass-fiber-reinforced plastic (GFRP) pipelines and prevent critical stresses. On account of their flexibility and low spring rates they are also to be found on sensitive plant components with enamelled equipment, glass and graphite apparatuses as well as graphite heat exchangers. Hence, they offer a compact alternative to the material-intensive and cantilevered horseshoe bends for the compensation of thermal expansion of pipe systems.

PTFE expansion joints are also used for the absorption of oscillations and vibrations, for example on pumps. In this case use of very special properties of the material is made: the low tendency towards material fatigue and the complete absence of a tendency to brittle fracture in comparison with other plastics or elastomers and certain metals.

Here, the convoluted liners are also made of low-void paste extrudates for safety reasons. This securely avoids the possible enlargement of defects under mechanical loads and movements extending as far as cracks. In addition to optimum liner quality, the even wall thickness of the PTFE is decisive for its lifetime. Dr. Schnabel GmbH has developed a special manufacturing method for Polyfluron expansion joints that avoids the concentration of stresses in the critical areas of the convolutions – the peaks and troughs – and thus enables maximum operational reliability and safety. Using simulations the operating pressure limits can be calculated at elevated temperatures of, for example, 150 °C (**Fig. 4**). This way it is possible to safely determine even large diameters for which the execution of practically-oriented bursting tests is barely possible. ■