Industrieverband
langlebige Kunststoffprodukte
und Mehrwegsysteme e.V.

pro-K Fluoropolymergroup

Technical Brochure 02:
Introduction into the processing of PTFE resins

Preamble

The fully fluorinated polymer PTFE is the most widely used fluoropolymer and based on its unique properties is established as an indispensable construction material in modern industries.

The main extraordinary properties of PTFE are resistance to most chemicals, a broad service temperature range, the excellent electrical properties, resistance to embrittlement, ageing resistance and very high purity.

This introduction provides a survey about the history and production of PTFE and the different polymerisation processes and describes the properties of suspension-PTFE, modified suspension PTFE, PTFE compounds and fine powder PTFE. Furthermore, the processing procedure will be explained and possible applications will be demonstrated.

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The brochure presents the state of knowledge as of February 2020.

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Content

1. History

The history of PTFE began more or less by accident during the research on fluorinated refrigerants. When trying to synthesize a safe, odourless, nontoxic and non-flammable refrigerant from tetrafluoroethylene a white, waxy powder was built - the hour of birth of PTFE - connected with the name of Dr. Roy Plunkett (DuPont) who thus became the inventor of the most important fluoropolymer.

Today, many decades after his invention, modern life cannot be thought without PTFE in its manifold variations, with different recipe combinations.

2. Manufacturing of PTFE

Fluorospar is used as basic material for the synthesis of tetrafluoroethylene (TFE) - the monomer basic material for the manufacturing of PTFE.

At the beginning fluorospar is reacted with sulphuric-acid to provide hydrogenfluoride and potassium sulfate, in subsequent reactions hydrogenfluoride is reacted at high temperatures with chloroform to finally provide TFE.

The radicalic polymerisation of TFE is started and controlled with an initiator system and polymerisation aids. This strong exothermic reaction creates a huge amount of energy which must be removed safely and reliably from the reactor.

Basically the polymerisation of TFE to PTFE can be differentiated into a suspension and an emulsion polymerisation process. Whereas the emulsion polymerisation occurs in an aqueous dispersion containing emulsifiers and dispersion aids the suspension polymerisation is done in an aqueous suspension without emulsifier.

Due to the different polymerisation- and work up conditions emulsion (E)-PTFE - also called fine powder PTFE - shows a particle structure which is built from very small primary particles (size of 200 nm) and a superficial secondary structure called coagulate with a particle size distribution of 400 - 600 µm.

In contrast suspension PTFE consists of irregularly formed compact polymer particles of around 2 mm – the so called reactor beads - which are milled in special mills to a particle size of around 10 µm or optionally are aggregated to free flowing powders with a particle size between 100 and 700 µm.

Fine Suspension-(S)-PTFE is called „non free flowing“ or „standard-flow“, whereas agglomerates are named „free flowing“ or „free-flow“.

Depending on the polymerisation process, recipe and powder properties different processing conditions apply and thus finally defining the appropriate applications.

Depending on the application and the product requirements specific properties can be improved by adding fillers or enforcing resins of different kind and amount to S-PTFE as well as to E-PTFE.

These PTFE-compounds - based on standard or chemically modified PTFE - enlarge the possible applications in engineering, automobile and especially in the chemical plant engineering.

3. General properties of PTFE

3.1 PTFE

PTFE is a partly crystalline polymer, which shows a melting point of about 342 °C and a crystallinity of 92 - 96 % in the virgin resin.

Above the crystalline melting point PTFE becomes translucent whereas below the melting point it appears white and opaque.

The specific gravity of finished products, that have been processed without voids, is - depending on the processing conditions - between 2,13 and 2,20 g/cm³, which corresponds to a crystallinity of 50 to 70 %.

Sintered finished goods show a melting point of 327°C.

PTFE shows some crystalline transitions, the most important one at 19 °C. This is characterized by a change in the crystalline configuration of triclinic to hexagonal and an increase in volume of about 1 %.

The basic properties of PTFE derive from its specific linear helical molecular configuration of the Fluorine and Carbon atoms. Both, the carbon- carbon as well as the carbon-fluorine bonds are extraordinary strong. Additionally the carbon backbone is hermetically shielded by fluorine atoms thus complicating a chemical attack making PTFE stable and resistant to chemicals.

Further properties like the low surface tension, the low friction coefficient or the excellent stability against temperature and flames are essentially based on the linearity, non-polarity and the high bonding energy respectively on the shielding by fluorine atoms.

In the following the basic properties are summarized which recommend PTFE since many years for challenging applications under critical and extreme conditions:

- High molecular weight and high melting point.
- Large range of temperature application of -250 to +260 °C
- Nearly complete resistance against chemicals and insolubility
- Anti-adhesive surface and extreme low friction coefficient
- Excellent (di)electric properties
- No water absorption
- High UV- and weathering resistance (no embrittlement by ageing)
- Very high purity; without additives
- High flame resistance
- Physiological harmlessness

3.2 Modified PTFE

An advancement of PTFE is the modified PTFE. This PTFE of second generation contains a small amount of a fully fluorinated modifier, Perfluoropropylvinylether (PPVE) and shows only a molecular weight of 20 % compared to standard PTFE. The shorter molecular chains tend to have a higher crystallinity than standard PTFE, which would reduce the mechanical properties of the material. The modifier however prevents crystallisation effectively.Thus modified PTFE combines the thermoplastic properties, which are due to shorter molecular weight, with the excellent mechanical properties of standard PTFE.

In modified PTFE the smaller medium size of crystallites and a more narrow distribution of the crystallites cause a more homogeneous and finer microporous structure which can be recognized via a higher transparency.

By this modification some inherent deficiencies of PTFE like the porosity, the high permeation or the strong cold-flow could be reduced.

Thus we have a PTFE with significantly improved properties which allow new applications and since many years take its place in industrial applications.

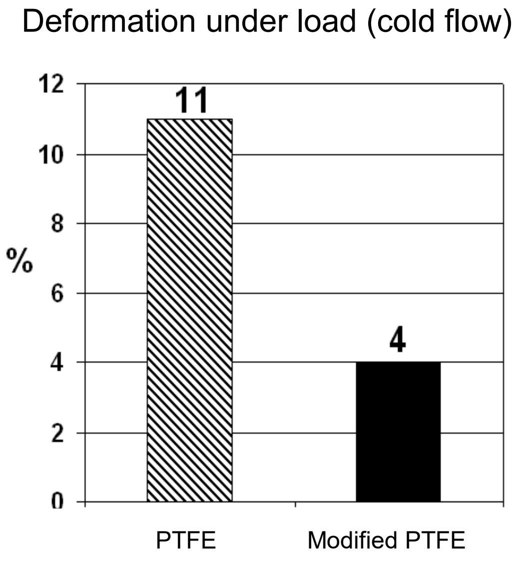
The main applications are in the chemical engineering, semi-conductor biotechnology and transportation.

In addition to the above described properties modified PTFE shows the following improved properties:

- More dense, less void containing polymer structure
- Less permeation

- Improved mechanical properties like tensile and elongation and stiffness especially at higher temperatures
- Substantially less deformation under load („cold flow“) and improved resilience
- Less creap behaviour, above all at higher temperatures and/or high load
- Smoother surfaces and higher transparency
- Good weldability with specific melding processes

In the following graph you find four essential properties in comparison to standard PTFE:



Relevance for the practice

•HIgher stability

•Assembly:
  –reduces the mount for adjustment
  –Shortassembly times

•For sealing applications
  –Less decrease in seatingstress
  –Resetting behaviour
  –Alternating stress
  –Better sealing overtime

Conditions: ^^Load 15 MPa
:time 100 h
Remaining deform. After 24 h

Fig. 1: Reduced deformation under load („cold flow“) of modified PTFE

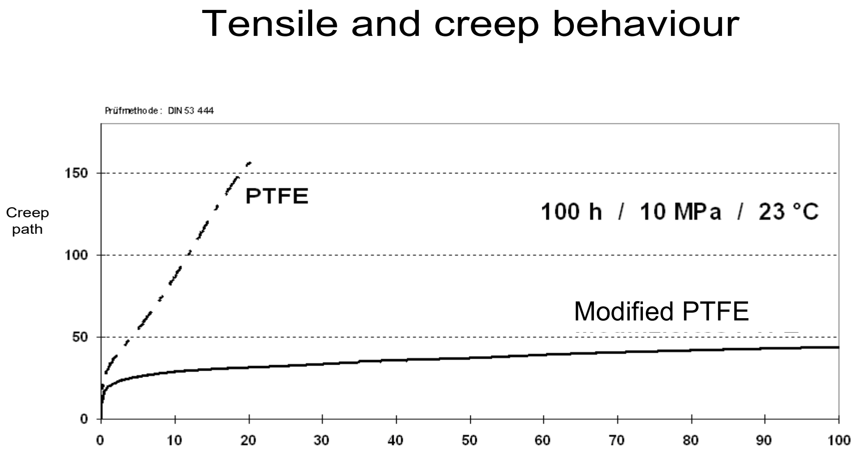
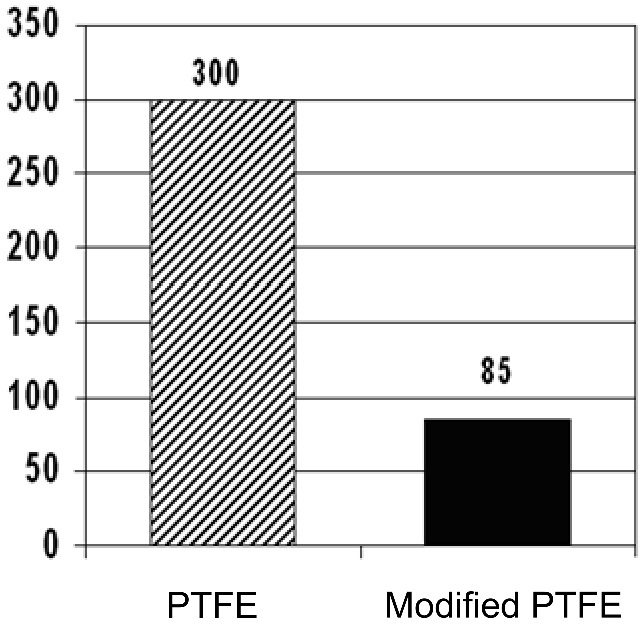


Fig. 2: Reduced tensile and creap behaviour of modified PTFE

Stretch void index



The improved composite of particles reduces the stretch void index (SVI) by a factor of 3 or more

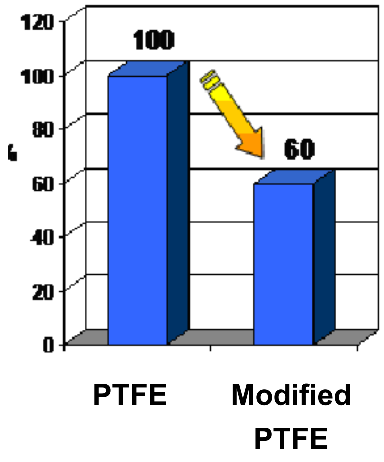
Impact for practice:

- The smalle the SVI the less voids are built during stretching
- Materials with small SVI are the stretched (assembling) condition more dense and less permeable

- SVI: Index for the building of voids during stretching

Fig. 3: Reduced Stretch-Void-Index of modified PTFE

Permeation properties



Impact for the practice:

- Improved barrier properties
- Reduced emission with same thickness
- Reduced wall thickness with same emissions
- Low permeation after processing (SVI effect)
- Reduced effort for handling of residual permeates: ventilation, insolation

Fig. 4: Reduced permeation of modified PTFE

In order to improve certain properties with regard to their application modified PTFE can also be compounded with fillers of different kind and amount. These compounds combine the advantages of modified PTFE with the individual advantages of the chosen filler or enforcements.

3.3 Compounds based on virgin PTFE and modified PTFE

3.3.1 Definition

PTFE-Compounds are physical mixtures of PTFE or modified PTFE with fillers or different enhancements. Like unfilled Suspension-PTFE, PTFE-Compounds are available as free flowing and non-free flowing powders. Beyond many extraordinary properties unfilled PTFE shows some disadvantages due to its polymer basics. The most important ones are the relative low hardness and a low wear resistance of unfilled PTFE. Another one is the so called „cold flow“, which may cause some problems for specific applications.

3.3.2 Possibilities of modification and properties

As mentioned in 3.2, some inherent weaknesses of PTFE may be reduced by the use of modified PTFE. For instance significant improvements can be achieved for the cold flow and tendency to creep.

Consequently there are quite some possibilities for adaption via use of different basic polymers (virgin PTFE or modified PTFE) and via the choice of fillers or enhancements as well as their concentration. By combination of these possibilities - especially by the simultaneous use of different fillers – nearly unlimited formulations with customized properties can be created for the particular application.

Fillers or enhancements may be organic or inorganic nature, however in each case they must resist the high temperatures necessary for the sintering process. The following chart combines the possibilities of influencing the properties as well as their quantitative effects.

Parameter variation	Tensile Properties	Cold Flow	Friction coefficient	Abrasion	Chemical resistance	Expansion coefficient	Thermal conductivity
Matrix polymer **Virginal PTFE** **Modified PTFE**	→/↗ (0/+)	↘ (+)	→/↗ (0/-)	→ (0)	→/↗ (0/+)	→ (0)	→ (0)
Filler Inorg./ organic	↘ (-)	↘ (+)	↗ (-)	↘↘ (+)	↘ (-)	↘ (+)	↘ (+)

Trends: (o) = neutral, (+) = positiv, (--) = negativ

Fig. 5: Influence on the properties of PTFE-compounds

Frequently used inorganic fillers are:

- Glass (fibers, spheres, hollow spheres, milled glass)
- Carbon (hard carbon, soft carbon, conductive pigment, graphite, carbon fibres)
- Bronze (spheric, irregular, dendritic, oxidizing, non-oxidizing
- Molybdenumdisulfide (MoS_2)
- Steelpowder, stainless steel
- Ceramics (e. g. Alumina)
- Wollastonite

Frequently used organic fillers are:

- Polyphenylene sulfide PPS
- Polyetheretherketone PEEK
- Aromatic Polyester
- Polyimide PI
- Polyphenylene sulfone $PPSO_2$
- Polyamidimide PAI
- Aramide

Depending on the nature of the filler certain properties are specifically changed.
The following table gives a survey:

	Filler						
Property	**Glass fibre up to 40 %**	**Soft Carbon up to 35 %**	**Hard Carbon up to 35 %**	**Grafite up to 15%**	**MoS2 up to 5 %**	**Bronze up to 60 %**	**Stainless Steel up to 60 %**
Wear	↘	↘	↘↘	↘	→	↘↘	↘
Abrasion	↗	→	→	↘	↘	→	↗↗
Chem. resistance	↘	↘	↘	↘	↘	↘	→
Heat conductivity	→	↗	↗	↗	→	↗	↗
Slipping properties	→	→	→	↗	↗↗	→	→
Friction coefficient	↗	↗	↗	↘	↘	↗	↗
Hardness	↗	↗	↗↗	↘	→	↗	↗
Stiffness	↗	↗	↗	→	→	→	→
Dry running conditions	→	↗	↗	↗	↗	→	→

Trend: Blue = neutral, green = positive, red = negative

Fig. 6: Influence of fillers on the properties of PTFE compounds

3.3.3 Example of use for PTFE-compounds

improved property	example of use
PTFE with glass fibres	
- Higher resistance to pressure and abrasion - Better heat conductivity	- conical nipple and valve body seat of armatures - Insulations for electric machinery - starting discs
Limits of application: only partly resistant to alkalines and acids, resistant against organic solvents	
PTFE with carbon	
- High resistance to pressure and hardness - Good slip properties and resistance to abrasion - Good heat conductivity - Low volume- and surface resistance	- Construction parts with antistatic requirements - friction bearing, valve box, valve body seat for the chemical plant engineering - Piston seal-/guiding elements for dry operating compressor - Radial Shaft Seal
Limits of application: Depending on carbon grade e.g.brittle, abrasion by oxydizing media	
PTFE with carbon fibres	
- Very low cold flow - Good resistance to abrasion - Good electric conductivity	- friction bearing - coating of rolls
PTFE with graphite	
- Good sliding properties and low friction coefficient - Good heat- and electric conductivity - No static charge	- Slip films for antistatic requirements
Limits of application: High abrasion with hard metals/reverse device, Abrasion of filler by strongly oxydizing media	
PTFE with bronce	
- Good sliding properties and abrasion properties - High pressure resistance - Low cold flow - Good heat conductivity	- Glide elements in mechanical engineering - friction bearing
Limits of application: Abrasion by acids and water possible	

3.3.4. Processing of PTFE-Compounds

For the processing of PTFE-compounds basically the same requirements apply as for virgin S-PTFE. The major differences exist with regard to the moulding pressure to be applied. Due to the fillers compounds generally need a higher specific pressure then unfilled PTFE.

Some fillers or combination of fillers should be processed at a maximum temperature of 360 - 365 °C - that is 10 -15 °C below the regular sinter temperature of PTFE - to avoid undesirable reactions or damage of fillers. Further information for the processing of PTFE-Compounds is provided by the producers of fluoropolymers.

4. Processing of Suspensions-PTFE (S-PTFE)

4.1 Basics and general moulding processing

Though being a thermoplastic polymer PTFE and modified PTFE cannot be processed like other thermoplastics by melting due to their high molecular weight and high melt viscosity but by different moulding and sinter techniques. The essential process steps are the following:

4.1.1 Moulding

The PTFE powder should be moulded at room temperature (23 °C +/- 2 °C) to a „Preform“. Thus the powder is compressed and with a defined pressure compacted.

The maximum pressure depends on the consistence of the powder: a non-free flowing S-PTFE powder requires about 15 MPa, whereas a free flowing powder needs 25 - 30 MPa. PTFE-Compounds are moulded at up to 80 MPa depending on the nature and amount of the filler.

The moulding process should occur slowly and smoothly without interruption. When the maximum pressure is reached a dwell time should be applied to enable the flowing of particles and to reduce the stress peak or avoid inconsistencies. After the slow decompression the mould is stored some time without stress to enable the elimination of air respectively stress-relaxation. The bigger a mould is the more important is the uniform moulding of the preform and the stress relaxation.

4.1.2 Sintering

After moulding the preforms are exposed to a defined sintering cycle. This is a defined heating which is adapted to the preform and a time controlled sintering at a maximum temperature of 370 - 380 °C. Above the melting point of 342 °C PTFE is transformed into an amorphous condition and the compacted particles sinter into a homogeneous structure. The sintering is performed in exactly controlled and regulated sinter ovens with an individual sinter program. Especially with bigger parts it is recommended to run slowly through the melting temperature range as there is a significant increase in volume and stress may occur.

Despite the melting temperature is reached resp. exceeded the sintering of the moulds occurs “form-free” because the very high gel stability due to the high molecular weight of PTFE.

4.1.3 Cooling

When the mould is completely sintered it is cooled down under exactly defined conditions which is in most cases very slowly. Especially the range between the sinter temperature and 260 °C should be passed slowly and cautiously –optionally a dwell time at 310 - 315 °C is recommended. Reaching the crystallisation temperature the moulds shrink and may cause severe stress. Therefore temperature differences within the moulds due to different cooling conditions (inside/outside) should be reduced. The more uniform the mould is cooled the less stress is created and less cracks are built.

After the complete cooling of the moulds they are usually subjected to a machining process like skiving, skinning, drilling or shaping.

These basic processing of S-PTFE apply with the conventional moulding with hydraulic presses as well as - slightly modified - with automatic moulding, isostatic moulding or ram-extrusion.

4.2 Automatic moulding

Automatic moulding is usually used for high numbers or simple geometries of components. Only free flowing S-PTFE is filled from a hopper reservoir into the moulding, automatically moulded and afterwards ejected. Then this process is repeated. The thus produced moulds are separately sintered in an oven.

4.3 Isostatic moulding

Isostatic moulding is done when PTFE powder is compressed in a moulding tool with homogeneous pressure created by a liquid which acts on an elastic, deformable balloon resp. membrane.

By this process complicated formed components can be produced with high reproducibility and economically. The moulding is followed again by a defined sintering process.

4.4 Ram-extrusion

Ram-extrusion is done by filling free flowing S-PTFE from a reservoir via a hopper into the feed opening followed by a vertical moving extrusion die compressing the powder in the shaping extrusion cylinder. After the die has been sitting a defined dwell time on the powder it is lifted, new powder is refilled and the moulding process is repeated. Compacting serves several jobs: to compress the powder, to allow the incorporated air to escape and to transport at the same time the compressed powder within the moulding tool.

Since the ram-extrusion tool contains heating zones below the compressing zone the single batches are sintered together during the transport through the ram-extrusion cylinder during which a specific extrusion pressure is built caused by the wall friction and the polymer properties. As mentioned above it is necessary to use very well flowing PTFE grades.

For the extrusion of thin walled profiles or rods specifically pre-sintered S-PTFE grades are used. For applications with high profiles of requirements modified S-PTFE has proven to be superior.

Using the ram-extrusion rods or profiled semi-finished goods can be produced quasi continuously and economically.

5. Processing of emulsion-PTFE (E-PTFE)

5.1 Basics

As described in chapter 2 Paste-PTFE consists of very small primary particles that have been agglomerated like snow balls to a secondary particle of roughly 500 µm. These particles prove to be extremely sensitive to shear and are mixed with a lubricant (gasoline) before processing –called paste extrusion. This lubricant diffuses into all pores and cavities and acts as spacer in the following shear process defining the amount of shear energy brought into the system.

Due to the reduction of the diameter passing the extrusion cone the PTFE-lubricant mixture is exposed to a deformation defined by shear. Depending on the shape and geometry of the cone the shape of the extruded part is determined. After the extrusion several processing steps may occur depending on the final application, which may or may not require a sintering process.

In the following you can find a detailed description of the processing steps in combination with the finished articles.

5.2 Preparation of the extrusion mixture

To achieve certain properties relevant for the processing it is recommended to store the resin in cooled rooms, ideally at 15 °C, which is below the transition point of 19 °C.
In case that the powder is clumped together or contains agglomerates despite the provisions taken the mixture shall be sieved (be sure not to squeeze the powder or contaminate it). The separated particles shall be cooled in the refrigerator between 5 and 10 °C for two or three days before they are carefully shaken to break the agglomerates and sieve them at temperature < 19°C. Usually the agglomerates dissociate into small free flowing particles.
Fig. 7 shows the cooling curve of a 25 kg drum of PTFE at 30 °C with an outside temperature of 15 °C. The temperature was measured with a thermo couple sitting in the centre of the PTFE containing drum. It takes more than 35 hours to cool the resin below the recommended processing temperature of 19°C. Therefore it is recommended to store PTFE containing drums before processing for two or more days at 12- 15 °C.

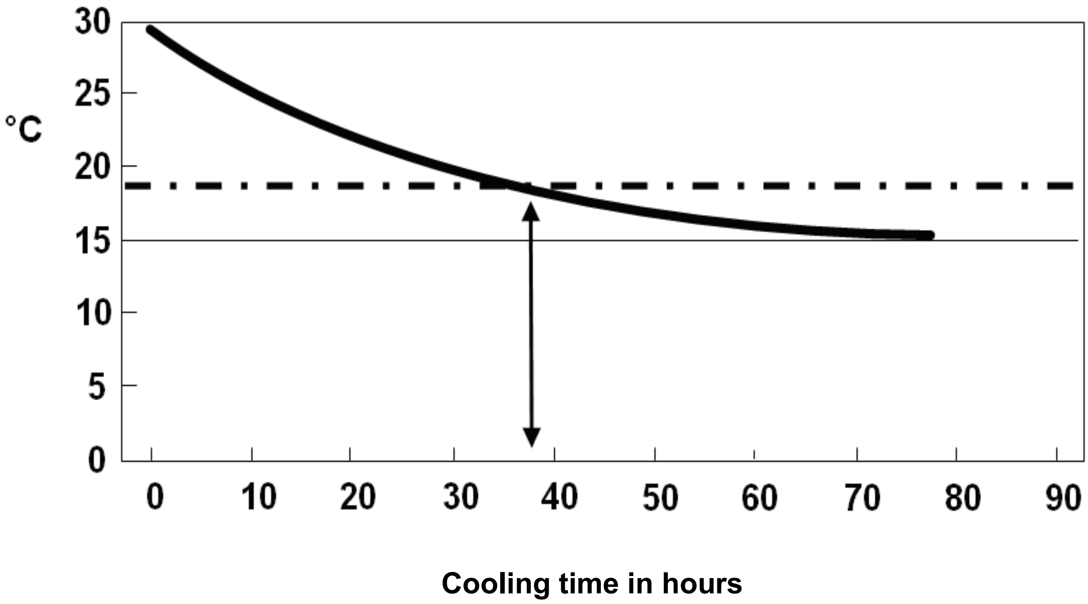


Fig. 7: Cooling time of a 25 kg paste-PTFE-drum at a storage temperature of 15 °C

To avoid voids in finished articles it has to be made sure that there is no strong mechanical strain during processing the polymer powder since this is very sensitive to shear. Therefore it is recommended that the powder is carefully charged resp. shovelled in order to avoid squeezing of the particles.

Before filling the powder in the mixer it has to be sieved to destroy agglomerates and to aerate the resin. The mesh size of the sieve should be 3- 4 mm. It is also possible to use vibrating sieves, which allow to destroy stronger agglomerates. Bigger particles should be removed from the sieve and collected in a separate bin. The removed agglomerates can be reworked by cooling and repeated sieving. It is important to have utmost cleanliness during sieving. To assure that there is no moisture absorption by condensation of humid air the polymer drum should have ambient temperature and is closed immediately after the resin has been taken out. Ideally the store room and the processing rooms have the same temperature.

PTFE is an excellent electrical isolator. Therefore it is important that during the batching there is no high velocity of the powder, since the resin could be charged electrostatic and cause ignition of the lubricant. Therefore it is strongly recommended that all apparatus that come into contact with PTFE and lubricant should be made from metal and are grounded.

Proved lubricants for the paste extrusion are aliphatic hydrocarbons (caution flammable) of different boiling points. The choice of the lubricant depends on the kind of the extruded articles. For thin walled articles, which require a calendaring process like films, usually high boiling lubricants are applied. However for thick walled goods like liners lubricants with a low boiling point are preferred.

The selected lubricant should be absorbed readily by the PTFE powder and should be removed easily after extrusion. It must not cause decolouration during sintering. Depending on the application and the character of the lubricant the amount necessary is 17 -25 % (w/w). The lubricant should not be added on the rim but into the centre of the mixer. Mixing should be performed below a temperature of 19 °C since the granular structure of the paste powder is more stable and the voids between the primary particles are completely filled with lubricant.

Depending on the kind of mixer (rolling mill or tumbling mixer) the mixing time should be 20 - 30 minutes with a rotating speed of 20 - 30 rpm/min. It is important that the powder ripples but does not fling.

The lubricant should be absorbed homogeneously by the resin and the mixer shall be closed tight to avoid loss by evaporation. The mixer should be filled to 2/3 of his volume to achieve a homogeneous mixing.

Due to the danger of deflagration of the lubricant by electrostatic charge it is essential that all apparatus are grounded. The concentration of lubricant in the working area has to be checked by suitable detectors and good ventilation has to be provided.

To achieve a homogeneous distribution of the lubricant in the PTFE the blend should be matured at slightly elevated temperatures (30 - 40 °C). Thus the mixture reaches a homogeneous temperature of the mixture and a complete penetration of the crotch volume.

The maturing process should last at least five hours or better overnight in tightly closed bins. More time is not necessary. A homogeneous distribution of the lubricant and a complete equilibration of the temperature of the PTFE-lubricant blend are essential for a homogeneous and constant quality of the extrusion process and finished article.

5.3 Moulding of the preform

After the mixture has been matured the preform is moulded. During this process step the mixture of PTFE and lubricant is compressed in a moulding press to a cylindrical preform. The goal of this process is to remove included air from the PTFE-lubricant mixture and to give the mixture a shape that allows a smooth introduction into the extrusion cylinder. The cylinder of the preform moulding press should be three times as long as the preform since the powder is compressed to a 1/3 of its original volume. The PTFE-lubricant mixture should be compressed as slowly as possible to allow the air to escape completely from the mixture. If necessary a vacuum may be applied to the ventilation fitting. The pre-compression should last some minutes at 10- 50 bar.

The quality of the finished goods depends among other aspects from a preform without voids. Therefore the pressure has to be reduced very slowly and the preform shall be taken from the cylinder very carefully. The preform must be processed immediately to avoid evaporation of the lubricant on the surface. Inhomogeneous distribution of the lubricant causes deviations in dimension and quality of the finished good.

The preform shall be introduced into the cylinder of the paste extruder whose diameter should be 1 - 2 mm bigger than the outside diameter of the preform.

5.4 Extrusion

Because of the different handling the extrusion is described in detail in the following chapters. The paste extrusion is performed with a relative simple piston press, which is pressing the preform through the extrusion die.

5.5 Production of films, tapes and sealing rods

The production of films, tapes and sealing rods can be performed with paste PTFE with or without stretching, with or without sintering. The following applications are common:

- Threat seal tapes, multilayer flat or plate sealings;
- Electrical insulation tapes for wrapping insulation; tape cables or yarns.

The essential process steps for the production of films and tapes are:

- Preparation of the extrusion mixture (chapter 5.1)
- Moulding of preform (chapter 5.2)
- Profile extrusion
- film calandering
- film drying
- stretching film mono or bi axial
- if necessary sintering of film, cutting and tailoring

The concentration of lubricant amounts to 18 - 25 % (w/w).
Compared to the extrusion of hoses it is recommended to use higher boiling lubricants (180 - 250 °C) to avoid loss of lubricant during the calandering. This improves the calandaring properties (edge wavyness, splicing).

5.5.1 Extrusion of profiles

The construction of extruders for the production of profiles may be very simple. Basically it is sufficient to have a cylinder with a die, a piston with mechanical or hydraulic actuator which operates with constant speed independently from the pressure. This is necessary as the pressure may vary during the extrusion.
For the profile extrusion a small extruder is sufficient which can achieve the necessary reduction ratio of maximum 100 : 1.

To reduce the loss of material that remains in the cone of the extruder it is possible to place one preform on the other one. The surfaces of the preforms that come into contact have to be roughed with a fork or similar in order to improve the interconnection. Otherwise voids may be built.

The shaping tool consists of a conical transition and a die with parallel guiding element. The angle of the cone is 20 - 40°. In practice a rod has proven to be the most suitable extrusion profile. For broad tapes a square profile or so called dog bone is preferred.

The tools or surfaces that come into contact with the preform shall be made from stainless steel and shall be polished. Avoid steps or edges for the transition between cylinder and cone. The very best profiles can be achieved when the extrusion cylinder and the die are heated to 30 - 40 °C.

After the extrusion the string is spooled or calandered. In case the string has to be stored please use a tightly closed bin in order to avoid loss of lubricant.

5.5.2 Calandering

For calandering of profiles two roll calanders are used which have a suitable guidance of strings. The shape of the guidance looks like a fishtail or coat hanger.

The calander rolls usually have a diameter of 300 - 400 mm and a width of 400 mm. For the surface tool a temperature of 40 °C and a rotation speed of 30 rpm are recommended depending on the diameter of the roll. To obtain the right thickness of the film an accurate calibration of the roll split across the whole width is necessary.

The surface of the roll should not be highly polished, but have a slight roughness perpendicular to calandering direction to provide a better cross section of the film. This can be achieved by polishing the roll with a sand paper of graininess 200.

The calandering from the profile to the film usually happens in one step. For thick walled profiles however it can be performed in several steps to the final width and thickness.

The calandered width of the film depends on the PTFE grade and the following factors:

- Shape of the profile
- Shape of the fishtail guide and their distance to the rolls
- Thickness of film
- Concentration of lubricant
- Surface of the rolls

With a dog bone shaped profile and the above described calander films of a thickness of 100 µm and width of 240 - 270 mm can be achieved.

5.5.3 Drying of films

Films are dried at temperatures of 160 - 200 °C. The speed through the drying oven resp. the length of the oven has to be chosen that way that the complete lubricant is removed. Calandering and drying should be performed independent from another as the two processes in most cases optimally run with different speed.

Attention: During drying flammable mixtures of air and lubricant may be generated in a range of concentration 0,8 - 6,5 vol% (please note the safety data sheet of the used lubricant and the safety guidelines for handling of flammable vapors).

To avoid flammable air- lubricant mixtures make sure there is enough ventilation and the lower explosion limit is fallen below.

5.5.4 Stretching of film

For certain applications (screw sealing rod) dried films are stretched. In practice the stretching of free running PTFE film is performed at temperatures of 280 - 300 °C.

During stretching the film is expanded by two rolls that run with different speed in the same direction. The film is fixed by roll systems that consist of a combination of rubber and metal rolls.

Depending on the PTFE grade the film can be stretched to a ratio of 1 : 10 up to 1 : 15 without generation of voids where there is only slight reduction of thickness in length and width. The material becomes thus highly porous. The stretching causes a significant reduction of the specific gravity of the film.

Stretched films are differentiated by mono and biaxial stretching. Mono axial stretched PTFE is used as thread seal tapes. Biaxial stretched PTFE is often used in textiles to provide breathable, water impermeable membranes. The distance of the fibres is big enough that water steam can move through the membrane whereas water drops cannot pass it and remain outside.Furthermore films and tapes can also be sintered before stretching to obtain high tensile films, tapes or yarns.

5.5.5 Production of non-stretched and stretched sealing rods

Sealing rods are usually round or square extruded rods which according to their application are used stretched or non-stretched. For the production of sealing rods a similar technology is used as for tapes. The profiles are made by extrusion similarly as tapes using special dies depending on the dimensions of the rod. Afterwards the rod is dried. Stretched sealing rods are expanded in stretching devices using similar apparatus and conditions as with films.The goal is to reach specific gravities of 0,65 g/cm^3 which equals a stretching ratio of 1:3 to 1:4. Homogeneous dimensions of the strings are provided if the rods are conducted through special calander rolls. During the same process an adhesive tape can be applied to get a fixing aid during assembly of the sealing rods.

5.6 Manufacturing of tubes/hoses

The paste extrusion allows to produce extremely thin walled Micro- or Spaghetti tubes and thin walled industrial tubes from paste PTFE. Their dimensions comprise from 0,1 mm to 25 mm inner diameter and thicknesses from 0,1 mm to 2 mm. By further processing heat shrink tubes, flexible hoses and wire coated hoses can be manufactured. The necessary steps are as follows:

- Preparation for hose extrusion: sieving, addition of lubricant, ageing ➔ Preforming
- hose extrusion, drying, sintering ➔ finished product.

5.6.1 Lubricants for the hose extrusion

In contrast to the tape production the hose extrusion is performed with lubricants of a lower boiling point (100 - 150 °C) in order to easily remove the lubricant during the short transfer time in the drying oven.

5.6.2 Hose extrusion - Paste extruder

The production of paste hoses is performed with special extruders, which may be arranged vertical as well as horizontal and with an inner mandrel which defines the inner diameter of the hose. Afterwards the hose is dried and sintered. The preparation and the manufacturing of the preform is described in chapter 6.1 and 6.2.

The extrusion is carried out discontinuously. After each preform the extruder is stopped, the piston is returned and a new preform is introduced. Big extruders may process several preforms with a total amount of 100 kg in one step. It is not possible to increase the diameter of the preform arbitrary as this might lead to excessive reduction ratios which result in deficient extruded products due to high local shear. Limits are defined by the polymer resin as high reduction ratios cause high extrusion pressures. Thus it is necessary to provide suitable cylinder diameters for the particular dimension of the hose. The diameters of the cylinder may vary in a range between 25 mm to 250 mm, as the different grades for hoses show different maximal reduction ratios.

The extruder gear must ensure that the extrusion speed setting is constant independent from a varying extrusion pressure. This is necessary in order to provide constant drying and sinter conditions in the inline oven that guarantee consistent dimensions and quality of the hoses. The extruder gear may be hydraulic or mechanic. In praxis it has proven that hydraulic operating extruders provide more exact extrusion conditions and may be manufactured with less effort/cost.

In contrast to the profile extrusion the hose extrusion need a mandrel in the extrusion tool. This is fixed on a cross head or frame plate and without fixing in the area of the die. During the extrusion the piston presses the polymer over the mandrel. To achieve a consistent wall thickness an exact centering of the mandrel in the die is necessary. This is provided independently by the centering of the mandrel and the material flow. Flexible mandrel cone heads made of Polyacetal or Polyimid have proven to work reliably. This tool consists of a conic transition piece and the die with parallel guidance.

To achieve a smooth surface of the hose the die and/or the cylinder are heated to a temperature of 30 - 60 °C. The tools or surfaces that come into contact with the product should be made of stainless steel and be polished. The necessary extrusion pressure primarily depends on the reduction ratio and the chosen PTFE grade, secondly on the concentration of the lubricant, temperature, angle of the die, length of the hoop and the extrusion speed. In cases of too high extrusions pressures there may be high strain to the extruder and over shearing in the hose (cracks, deformations etc.). If the extrusion pressure is too low the extruded part may show deficiencies like surface roughness.

The extrusion speed depends on the dimension respectively on the wall thickness and the length of the drying and sinter oven. It may vary between 1 to 20 m/min.

5.6.3 Drying and sintering of hoses

The extruded hose is dried and sintered in a continuous furnace. In the drying zone the lubricant is evaporated above its boiling point and below the sinter temperature of PTFE (150 to 250 °C). The evaporation speed depends on the temperature of the oven, the residence time, the wall thickness and the dimension of the hose. To avoid flammable air-lubricant mixtures sufficient ventilation is required.

After it is dried the hose is sintered at a temperature of 360 to 380 °C. High extrusion speeds require higher oven temperature or longer ovens. The sinter condition is determined by the dimension of the hose, the extrusion speed, the temperature and the length of the oven.

During drying and sintering the dimensions of the hose changes. The shrinkage across is expected to be 0 - 15 % whereas the shrinkage in length is 15 - 25 %. This change in dimension must be considered for the selection of the extrusion tool and is influenced by the concentration of the lubricant, the temperature profile and the weight of the hose that is affecting the extruded part of the hose.

5.6.4 Possible applications of PTFE hoses

Chemical industry	For aggressive media e.g. for road tanker, sample hoses for the control of operations, Laboratory equipment
Pharmaceutical and food industry	
Mechanical engineering	Steam lines for inlay and vulcanisation presses, extruders, calander, cleaning devices, polymer foaming plants, paint shops, adhesion pipelines for the processing of wood, hydraulic systems, air conditions and refrige-ration plants
Automotive and machinery industry	Exhaust gases recirculation, push-pull cable, gasoline hoses
Electric- and electronic industry	Insulations for electronic components

5.7 Production of thick walled pipes

Liners are thick walled pipes with a thickness of 2 -15 mm for the corrosion resistant coating of steel pipes. In the following only the manufacturing of seamless lined pipes by paste extrusion is described. Alternative linings with S-PTFE (isostatic moulding, Ram-extrusion, skived films) and unsintered wrapping tapes are not subject of this chapter.

5.7.1 Preparation of samples and lubricant

The preparation is not different from the production of hoses. The lubricants described there can also be used for the manufacturing of liners. The liner extrusion is usually done with reduction ratios of 10 - 50. This is the reason for the low extrusion pressure and the low green strength of the lined pipes. The green strength is defined as the stability of the extruded pipe immediately after leaving the extrusion die. At that moment the PTFE still contains lubricant and is very sensitive to mechanical stress. To increase the extrusion pressure and thus the green strength PTFE liner grades have a high inherent pressure. Additionally low amounts of lubricant are used, which empirically amount to 17 to 20 parts relative to 100 parts of PTFE.

5.7.2 Liner extruder

For the extrusion of liners the same piston type extruders may be applied as described with the extrusion of hoses. Because of their high weight these extruders are horizontally installed and due to the big dimensions of the pipes need significantly bigger extrusion cylinders. If necessary the extruded liner is transferred above a supporting tube and put into a half shell to take into account the low green strength. The support tube and half shell must be corrosion resistant, otherwise discolorations may occur.

In contrast to the hose extrusion the diameter of the mandrel may be bigger than the mandrel bar to obtain big liner dimensions. This requires highly dimensioned bars made of high tensile steel, as the mechanical strain may be very high.

5.7.3 Liner extrusion process

Based on their high weight and their brittleness across the extrusion direction the liners are extruded directly on support pipes immediately after the extruder to avoid the collapse. Smaller pipes are extruded into protective pipes to avoid damage. The design of the support pipes have to take into account the change in volume during drying and sintering. The support pipes have to be made from corrosion resistant material due to the high sintering temperatures.

5.7.4 Drying and sintering

The pipe sections, which may be as long as 10 m are horizontally dried and sintered in the oven. The pipes are put together with their support pipes in a half shell made of metal to avoid deformation of the liner pipes during drying and sintering. The drying conditions must be adjusted to the dimensions of the semi-finished product and the boiling point of the lubricant in order to completely remove the lubricant during drying which would affect the sintering. Remaining lubricant can cause discoloration, cracks or blisters.

For drying and sintering of the liner pipes the following times and temperatures are recommended depending on the thickness of walls and dimension:

Drying:	Two to three hours at 150 to 200 °C
Sintering:	One to three hours at 360 to 380 °C

Depending on the required crystallinity the cooling occurs quickly or slowly. The transfer speed of the gel point at 310 - 320 °C is essential. Quick cooling reduces the crystallinity and improves the flexibility. Slow cooling increases the crystallinity and the specific gravity but reduces the permeability.

For safety and health reasons it is important to provide a sufficient ventilation of the vapors which are built during drying and sintering.

5.8 Production of cable insulators

The excellent dielectric properties of PTFE in combination with high resistance to temperature, nearly universal chemical resistance and non-flammability are crucial for their application as insulation material for cables and wires. In analogy to the hose extrusion the paste extrusion with special wire-cable extruders has well proven. The different processing steps are described in the following chapter.

5.8.1 Preparation of the extrusion mixture

Especially for the cable extrusion the prepared blend of paste PTFE and lubricant shall be sieved through a filter of mesh 3 - 5 mm into the preform mould. As cable insulations mostly have a low wall thickness agglomerates that have not been removed cause defects. Afterwards it is important that moulding the preform is performed as slowly as possible to enable the air to escape completely from the lubricant containing PTFE powder. Furthermore the pressure for the preform should not exceed 80 bar and should be kept for 5 - 10 minutes. The quality of the wire- and cable insulation depends mainly on a defect free preform, which should be given high attention. The preform is slowly removed to avoid cracks. It should be further processed immediately or kept in a closed bin to avoid loss of lubricant.

Lubricants with a low boiling point are preferred as the dwell time in the drying oven may be short due to the high extrusion speed. The amount of lubricant may be varied in a wide range in order to reduce the extrusion pressure at high reduction ratios. However there is only a narrow range of lubricant concentration to minimize the amount of electrical defects.

5.8.2 Cable extruder

The extrusion system resp. the cable insulation plant consists of a wire pay-off including dancer roll for wire stress release, the extruder itself, a drying and a sinter oven with opt. deflection roller, the wire haul-off followed by the electrical breakdown testing device and the wire take-up system.

The cable extruder may be arranged vertically or horizontally. A guide tube for the wire is used instead of a mandrel sitting in the midst of the extrusion cylinder to achieve a constant thickness of the isolation. Because of the high extrusion speed at the cable manufacturing long drying and sintering ovens are necessary. In order to use the space of the production area well they are placed parallel to each other and therefore need an idler pulley. For construction reasons it is often necessary to deflect the wire 180 ° after leaving the drying oven before it enters the sintering oven. Alternatively the wire may be deflected several times inside the oven to increase the dwell time in the oven. After leaving the sinter oven the isolated wire passes a thickness gauge and is finally checked for the dielectric strength.

5.8.3 Cable extrusion process

The preform with an inner drill hole is placed into the extrusion cylinder of a paste extruder and pressed through a die by a piston. The extruded PTFE resin jackets the wire which is conducted through the die at the same time. As the extrusion pressure may vary during the process it has to be taken into account when configuring the wire extruder that the speed of the piston and hence the extrusion speed remains constant. This is especially very important if the extrusion is carried out at high reduction ratios. When leaving the extruder the diameter of the extruded wire is bigger than the inner diameter of the die. This is called the swell rate of PTFE, which may be explained by the release of elastic deformation energy of the polymer particles.

In order to reduce the number of electrical breakdowns it is recommended to preheat the PTFE-lubricant mixture up to 25 °C. Furthermore the extrusion cylinder and the extruder die shall be heated up to 40 to 60 °C to provide a smooth surface of the extruded insulation with a low number of dielectric breakdowns.

5.8.4 Drying and sintering

After the extrusion the insulation has to be dried at 150 - 200 °C. If lubricant remains in the extruded product brownish discoloration, cracks and electrical defects may occur. The sintering is done preferably above 327 °C, especially between 360 and 380 °C.

With increasing thickness of the insulation the coated wire must be transferred more slowly. PTFE serves as a good insulation for heat and prevents that the insulation is completely dried and sintered if the drying and sintering time and temperature is not high enough. Please make sure the ventilation is sufficient as with thick insulation big amounts of lubricants may be evaporated.

6. PTFE-applications

Based on its chemical and thermal resistancy S-PTFE as well as E-PTFE is applied in the chemical plant engineering, where it is used for highly corrosive and temperature resistant coatings and liners.
Especially modified PTFE contributes essentially to the long life cycle of chemical plants due to its high impermeability and low voids.

For fittings and valves virgin PTFE as well as modified PTF is applied, the ladder one is used especially for membranes and bellows with low permeability.

PTFE is also established for many years in the area of sealings and bearings, where the improved properties of modified PTFE provide low leakage/emission rates, longer cycle times and hence better plant utilization.

In the semi-conductor industry PTFE is preferred because of its purity and low amounts of ions.

In addition to its anti-adhesive surface properties and easy cleaning PTFE is also appreciated because of its purity and physiological harmlessness in the food industry and biotechnology. Here modified PTFE is increasingly applied too.

In the electric and electronic industry PTFE resp. modified PTFE is used because of its strong insulation properties and high dielectric strength.

The excellent dielectric properties and inherent non-flammability is of tremendous importance for the safe data transmission in the automotive or airplane industry.

Finally PTFE is applied as stretched membranes in water repellent and breathable textiles.

7. Safety guidelines for handling PTFE

In addition to the general occupational safety conditions, the "Instructions for safe handling of fluoroplastics" issued by PlasticsEurope must also be observed when processing PTFE. The instructions can be downloaded from the pro-K website www.pro-kunststoff.de.

The following companies contributed to this brochure:

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