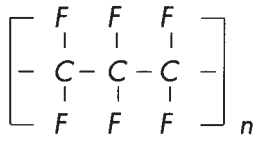
POLYTETRAFLUOROETHYLENE (PTFE)

PTFE is a partly crystalline polymer of fluorine and carbon having unbranched, linear structure. During polymerization, gaseous tetrafluoroethylene is converted to polymeric polytetrafluoroethylene in the presence of certain catalysts and emulsifiers.

Structural formula



The carbon-fluorine bond is one of the strongest bonds in inorganic chemistry. It can be broken only under extreme conditions. The structure of the macromolecule is assumed to be linear. The molecular weight cannot be determined with standard methods; specially developed techniques yield values of at least 10^5. PTFE is a partly crystalline polymer. A crystallite transformation takes place at 19°C. Figure 1 shows the different crystallite forms above and below this transformation temperature.

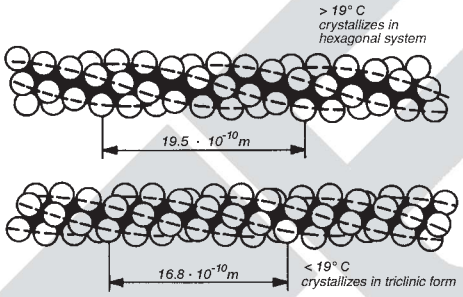


Figure 1: Model of the molecular chain

The fact that a volume expansion of about 1% takes place and that the relative length change is nonlinear can be attributed to this transformation of the crystalline lattice.

Properties

The unusual properties of PTFE can be explained on the basis of its chemical structure.

- ✻ Thermal stability from -270°C to 260°C,
- ✻ universal chemical resistance,
- ✻ excellent non-stick properties,
- ✻ low coefficient of friction, good sliding properties,
- ✻ physiological safety,
- ✻ good electrical insulation characteristics.

Thermal properties

PTFE has great thermal stability. Its chemical and electrical properties, flexibility and extensibility are conserved even in the cryogenic range. PTFE does not become brittle even in liquid helium (-269°C). The maximum permissible temperature for continuous use depends on the particular mechanical stress and strain conditions. At low load, the upper temperature limit for continuous stress and strain is 260°C . The thermal insulation ability is high, while the thermal conductivity is extremely low (0.25 to 0.5 W/K·m). Better thermal conductivity can be achieved in compounds containing conductive additives. PTFE achieves level 1 during incandescence resistance tests per DIN 53459 or ISO/R 181, and it is nonflammable and incombustible under normal conditions. The crystallite transformation at 19°C results in a volume change of 1%. Figs. 2 and 3 show the relative length change as a function of temperature and the variation of the coefficient of linear thermal expansion respectively.

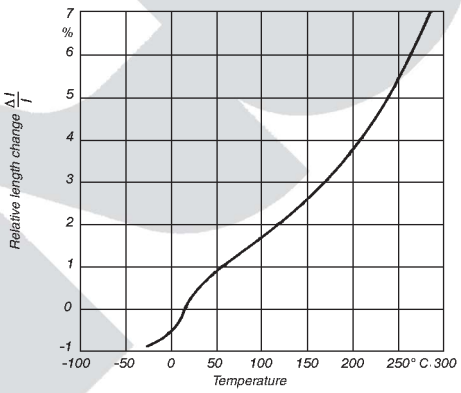


Figure 2: Relative length change of PTFE as a function of temperature

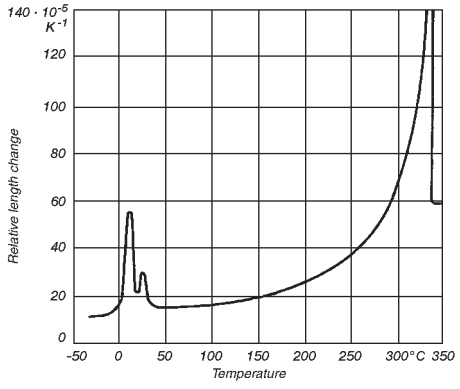


Figure 3: Coefficient of linear thermal expansion of PTFE as a function of temperature

Mechanical properties

Most mechanical properties depend strongly on the processing conditions, which influence density, strength, elasticity, hardness and dielectric characteristics.
Any mechanical data cited in the following must be regarded merely as average values. Furthermore, no indication will be given as to whether the values were determined across or along the processing direction. Exact values can be found in the supply-specific test products per DIN/ISO/EN. The mechanical properties are strongly time-dependent and temperature-dependent. PTFE undergoes the same kind of deformation as other thermoplastic materials in response to load magnitude, temperature and loading duration. These factors have an additional determining influence on degree of deformation, beyond that of the processing method used.
If deformation already begins at room temperature, the behaviour is referred to as "cold flow" or "creep". In other words, the law of linear proportionality between stress and deformation is not obeyed under these conditions. The behaviour of PTFE under long-term stress and strain can be improved by addition of suitable fillers.

Tensile strength

Behaviour under short-term stress and strain

Tensile strength values depend on specimen thickness and also differ by virtue of the different shapes of the specimens per the DIN and ASTM measuring techniques.

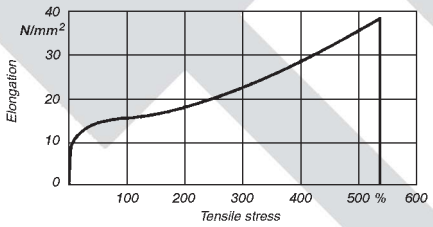


Figure 4: Stress-strain diagram of PTFE

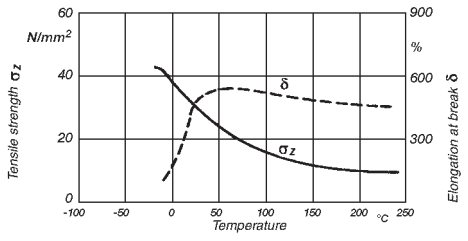


Figure 5: Tensile strength and elongation at break of PTFE as a function of temperature

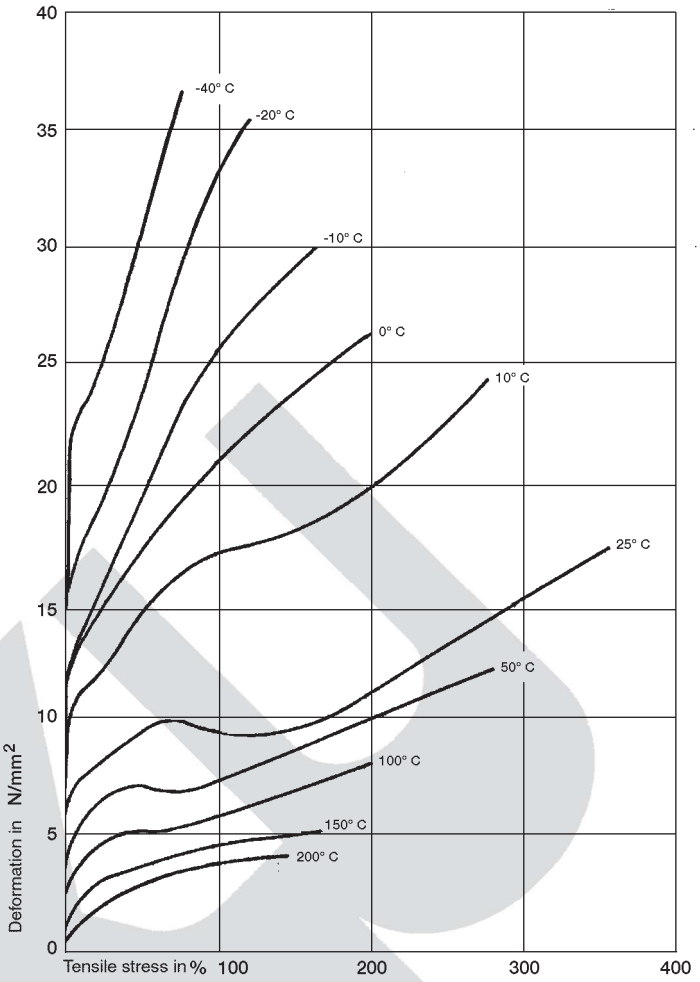


Figure 6: Stress-strain diagram at several temperatures

Behaviour under long-term stress and strain

Figures 7a to 7c illustrate the time yield limits of PTFE as a function of loading duration.

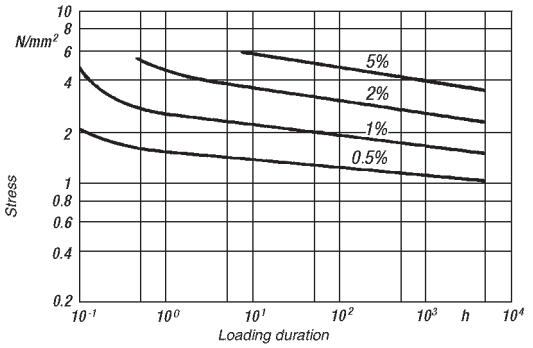


Figure 7a: Time yield limits of PTFE as a function of loading duration for four different elongations at 20°C

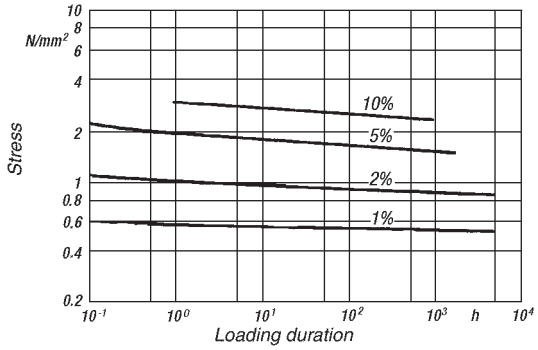


Figure 7b: Time yield limits of PTFE as a function of loading duration for four different elongations at 100°C

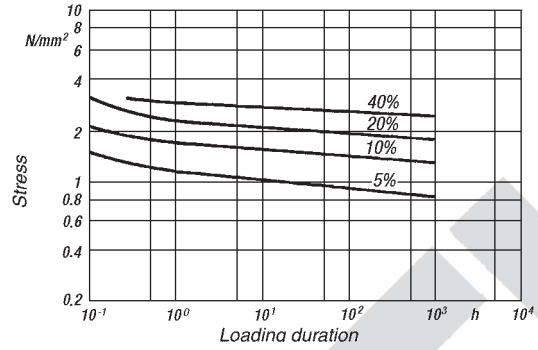


Figure 7c: Time yield limits of PTFE as a function of loading duration for four different elongations at 200°C

Compressive stress and strain

The tensile strength and elongation at break in the tensile test are used mainly for quality control purposes. Since PTFE is used only infrequently under tensile stress and strain, much greater practical importance is attached to the measurements on specimens under compressive stress and strain.

Behaviour under short-term stress and strain

The following values, which are also listed in Table 1, were obtained for yield points in the compression test per DIN 53454:

1%	yield point	10 N/mm^2
10%	yield point	18 N/mm^2

Behaviour under long-term stress and strain

Figs. 8a to 8c illustrate the behaviour of PTFE subjected to prolonged compressive load followed by relaxation.

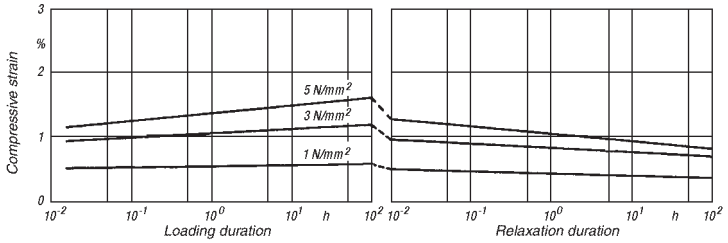


Figure 8a: Compressive strain and recovery as a function of time at 20°C

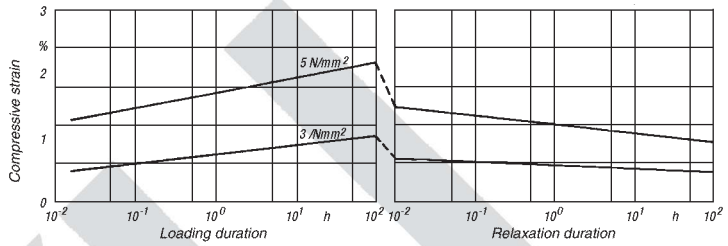


Figure 8b: Compressive strain and recovery as a function of time at 100°C

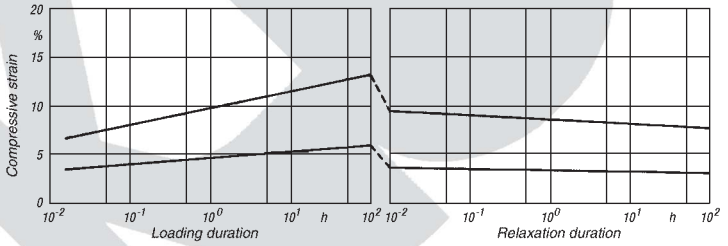


Figure 8c: Compressive strain and recovery as a function of time at 150°C

Flexural stress and strain

As shown in Table 1, a flexural stress of 14 N/mm^2 at 3.5% is obtained in the flexural test per DIN 53452.
The flexural-strength test per ASTM D-790 is passed without break. The fatigue limit under completely reversed bending stress, which depends strongly on crystallinity, exhibits high values. The modulus of elasticity in bending is 620 N/mm^2 at 23°C, and even at 100°C is 3200 N/mm^2.

Impact strength and notched bar impact strength

As the values in Table 1 prove, PTFE has high impact strength. The specimens exhibit pronounced ductile fracture both in the tensile test and in the impact flexural test, even at temperatures as low as about -150°C. Fig. 9 shows the notched bar impact strength as a function of temperature.

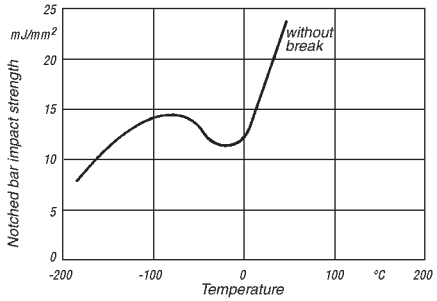


Figure 9: Notched bar impact strength as a function of temperature (DIN EN ISO 197 397)

Fatigue behaviour

By virtue of its flexibility, PTFE withstands a large number of load cycles. The dynamic modulus of elasticity measured in the bending vibration test and the loss factor tan δ are strongly temperature-dependent, as is the case for all mechanical strength values.

Table 1 **Mechanical properties of PTFE**

Property	Value	Unit	Test method
Density	2.15 to 2.18	g/cm³	DIN 53479 ASTM 1457-69 T
Tensile strength	20 to 40	N/mm²	DIN EN ISO 527 ASTM D 1457-69 T ASTM D 1710-63 T
Elongation at break	250 to 500	%	(as for tensile strength)
Modulus of elasticity in tension	750	N/mm²	DIN 53457
Compressive strength			DIN 53454
1% yield point	10	N/mm²	
10% yield point	18	N/mm²	
Flexural strength	without break	N/mm²	DIN 53452
3.5% flexural stress	14	N/mm²	DIN 53452
Torsional stiffness	160	N/mm²	DIN 53447
Impact strength	without break	kJ/m²	DIN EN ISO 197 397
Notched bar impact strength	16	kJ/m²	DIN EN ISO 197 397
Number of bending cycles to failure	> 10^6	load cycles	DIN 53374
Ball indentation hardness (135 N test load)	27 to 32	N/mm²	DIN 53456 30 sec value
Shore hardness	D 55 to 59 C 85 to 87		DIN 53505

Table 2 **Physical and thermal values**

Property	Value	Unit	Test method
Melting range	320 to 340	°C	DTA
Volume change in the melting interval (10 K range)	5 to 8	%	-
Volume change between room temperature and melting range	27 to 28	%	-
Coefficient of linear thermal expansion between			DIN 52328
20°C and 100°C	$16 \cdot 10^{-5}$	K^{-1}	(dilatometer)
20°C and 200°C	$19.5 \cdot 10^{-5}$	K^{-1}	
20°C and 300°C	$25 \cdot 10^{-5}$	K^{-1}	
Specific heat			adiabatic
at 0°C	0.96	kJ/kg·K	calorimeter
at 50°C	1.03	kJ/kg·K	
Thermal conductivity	0.25 to 0.50	W/m·K two-plate method	DIN 52612
Temperature range for application	-200 to +260*	°C	
Dimensional stability under heat			
ISO/R 75, method A	50 to 60	°C	DIN 53451
ISO R 75/ method B	130 to 140	°C	
Vicat softening point VST/B/50	110	°C	DIN 53460, in air
Martens	72	°C	DIN 53458, 53462
Incandescence resistance	Level 1		DIN 53459
Heat of combustion	4600	kJ/kg	

* briefly up to +300°C

Hardness of PTFE

PTFE has only low hardness; it is relatively soft. The hardness can be increased only by addition of fillers.

Adhesion behaviour

By virtue of its molecular structure, PTFE has excellent non-stick behaviour. Even viscous and tacky substances do not adhere. PTFE is difficult to wet. The contact angle with water is 126°.

Sliding behaviour

The weak intermolecular binding forces mean that PTFE has, among other properties, the lowest coefficients of friction among all solid materials. The coefficient of friction measured at a given time depends on numerous factors, including load, sliding velocity, partner material and additional lubrication.

The following general observations can be made:

- the static and dynamic coefficients of friction are equal to one another
- at low load, the coefficient of friction rises steeply; with increasing load it decreases rapidly at first, then slowly. Figure 10 shows this relationship.
- with increasing sliding velocity, the coefficient of friction increases up to about 50 m/min, but beyond that point it is only slightly velocity-dependent. Figure 11 shows the curve.
- with increasing temperature, the coefficients of friction increase up to 20°C and then remain largely constant. At low temperatures, the coefficient increases slightly starting from -45°C and then also remains almost unchanged.

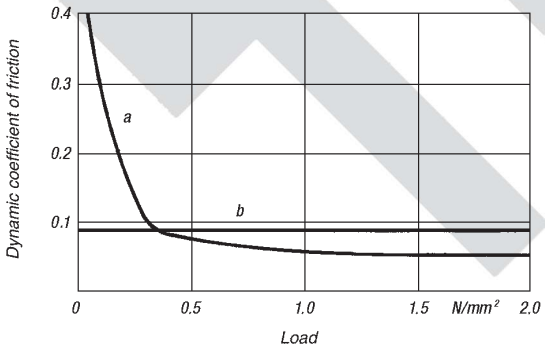


Figure 10: Dynamic coefficient of friction of PTFE as a function of load

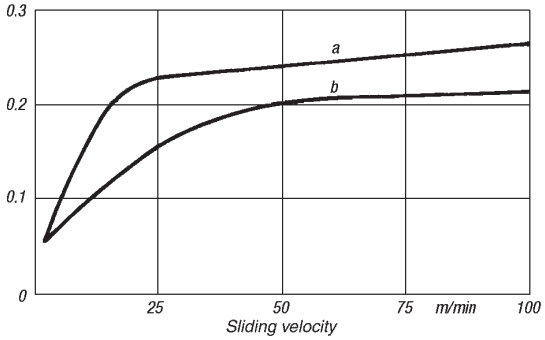


Figure 11: Dynamic coefficient of friction of PTFE as a function of sliding velocity

Wear behaviour

Because of its molecular structure and the nature of the processing processes, the abrasion resistance of PTFE is low. Abrasion tests lead to greatly divergent values, because of the different test setups. PTFE compounds exhibit good abrasion resistance even at relatively high loads.

Weathering resistance

Even under extreme climatic conditions, the properties of PTFE do not change. The aging resistance is extremely high.
Water absorption is undetectable, even after prolonged storage time.

Physiological safety

In the temperature range up to 200°C, PTFE in non-compounded form is physiologically neutral. Breakdown products must be expected above 300°C, the temperature at which thermal decomposition slowly begins.

Chemical resistance

PTFE has universal chemical resistance by virtue of the strength of the carbon-fluorine bond and of the fact that the carbon chains are shielded almost completely by a helical arrangement of fluorine atoms. Even aggressive substances such as hydrochloric and hydrofluoric acid, fuming sulphuric and nitric acid, hot sodium hydroxide solution, chlorine gas, hydrogen peroxide, esters, ketones, alcohols and acid chlorides, etc. do not attack PTFE.

It is only at temperatures close to the crystallite melting range of 327°C that PTFE is susceptible to attack by highly fluorinated oils. At room temperature, fluorine-containing hydrocarbons swell PTFE reversibly. Alkali metals in molten or dissolved form attack PTFE and cause brown discoloration, extracting fluorine from the molecule. At high temperatures the resistance to molten alkali metals, chlorine trifluoride and elemental fluorine deteriorates.

Table 3

PTFE is resistant against (among others) the following chemicals:

Abietic acid
Acetic acid
Acetic anhydride
Acetone
Acetophenone
Acrylic anhydride
Allyl alcohol
Aluminum chloride
Ammonia, liquid
Ammonium chloride
Aniline
Benzonitrile
Benzoyl chloride
Benzyl alcohol
Borax
Boric acid
Bromine
n-Butylamine
Butyl acetate
Butyl methacrylate
Carbon disulphide
Cetane
Chlorine
Chloroform
Chromic acid
Cyclohexane
Cyclohexanone
Dibutyl phthalate
Dibutyl sebacate
Diethyl carbonate
Diisobutyl adipate
Diethyl ether
Dimethyl formamide
Dioxane
Ethyl acetate
Ethyl alcohol
Ethyl ether
Ethylene bromide
Ethylene glycol
Fluoronitrobenzene
Formaldehyde
Formic acid
Furane
Gasoline
Hexachloroethane
Hexane
Hydrazine
Hydrochloric acid
Hydrogen fluoride
Hydrogen peroxide
Iron(III) chloride
Iron(III) phosphate
Lead
Magnesium chloride
Mercury
Methanol
Methyl acetate
Methyl ethyl ketone
Methyl methacrylate
Naphthalene
Naphthols
Nitric acid
Nitrobenzene
Nitrogen tetroxide
Nitromethane
Octane
Oils
Ozone
Pentachlorobenzamide
Perchloroethylene
Perfluoroxylene
Phenol
Phosphoric acid
Phosphorus pentachloride
Phosphorus trichloride
Pinene
Piperidine
Polyacrylonitrile
Potassium acetate
Potassium permanganate
Potassium chloride
Pyridine
Soaps and detergents
Sodium hydroxide
Sodium hypochlorite
Sodium peroxide
Styrene
Sulphur
Sulphuric acid
Tetrabromomethane
Tetrachloroethylene
Trichloroacetic acid
Trichloroethylene
Tricresyl phosphate
Triethanolamine
Vinyl methacrylate
Water
Xylene
Zinc chloride

The absence of certain chemicals from the above list does not mean that they are incompatible with PTFE. Under certain circumstances, many PTFE types develop environment-related stress cracks, if they are in the presence of some of these liquids and simultaneously subjected to continuous stress and strain.

Electrical properties

By virtue of its nonpolar structure, PTFE has excellent dielectric properties. The volume resistivity is almost independent of temperature and higher than $10^{18}\ \Omega \cdot$ cm up to 150°C. Even after specimens have undergone prolonged storage in water, this does not decrease markedly. The surface resistance in the absence of humidity is about $10^{17}\ \Omega$, and is still greater than $10^{12}\ \Omega$ in the presence of air at 100% relative humidity.

The dielectric strength decreases at about 50°C and remains largely constant up to 250°C. The dielectric loss factor tan delta, which is smaller than 0.0001, is independent of temperature and frequency between -60°C and 250°C. The relative dielectric constant is almost independent of frequency in the range of 50 to 10^{10} Hz and changes only slightly in the temperature range from -50°C to above 200°C.
The main dielectric properties are listed in Table 4.

Table 4 **Dielectric properties**

Property		Value	Unit	Test method
Relative dielectric constant	at 50 Hz	2,1	-	DIN 53483
	at 10^3 Hz	2,1		
	at 10^4 Hz	2,1		
	at 10^5 Hz	2,1		
	at 10^6 Hz	2,1		
	at 10^7Hz	2,1		
Dielectric loss factor tan δ	at 50 Hz	$0{,}5\cdot10^{-4}$	-	DIN 53483
	at 10^3 Hz	$0{,}3\cdot10^{-4}$		
	at 10^4 Hz	$0{,}4\cdot10^{-4}$		
	at 10^5 Hz	$0{,}7\cdot10^{-4}$		
	at 10^6 Hz	$0{,}7\cdot10^{-4}$		
	at 10^7 Hz	$0{,}7\cdot10^{-4}$		
Dielectric loss factor tan δ	(at 10^3, 10^4 u. 10^5 Hz)		-	DIN 53483
	-50°C	$<1\cdot10^{-4}$		
	0°C	$<1\cdot10^{-4}$		
	+50°C	$<1\cdot10^{-4}$		
	+100°C	$<1\cdot10^{-4}$		
	+150°C	$<1\cdot10^{-4}$		
	+200°C	$<1\cdot10^{-4}$		
Dielectric strength		50...80	kV/mm	VDE 0303 Part 2
(spherical electrode)				(0.2 mm thick film)
Volume resistivity		10^{18}	Ω·cm	DIN 53482
Surface resistance		10^{17}	Ω	DIN 53482
Tracking resistance		KC>600	Level	VDE 0303 Part 1/9.64
Arc resistance		L4	Level	VDE 0303 Part 5

Processing

Due to of its high melt viscosity above the crystallite melting range of 320° to 340°C, PTFE cannot be processed by means of technical methods which are standard for the majority of thermoplastics. Specific processing methods comparable with those of powder metallurgy therefore had to be developed. Processing of the powdered polymer of various particle sizes and shapes is achieved by compaction at room temperature followed by sintering at temperatures above the crystallite melting point.

The processing conditions have a lasting effect on the basic properties of the polymer. These basic properties in turn influence some important properties of the semifinished product, especially tensile strength, elongation, density and dielectric characteristics. The basic properties influenced by the processing conditions are essentially molecular weight, crystallinity and pore density. Fig. 12 shows, as an example, the dependence of breaking strength on extrusion velocity and sintering temperature.

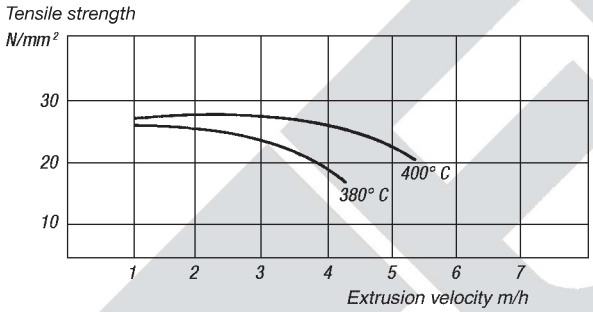


Figure 12: shows the dependence of tensile strength on extrusion velocity.

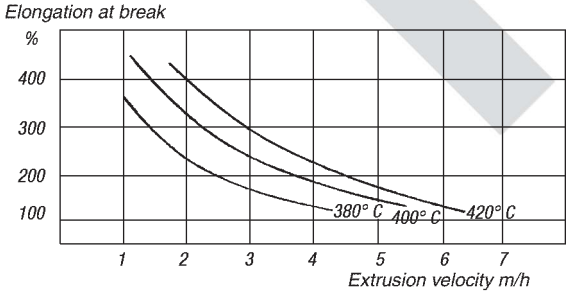


Figure 13: illustrates the dependence of elongation at break on extrusion velocity and sintering temperature.

Processing by moulding

Using metal moulds and hydraulic presses, PTFE powder is compacted at room temperature to preforms of simple geometric shape, after which it is re-sintered in hot-air ovens, which in special cases have a nitrogen atmosphere. The sintering cycle depends on the size and dimensions of the shaped parts, and involves monitored heating, controlled holding at temperature and precisely defined cooling. Depending on powder type, the compression pressure in the die during powder compaction ranges from 200 to 380 bar for unfilled PTFE and up to 1000 bar for compounds. The compaction ratio (density of the compact divided by bulk density of the moulding powder) can range between 3:1 and 7:1. The compaction speed – which depends on dimensions and compaction ratio – can be chosen between 10 mm/min and 100 mm/min. The usual sintering temperature is between 306°C and 380°C.

Automatic moulding

On the basis of metal powder processing as a model, geometrically simple parts can be automatically pressed at a correspondingly high output rate with short cycle times.

Isostatic moulding

In contrast to processing by moulding as described above, where compaction takes place only in one direction, isostatic pressing achieves compaction from all directions. In accordance with the known laws of pressure propagation in gases and liquids, the PTFE powder is pressed in elastic moulds by a pressure-exerting liquid medium, thus producing geometrically more complex shape parts for subsequent sintering.

Extrusion processing

Ram extrusion is a continuous pressure-sintering method. PTFE powder is introduced by a proportioning unit into an extrusion cylinder, compacted by means of a ram and at the same time further conveyed in the cylinder, which is heated to sintering temperature. The individual proportioning charges become sintered together as an endless extrudate.

Free-flowing, thermally pretreated powder types are suitable. They are processed at extrusion pressures of between 100 and 450 bar and temperatures of 340°C to 380°C in the heating section, which is divided into several control zones. Extrusion velocity, or in other words ram velocity, dwell time in the sintering zone and the use of braking units are strongly dependent on the size and shape of the extrudate.

Paste extrusion is another continuous process for pressing ultrafine PTFE powder with lubricant addition, subsequent evaporation of the lubricant and sintering of the extrudate. This process is used to manufacture thin-walled tubing and pipes.

Processing by chip-removing techniques

The semifinished products made by moulding and extrusion can be processed to finished parts by the standard chip-removing techniques – sawing, turning, milling, boring, grinding – on known machine tools, using bits resembling those for woodworking. The low thermal conductivity and the high coefficient of thermal expansion can lead to defects under unfavorable machining conditions. Cooling – usually with air – is therefore required at high cutting speeds. It must also be kept in mind that the crystalline microstructure of PTFE has a transformation point between 19 and 23°C, where a volume change of about 1% takes place.

Bonding of PTFE

Due to of the high solvent resistance and its non-stick properties, bonding of PTFE is only possible after the surfaces to be bonded have been pretreated. For this purpose it is necessary to activate the surfaces chemically. Etching agents in the form of solutions of alkali metals in liquid ammonia or as naphthylsodium in tetrahydrofuran have proved suitable for this purpose. (The colour of PTFE changes from white to metallic brown under the action of the etching agent.) The etching effect may be gradually lost due to aging and the ultraviolet component of daylight. Etched parts, especially commercially etched films, should therefore be stored in the dark until the bonding process. The bonding method is suitable when relatively large surfaces are to be joined with PTFE films. The choice of adhesive depends largely on operating conditions, for example thermal stability.

PTFE compounds

To achieve satisfactory results in the practical use of PTFE, the following criteria must be kept in mind:

- the thermal expansion is ten per cent greater than that of metallic materials
- the abrasion resistance is low
- starting from a certain load level, the material becomes permanently deformed due to cold flow
- the thermal conductivity is low.

Most of these properties can be modified by admixing organic fillers. Glass, carbon black and graphite, molybdenum disulphide, bronze and mixtures of these substances in proportions of 5% to 40% have proved useful as fillers. The following improvements in properties can be achieved by incorporation of such fillers:

- greater compressive strength
- smaller deformation under load (cold flow)
- better thermal conductivity
- greater wear resistance
- reduced thermal expansion
- changed electrical properties.

A detailed description can be found in the TEKU publication entitled "PTFE Compounds".

PTFE SEMIFINISHED PRODUCTS AND FINISHED PARTS

PTFE -fluoroplastic

Properties and characteristic data