

Solef®



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Solef®

Design & Processing Guide

**SPECIALTY
POLYMERS**

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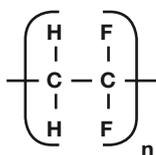
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Chemistry

Composition and Principle of Polymerization

PVDF is obtained by the polymerization of vinylidene fluoride, and corresponds to the following chemical formula:



The PVDF homopolymers on the market are polymerized according to two main processes (Table 1):

- The suspension process to produce “S-PVDF” or type II PVDF according to the ASTM D3222 standard
- The emulsion process to produce “E-PVDF” or type I PVDF according to the ASTM D3222 standard.

The suspension polymerization process leads to polymers with fewer structural defects (“head-to-head” or reverse monomer additions) in the molecular chains, i.e. polymers which are more crystalline. Thus the melting temperature

and crystallinity ratio are higher than those of the homopolymers with the same average molecular weights obtained by emulsion polymerization. Both polymerization processes are used by Solvay Specialty Polymers to make Solef® PVDF, depending on the specific grades.

Solef® PVDF homopolymers contain 59 % fluorine. The bond between this element, which is highly electronegative, and the carbon atom is extremely strong (dissociation energy of 460 kJ/mol).

Copolymers

In addition to the PVDF homopolymers, which are recognized worldwide for their excellent performance in a variety of applications, Solvay Specialty Polymers has developed a wide range of VF2-HFP copolymers, and VF2-CTFE copolymers to respond to specific needs of the market.

As a result of the Solvay Specialty Polymers manufacturing flexibility, PVDF can be tailored to meet a wide range of other property requirements.

Table 1: Characteristics of PVDFs on the market according to ASTM D3222 standard

Average Properties	Units	Type I Class 1	Type I Class 2	Type II
Density	g/cm ³	1.75–1.79	1.75–1.79	1.76–1.79
Melting temperature ⁽¹⁾	°C	156–162	162–170	164–180
Apparent melt viscosity⁽²⁾				
High viscosity	Pa·s	2,800–3,800	2,800–3,100	1,300–2,500
Average viscosity	Pa·s	2,300–2,800	1,300–2,800	1,300–2,500
Low viscosity	Pa·s	–	500–1,300	500–1,300

⁽¹⁾ According to the ASTM D3418 standard: +/- 1 mg, from 20 to 200 °C at 10 °C/min T_f = peak of the endothermic curve

⁽²⁾ According to the ASTM D3835 standard: $T^\circ = 232$ °C, $a = 60$ °, $L/D = 15$, $g = 100$ s⁻¹ (capillary rheometer)

Purity of the Resin

Solef® PVDF resins are extremely pure polymers and, unlike many other plastics, they do not require use of stabilizers, plasticizers, lubricants or flame-retardant additives. Thanks to their chemical inertness and to the virtual absence of released contaminations, natural Solef® PVDF resins are ideal materials for distribution of ultra-pure water and other chemically pure fluids used in the semi-conductor industry. High-purity Solef® PVDF grades are based on 100 % pure polymer without any added substance and are produced in a dedicated line to prevent

any possible cross-contamination. Pipes and equipment manufactured from these grades meet the most severe requirements of the semi-conductor industry. For instance, they easily comply with SEMI F-57 specification and they are capable of maintaining a level of resistivity of ultra-pure de-ionized water higher than 18 MΩ·cm.

Table 2 shows the results of extraction tests carried out with Solef® PVDF: after 7 day exposure to hot de-ionized water the concentration of all substances in water was below the detection limit.

Table 2: Ultra-pure water extraction data from Solef® PVDF pellets

Parameter	Detected Amount [µg/liter or ppb]	Detection Limit [µg/liter or ppb]
Aluminum	*	0.10
Barium	*	0.002
Boron	*	0.31
Calcium	*	0.10
Chromium	*	0.003
Copper	*	0.004
Iron	*	0.025
Lead	*	0.025
Lithium	*	0.003
Magnesium	*	0.02
Manganese	*	0.002
Nickel	*	0.07
Potassium	*	0.22
Sodium	*	0.25
Strontium	*	0.002
Zinc	*	0.015

* = below the detection limit

Comparison to Other Fluoropolymers

Table 3 presents a comparison of various properties of fluorinated polymers and PVDF.

While the perfluorinated polymers have a chemical resistance to a wider range of aggressive environments, their mechanical properties are inferior to those of PVDF. PVDF embodies an excellent compromise among general properties, combined with very easy processing and an advantageous quality-price ratio.

PVDF resin is characterized by a melting temperature which is significantly lower than that of the perfluorinated polymers. However, the mechanical properties (in particular the creep strength) of PVDF are superior in the temperature range between -20 and 150 °C (-4 and 302 °F). Table 4 illustrates this at 23 °C (73.4 °F).

In addition, the pressure resistance of Solef® PVDF pipes is superior to that of other polymers, as shown in Figure 1.

Conditions: Soak time: 7 days; Temperature: 85 °C (185 °F); Polymer to water ratio: 10 g/l; Pre-cleaning according to SEMI F40. Analytical method: ICPMS

Table 3: PVDF and the other fluorinated polymers

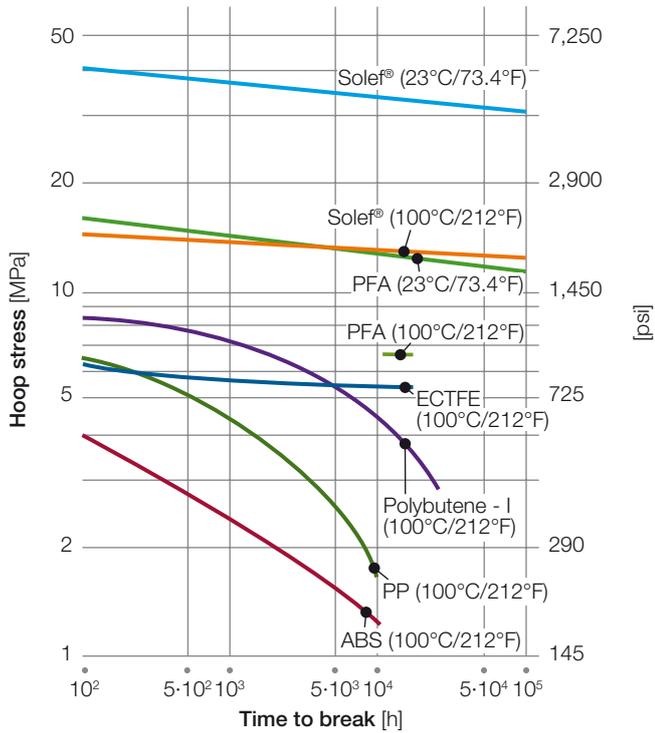
Average Properties	Units	PVDF					
		Homopolymer	PTFE	FEP	PFA	ETFE	ECTFE
Density	g/cm ³	1.78	2.17	2.15	2.15	1.72	1.68
Melting point	°C	160–172	330	270	305	–	242
	°F	320–342	626	518	581	–	468
Tensile properties at 23 °C (73 °F)							
Yield strength	MPa	45–55	10	12	16	25	30
	psi	6,500–8,000	1,450	1,700	2,300	3,600	4,300
Stress at break	MPa	40	30	22	30	40	54
	psi	5,800	4,300	3,200	4,300	5,800	7,800
Elongation at break	%	20–100	350	300	300	250	250
Modulus of elasticity	MPa	1,300–2,200	750	550	500	1,000	1,655
	kpsi	190–320	109	80	72.5	145	240
Shore D hardness	–	78	57	57	62	68	75
Deflection temperature under load of 1.82 MPa (264 psi)	°C	110–88	56	54	50	70	65
	°F	230–190	133	129	122	158	149
Thermal conductivity	W m ⁻¹ ·K ⁻¹	0.20	0.25	0.2	0.22	0.20	0.2
Coefficient of linear thermal expansion	K ⁻¹ ·10 ⁻⁶	120–140	130	110	120	90	100
Volume resistivity	ohm·cm	≥ 10 ¹⁴	10 ¹⁸	10 ¹⁸	10 ¹⁷	10 ¹⁴	10 ¹⁶

Table 4: Comparison of tensile creep characteristics of fluoropolymers at 23 °C (73.4 °F)

Material	Stress [MPa (psi)]	100 Hours Total Strain [%]	1,000 Hours Total Strain [%]
Solef® 1010	4 (580)	0.3	0.4
	8 (1,160)	0.7	0.9
	12 (1,740)	1.1	1.4
Halar® ECTFE	4 (580)	0.3	0.3
	8 (1,160)	0.7	0.8
	12 (1,740)	1.2	1.4
FEP	4 (580)	0.9	1.0
	8 (1,160)	3.3	3.8
	12 (1,740)	>40	Fail – full yield
Hyflon® PFA	4 (580)	1.2	1.3
	8 (1,160)	4.7	5.3
	12 (1,740)	39	52
PTFE	4 (580)	1	Fail – full yield
	8 (1,160)	10	Fail – full yield
	12 (1,740)	Fail – full yield	Fail – full yield

ASTM D2990, Compression molded plates, 3 mm thick

Fig. 1: Bursting resistance of pipes made of various fluorinated and non fluorinated polymers (at 23 °C/73.4 °F and 100 °C/212 °F)



Physical Properties

Structural Properties

Molecular Weight

Table 5 below presents several characteristics of the molecular structure of various grades of Solef® PVDF homopolymer and copolymer resins.

Crystalline Structure

The PVDF homopolymer is a strongly crystalline resin; while nearly transparent in the melting phase, it becomes translucent after crystallization.

Depending on processing conditions, several crystalline forms can be observed, the most important of which

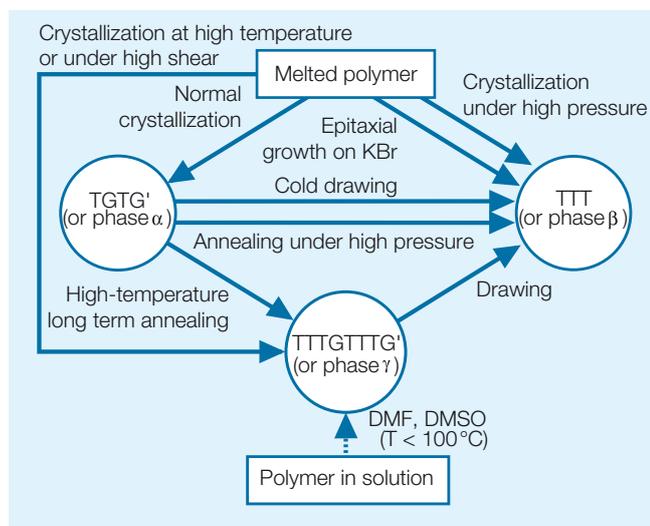
are designated by α , β and γ (or II, I and III, respectively). Phase α is the most commonly produced phase however this depends on certain processing or post-treatment parameters.

Figure 2 is a scheme of the various crystalline phases of PVDF which are obtained from the melted polymer or from a solution, and the modes of crystallization and/or (post-) treatment necessary to obtain them. These treatments are sometimes severe and generally do not correspond to conventional processing conditions.

Table 5: Molecular weights of Solef® PVDF resins measured by Gel Permeation Chromatography

Grades	Number Average Molecular Weight [$M_n \cdot 10^{-3}$]	Weight Average Molecular Weight [$M_w \cdot 10^{-3}$]	Polydispersity Index [U_N]
Homopolymers			
Solef® 1008	114	244	2.1
Solef® 1010	153	352	2.3
Solef® 1012	180	396	2.2
Solef® 1015	238	573	2.4
Copolymers			
Solef® 11008	127	268	2.1
Solef® 21508	132	240	1.8
Solef® 31508	149	274	1.8

Fig. 2: Various crystalline phases and modes of crystallization of PVDF (A. Lovinger)



In most cases, PVDF consists (in addition to an amorphous phase) of crystalline phase α , in the form of spherulites containing a very low fraction (often none) of phase γ .

Nevertheless, during drawing of films under special conditions, the form β is largely favored by molecular orientation. The films obtained are transparent and exhibit piezo- and pyro-electric properties, which are increased by polarization under an electric field applied in the direction of thickness.

Given the tremendous ease with which it crystallizes, PVDF homopolymer retains a high crystallinity level (above 50%) whatever the thermal treatment to which it is subjected during processing and any possible post-treatments. In addition, crystallinity increases significantly in the first days after processing (around 7 days), and stabilizes completely after 20 to 30 days by post-

crystallization in solid phase. Crystallinity is higher when the material is cooled more gradually, and above all when it is subjected to an annealing treatment at high temperature.

To develop an optimal crystallinity level which is stable over time and reduce internal stresses, it is useful after processing to perform an annealing at a temperature of 150 °C (302 °F) during 30 min/cm (75 min/in) of wall thickness, followed by a slow cooling.

Please contact Solvay Specialty Polymers for more details about the annealing procedure.

Rheological properties Melt Flow Index (MFI) (ASTM D1238, DIN 53 735)

Table 6 presents typical values at 230 °C (446 °F) for various Solef® PVDF grades.

Table 6: Average MFIs at 230 °C (446 °F) under different loads

Grades	Average Melt Flow Indices (MFI) at 230 °C (446 °F) in g/10 min Under a Load of		
	2.16 kg	5 kg	10 kg
Solef® PVDF resins			
1006	40	–	–
1008, 6008, 9009, 11008, 21508	8	24	–
31508	5	15	–
1010, 6010, 11010, 21510	2	6	18
1012, 6012	0.5	1.5	5
460	–	0.6	2.6
60512	–	1	3
Solef® PVDF compounds			
3108/0903	1.5	4.5	13.5
3208/0150	8	24	–
8808/0902	3	9	24

Figure 3 represents, for Solef® PVDF homo- and copolymer resins, the existing correlations between the MFIs under 5 kg and under 2.16 kg, as well as the MFIs under 10 kg and under 5 kg (at 230 °C/446 °F).

Melt Viscosity

Figures 4 through 7 give the apparent viscosities η of various Solef® grades as a function of the shear rate $\dot{\gamma}$ (s^{-1}).

Figure 8 gives the variation of the apparent viscosity at $\dot{\gamma} = 100 s^{-1}$ vs. temperature for several homo- and copolymer grades.

Fig. 3: Relation between MFIs at 5 and 2.16 kg and between MFIs at 10 and 5 kg

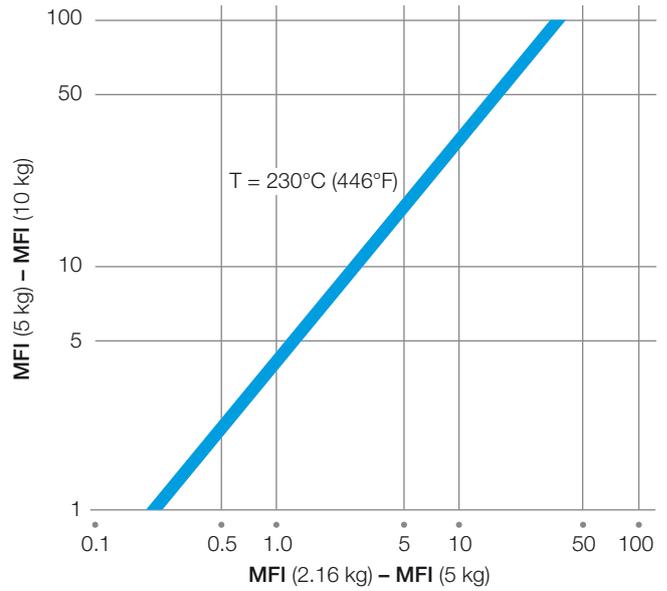


Fig. 4: Melt viscosity at 220 °C (428 °F) of various Solef® PVDF copolymer grades

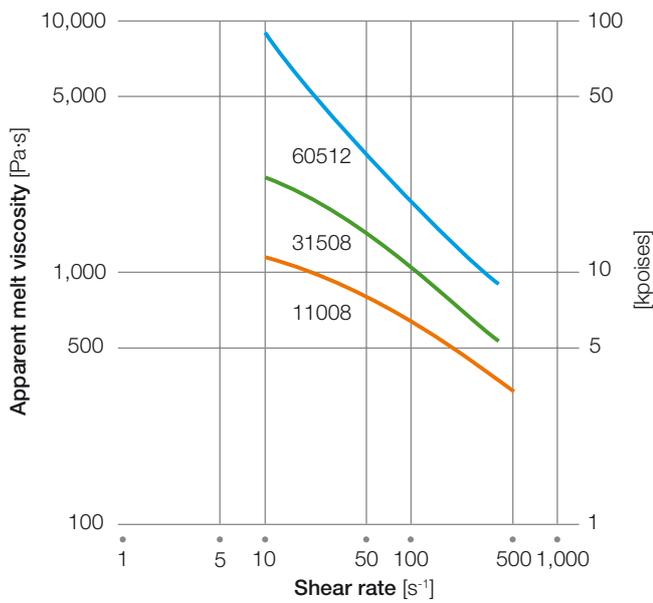


Fig. 5: Melt viscosity at 200 °C (392 °F) of the 1000 series Solef® PVDFs

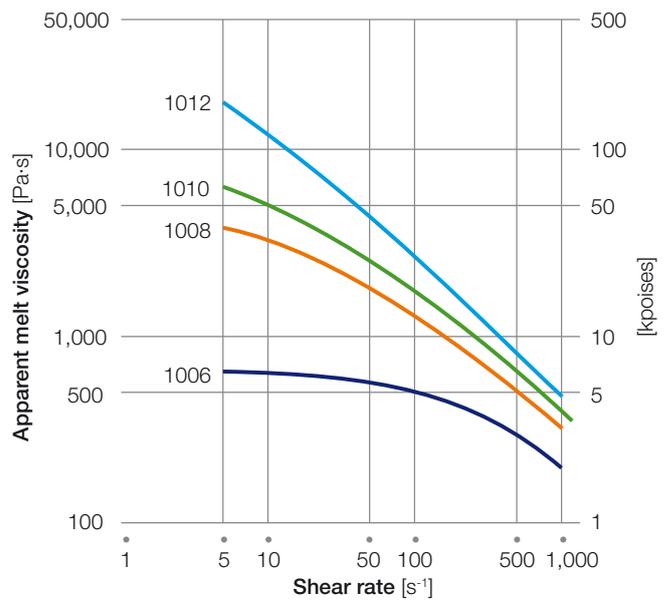


Fig. 6: Melt viscosity of Solef® 1010 at various temperatures

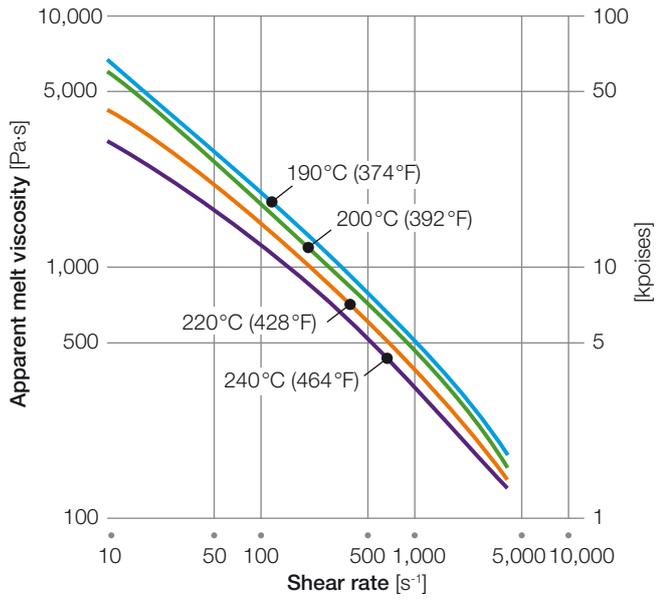


Fig. 7: Melt viscosity of Solef® 11008 at various temperatures

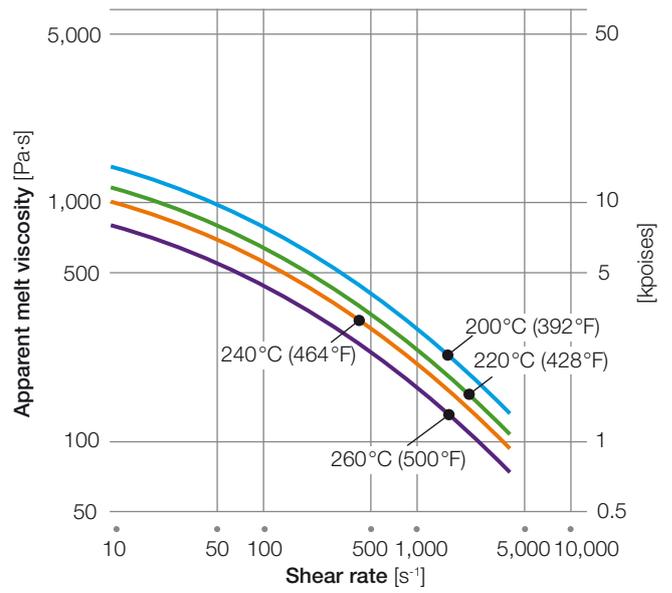
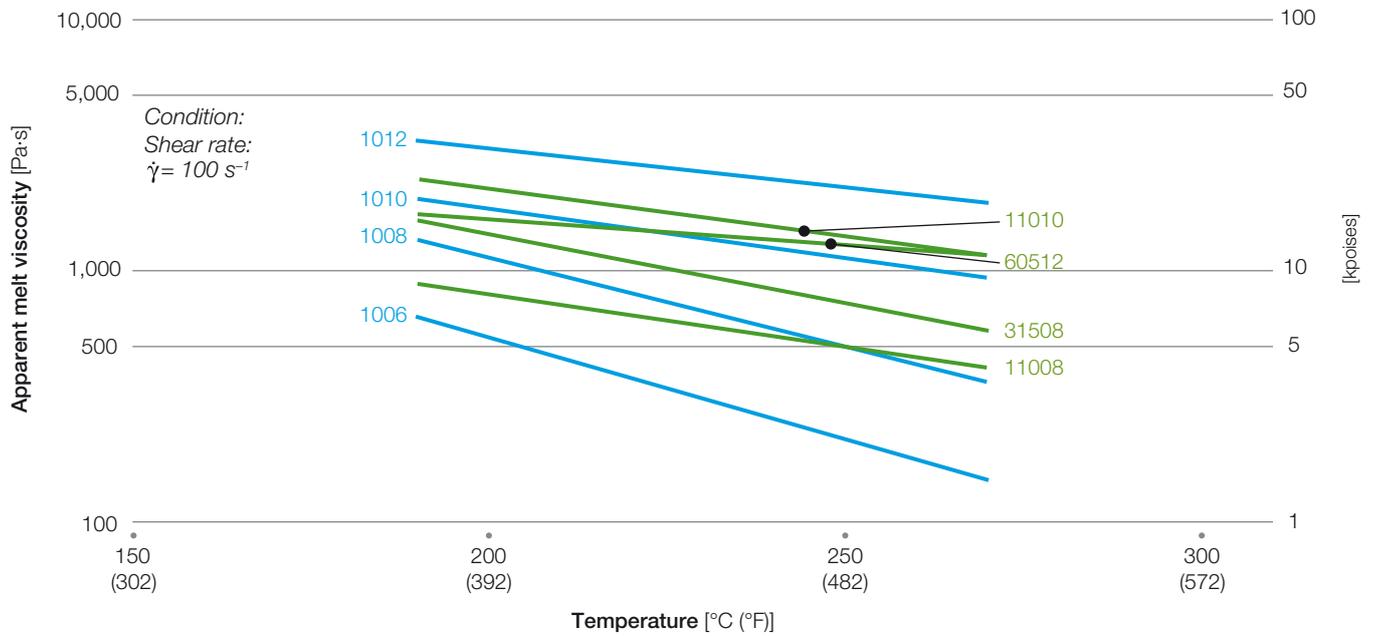


Fig. 8: Melt viscosity at 100 s^{-1} of various Solef® PVDF grades vs. temperature



Thermophysical Properties

DSC Curves

The crystalline melting temperatures and corresponding heats of fusion ΔH_f of Solef® PVDF resins, recorded by DSC under defined operating conditions (ASTM D3418), are presented in Table 7.

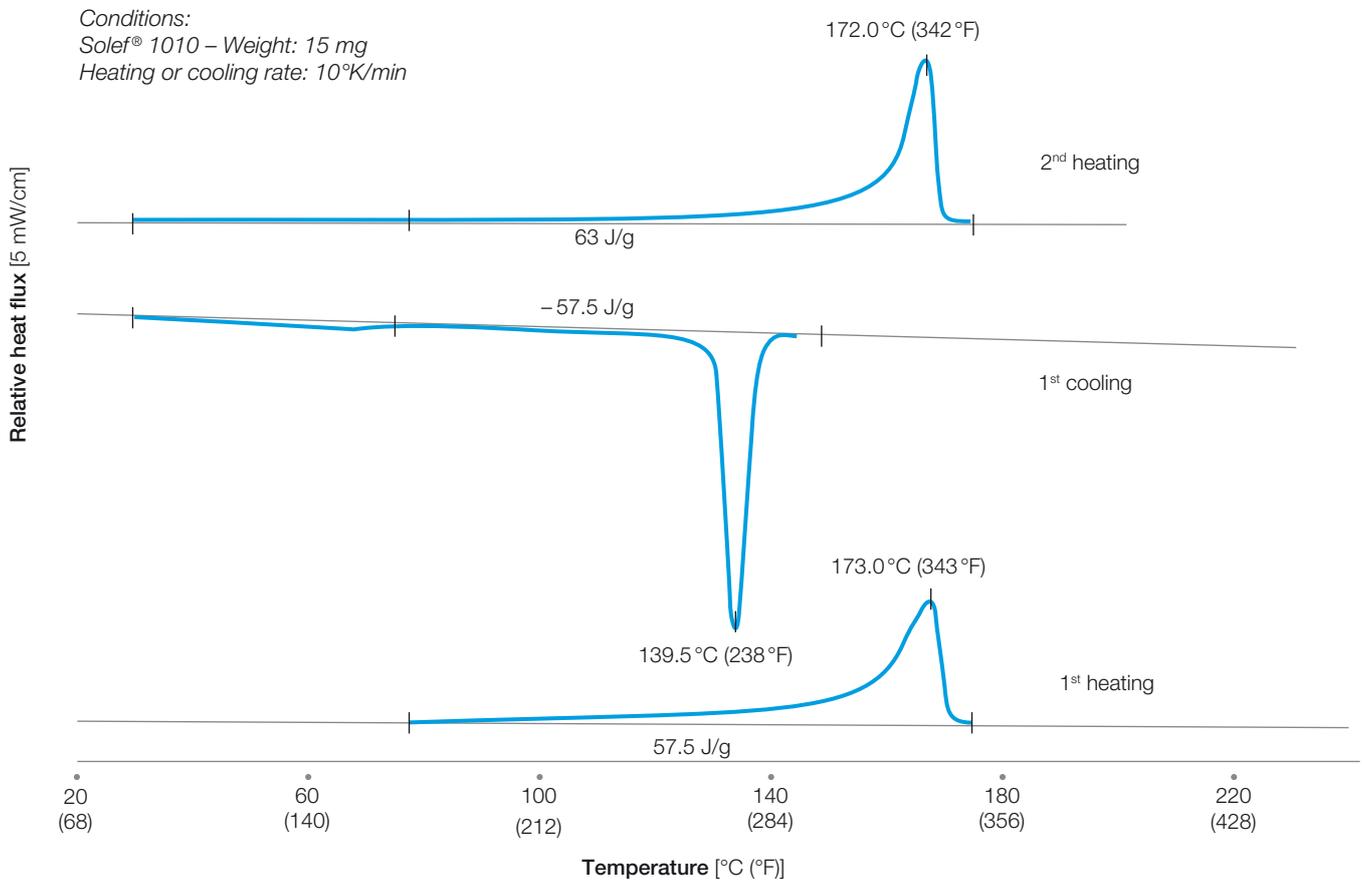
Figure 9 illustrates the relative heat flux curves as a function of the temperatures obtained in DSC of Solef® PVDF grade 1010 during a first heating up to 250 °C (482 °F), a cooling down to room temperature, and a second heating above the melting zone.

Table 7: Thermophysical data recorded by DSC

Grades	Melting Temperature T_f [°C (°F)]	Heat of Fusion ΔH_f [J/g (Btu/lb)]	Calculated Rate of Crystallinity [%]
Solef® PVDF homopolymers			
1000 and 6000 series	171–172 (340–342)	59–64 (25–28)	56–61
9009	162–168 (324–334)	53–60 (22–26)	52–55
460	160 (320)	46 (20)	44
Solef® PVDF copolymers			
11008 and 11010	160 (320)	37–39 (16–17)	–
21510	135 (275)	23 (9.9)	–
31508	168 (334)	26 (11.2)	–
60512	171 (340)	51 (22)	–

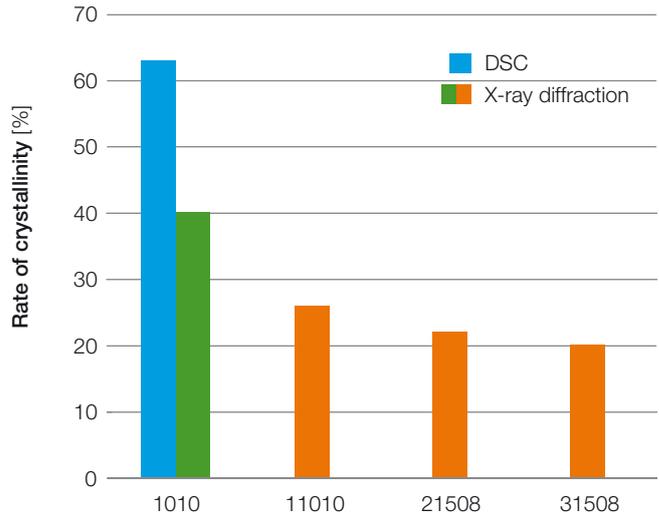
Conditions: Samples taken from pellets: weight of 15 ± 1 mg Measurements by DSC performed during the second heating (first heating to 250 °C/482 °F), rate of heating: 10 K/min ΔH_f measured between 80 °C (176 °F) and 2 to 3 °C (4 to 5 °F) higher than the end of the melting phases

Fig. 9: DSC curves of Solef® 1010



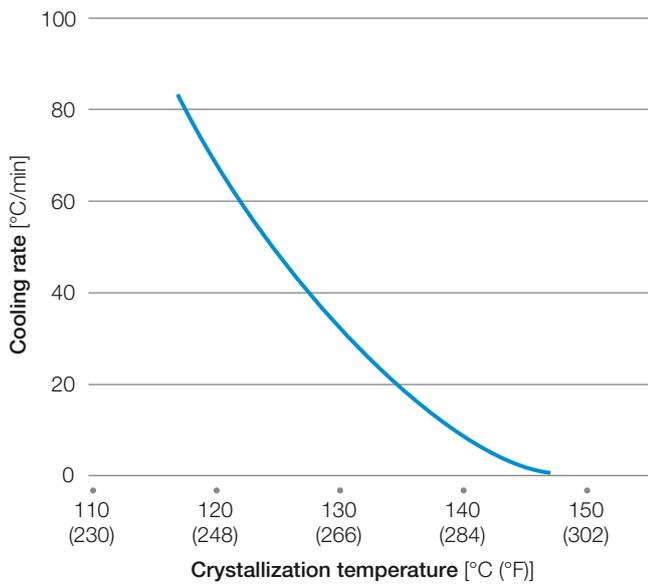
By way of comparison, the rate of crystallinity of Solef® PVDF homopolymers and copolymers, measured by X-ray diffraction, are shown in Figure 10. The rate of crystallinity is calculated in comparison to an assumed “100% crystalline” PVDF whose heat of fusion (obtained by extrapolation of measurements relating to increasing crystallinity levels) is estimated at 105 J/g (45.1 Btu/lb).

Fig. 10: Rate of crystallinity measured by DSC and X-ray diffraction



Thermophysical Data by DSC

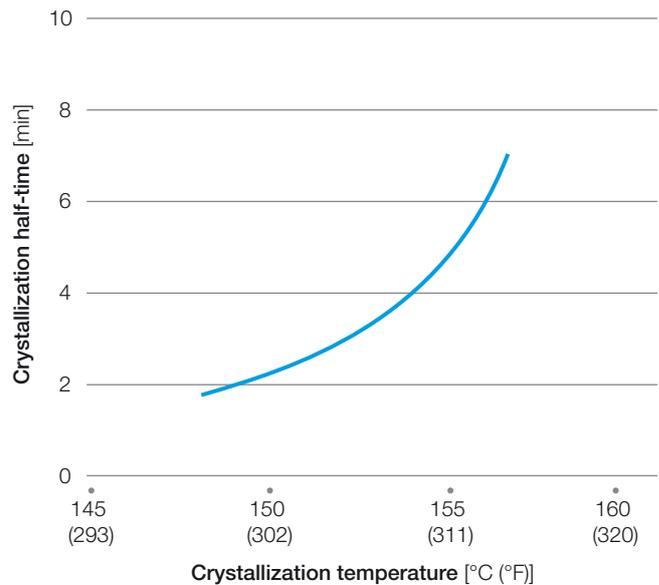
Fig. 11: Incidence of cooling rate on crystallization temperature recorded by DSC (non-isothermal crystallization)



Conditions:
Solef® 1010

- Pre-treatment: melting 5 min at 250°C (482°F)
- Non-isothermal crystallization

Fig. 12: Variation of crystallization half-time as a function of temperature (isothermal)



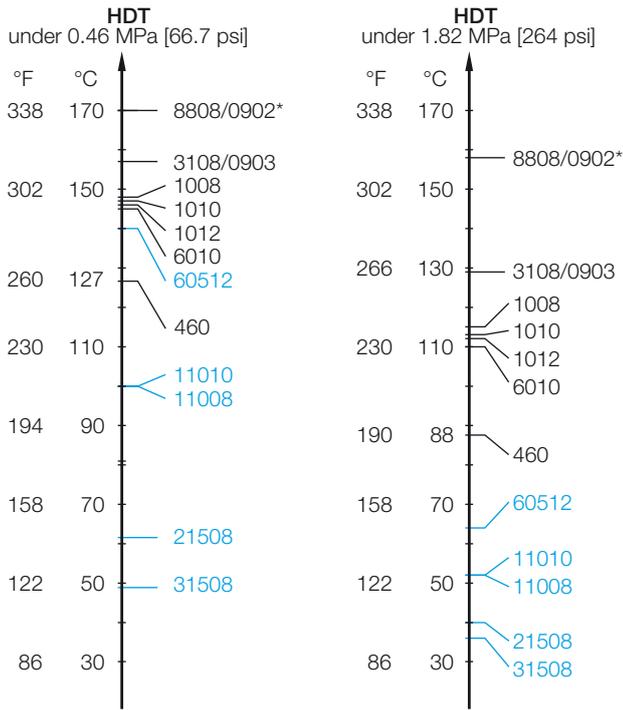
Conditions: Solef® 1010, Examination under polarizing microscope of the growth of the spherulites

Thermal treatment of the sample:

- Melting 5 min at 250°C (482°F)
- Quenching at the rate of 80°C/min until the chosen crystallization temperature T_c
- Isothermal crystallization at temperature T_c

Fig. 13: HDT of various Solef® PVDF grades

Conditions: Annealed compression moulded plates
* Injection molded specimens



Softening Temperatures
Heat Deflection Temperature (HDT)
(ASTM D648)

The heat deflection temperature under load (HDT) indicates the short term thermal behavior of a material under load. It is determined under a flexural stress of either 1.82 MPa (264 psi) or 0.46 MPa (66.7 psi).

Figure 13 presents the HDT values of various Solef® PVDF grades.

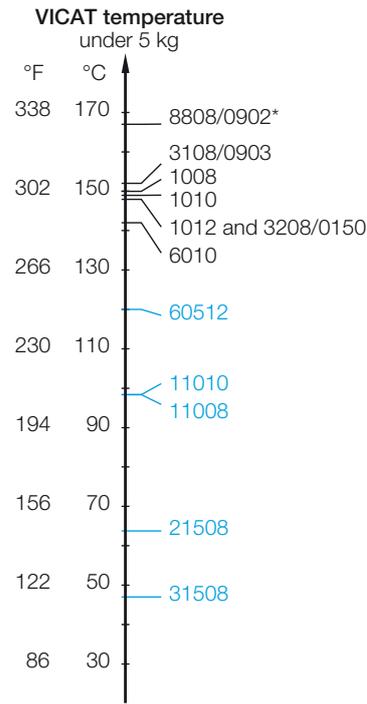
VICAT Softening Temperature
(ISO 306)

Like HDT, the VICAT softening temperature is also a short term thermal behavior index of a material under a point load of 1 or 5 kg (2.2 or 11.0 lb).

Figure 14 presents the VICAT softening temperature (5 kg/11.0 lb) for various Solef® PVDF grades.

Fig. 14: VICAT softening temperature (5 kg/11.0 lb) of various Solef® PVDF grades

Conditions: Annealed compression moulded plates
* Injection molded specimens



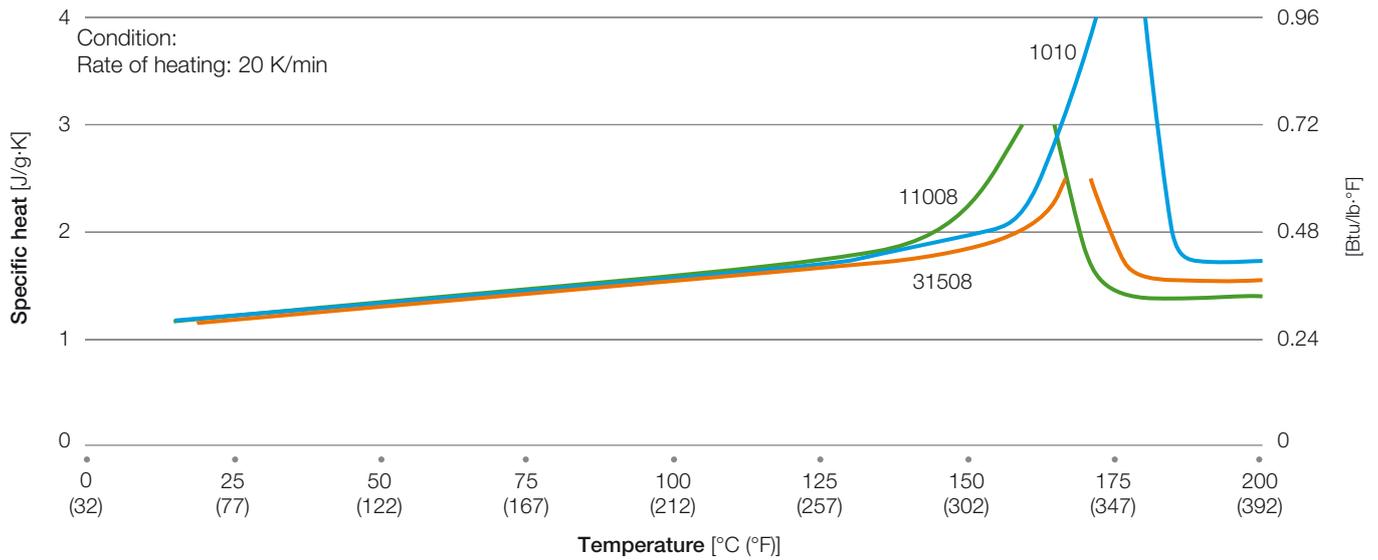
Specific Heat

The specific heat Cp measured by adiabatic calorimetry, varies as a function of the temperature. It is presented in Figure 15 for Solef® 1010, 11008 and 31508.

Cp increases slightly between 20 and 130 °C (68 and 266 °F). Beyond this temperature, the value of Cp presents a peak corresponding to the melting zone which becomes sharper as the resin is more crystalline. Beyond this zone, the variation of Cp is analogous to that recorded in the vicinity of room temperature.

Outside the crystalline melting zone, Cp varies approximately linearly from 1.2 J/g·K (0.29 Btu/lb·°F) at 20 °C (68 °F) to 1.8 J/g·K (0.43 Btu/lb·°F) at 130 °C (266 °F), whatever the resin. It varies from 1.4 to 1.7 J/g·K (0.33 to 0.41 Btu/lb·°F) at 200 °C (392 °F) depending on the type of resin.

Fig. 15: Specific heat of Solef® PVDF vs. temperature



Thermal Conductivity

The thermal conductivity λ of Solef® 1010 was measured as a function of the temperature, using the heating wire method (ASTM D2326-70). It is presented in Figure 16.

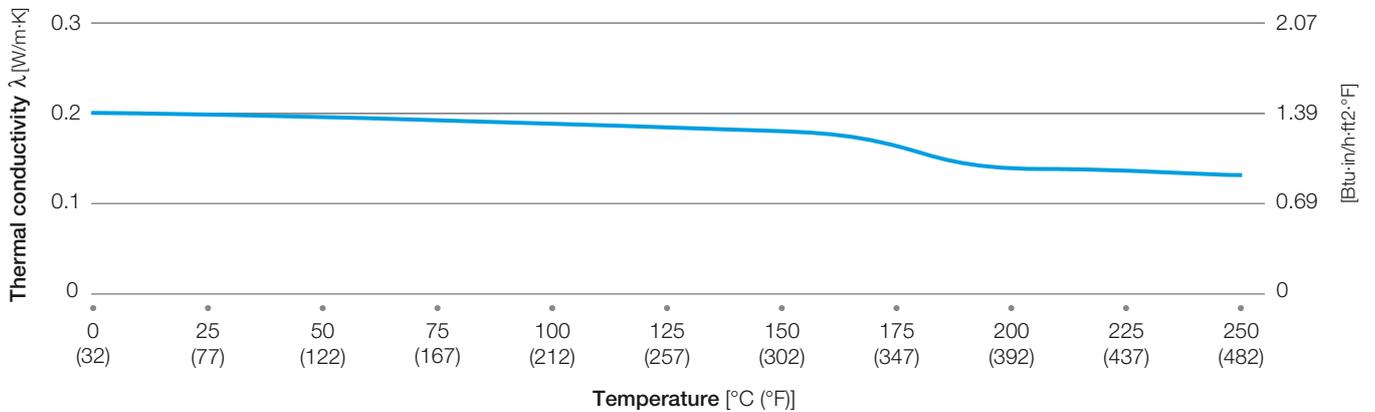
At 20 and 200 °C (68 and 392 °F) λ is respectively 0.20 and 0.14 W/m·K (1.39 and 0.97 Btu·in/h·ft²·°F).

Table 8 brings together the values of λ at 20 °C (68 °F) for various Solef® PVDF resins and compounds.

Table 8: Thermal conductivity of Solef® PVDF

Grades	Thermal Conductivity λ [W/m·K (Btu·in/h·ft ² ·°F)]
PVDF homopolymers	
Solef® 1000 and 6000 series	0.20 (1.39)
Solef® 460	0.19 (1.32)
PVDF copolymers	
Solef® 11010	0.19 (1.32)
Solef® 21508	0.18 (1.25)
Solef® 31508	0.18 (1.25)
Solef® 60512	0.20 (1.39)
PVDF compounds	
Solef® 3108/0903	0.30 (2.08)
Solef® 3208/0150	0.20 (1.39)
Solef® 8808/0902	0.33 (2.29)

Fig. 16: Thermal conductivity of Solef® 1010



Coefficient of Linear Thermal Expansion (ASTM D696)

The coefficient of linear thermal expansion α of Solef® PVDF was measured by thermal analysis TMA over a wide range of temperatures, from -40°C (-40°F) up to the maximum service temperature. The procedure consisted of a measurement of relative length of the specimen under a temperature increasing. The average coefficient α was determined in two temperature ranges:

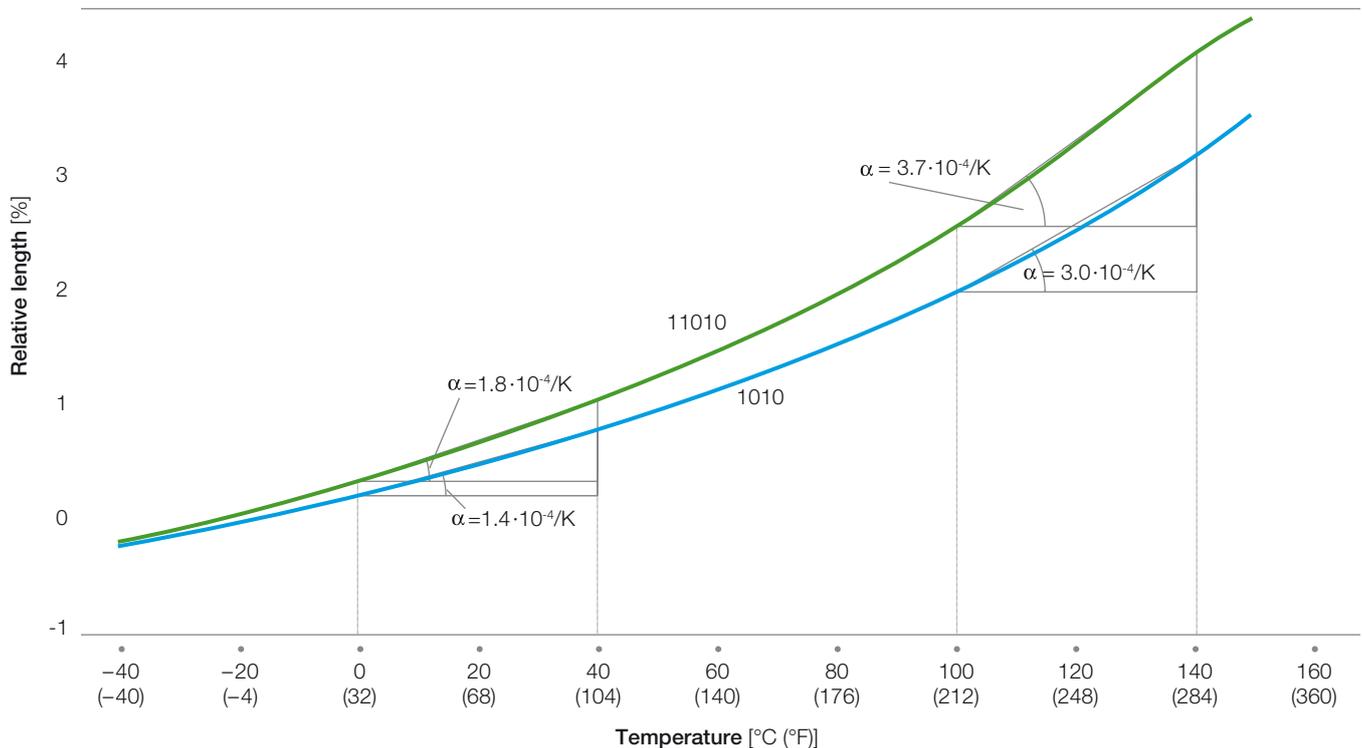
α ($20^{\circ}\text{C}/68^{\circ}\text{F}$): from 0 to 40°C (32 to 104°F)

α ($120^{\circ}\text{C}/248^{\circ}\text{F}$): from 100 to 140°C (212 to 284°F)

Figure 17 presents the thermal expansion curves for Solef® 1010 and 11010 grades and gives the values of α in these temperature ranges.

In addition, Table 9 brings together the values of α for various Solef® PVDF grades.

Fig. 17: Thermal expansion curve of Solef® PVDF measured by TMA



Conditions: Annealed compression moulded plates, Heating rate: 10 K/min

Coefficient α determined

– between 0 and 40°C (32 and 104°F)

– between 100 and 140°C (212 and 284°F)

Table 9: Coefficient of linear thermal expansion for Solef® PVDF

Grades	Coefficient of Linear Thermal Expansion [$10^{-4}/\text{K}$ ($10^{-4}/^{\circ}\text{F}$)]	
	at 20°C (68°F), (0 to $40^{\circ}\text{C}/32$ to 104°F)	at 120°C (248°F), (100 to $140^{\circ}\text{C}/212$ to 284°F)
Solef® 1000 series	1.35–1.45 (0.75–0.81)	3.00–3.30 (1.67–1.83)
Solef® 460	1.20–1.30 (0.67–0.72)	–
Solef® 11010	1.80 (1.0)	3.70 (2.06)
Solef® 31508	1.40* (0.78)*	–
Solef® 60512	1.55* (0.86)*	–
Compounds		
Solef® 3108/0903	1.30* (0.72)*	–
Solef® 3208/0150	1.30* (0.72)*	–
Solef® 8808/0902	0.80* (0.44)*	–

* Measurements according to the ASTM D696 standard

Density

(ISO R 1183, ASTM D792)

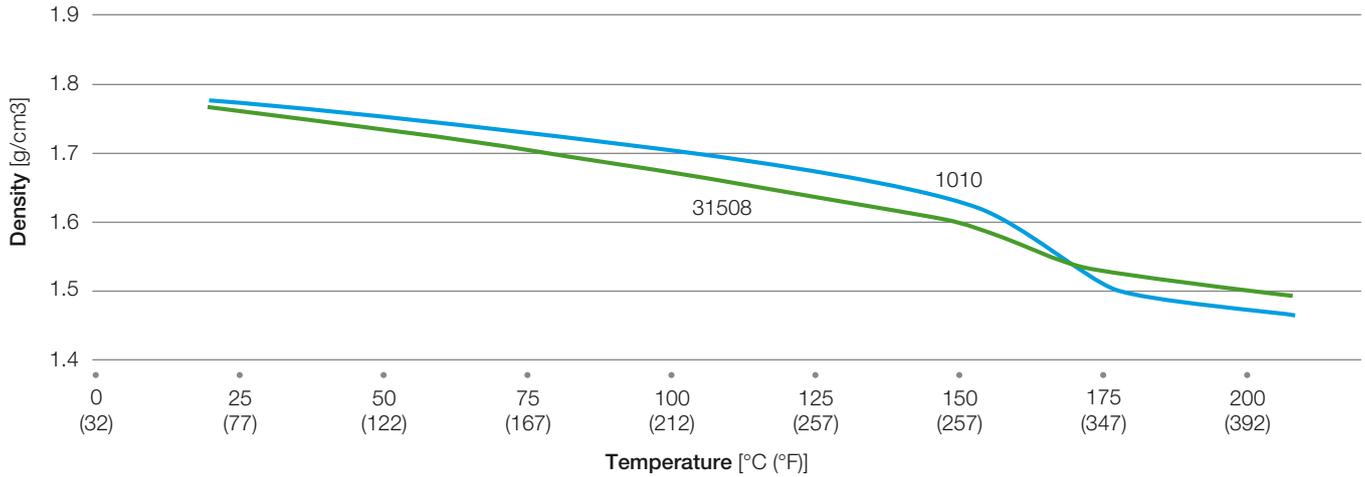
The density ρ (g/cm³) at room temperature of PVDF homo- and copolymer resins is between 1.75 and 1.79, whatever the grade. The density variation vs. temperature is presented in Figure 18 for Solef® 1010 homopolymer and Solef® 31508 copolymer. Table 10 presents the densities at 23 °C (73.4 °F) of filled or reinforced PVDF.

In addition, the bulk density of pellets, is between 0.94 and 1.00 g/cm³, whatever the grade of the resin.

Table 10: Density at 23 °C (73.4 °F) of Solef® PVDF compounds

Grades	Density [g/cm ³]
3108/0903	1.83
3208/0150	1.80
8808/0902	1.78

Fig. 18: Density of Solef® PVDF vs. temperature



Specific Volume – pvT Curves

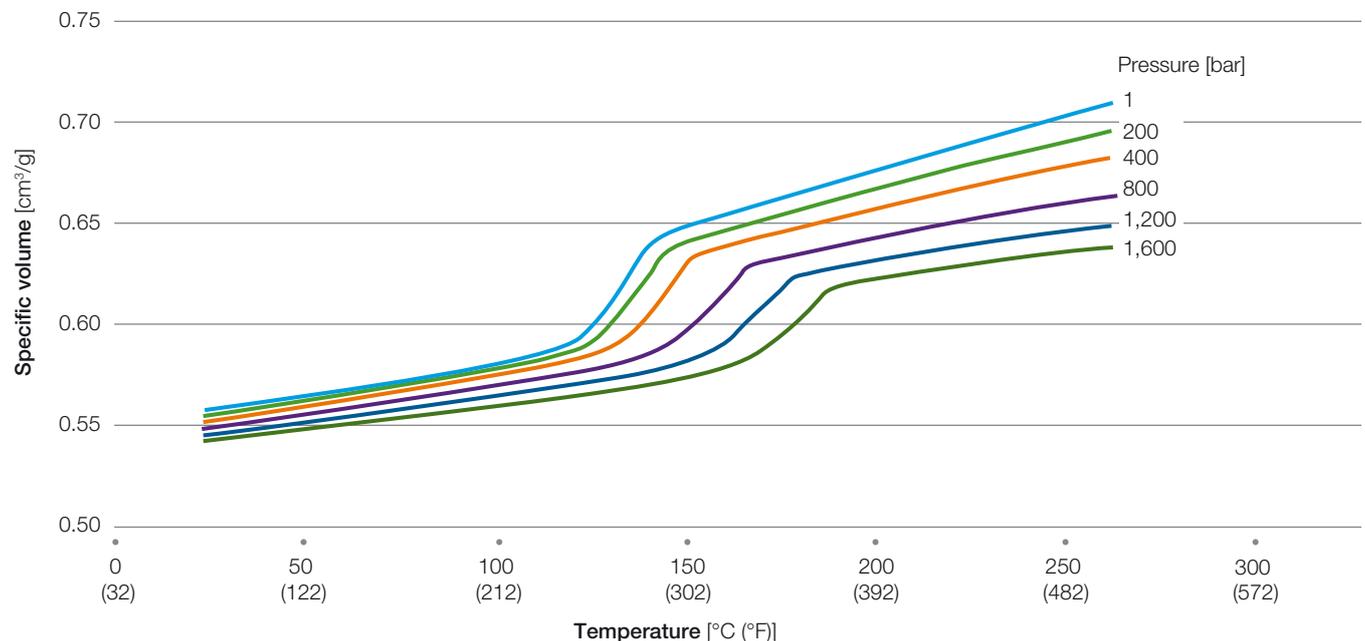
The specific volume v (cm³/g) of Solef® 1008 was measured under different pressures as a function of temperature. The variation curves are presented in Figure 19.

This diagram (or pvT curves) is obtained by measuring the volume occupied by a mass of material introduced into a

cylindrical space, and then brought to fusion and finally cooled under various pressures between 1 and 1,600 bars.

These curves are of special interest for injection molding, because they make it possible to optimize the holding phase of the injection molding cycle.

Fig. 19: pvT curves of Solef® 1008

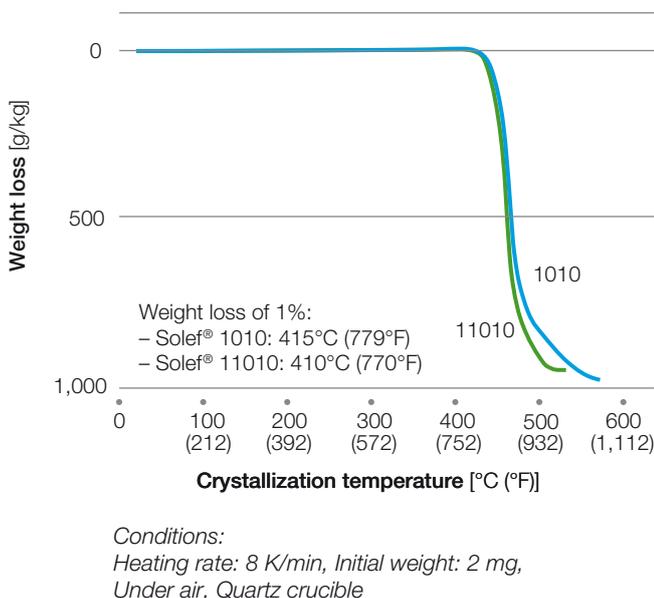


Short Term Thermal Stability – Thermogravimetric Analysis (TGA)

One method for evaluating the thermal stability of a material is the thermogravimetric analysis. In this test, a small sample of test material is heated while its weight is constantly monitored. The test is usually performed either in an inert nitrogen atmosphere or in air.

Figure 20 shows the result of thermogravimetric analysis under air of Solef® 1010 and 11010, performed at a heating rate of 8 °K/min. The curves for these two products are very similar in first phases of decomposition and weight loss.

Fig. 20: Thermogravimetric analysis under air of Solef® PVDF



The processing of PVDF resins is generally performed at temperatures between 200 and 250 °C (392 and 482 °F), well below the decomposition temperature. It is imperative not to exceed a temperature of 350 °C (662 °F), above which the polymer rapidly decomposes (significant dehydrofluorination).

The decomposition of PVDF can be sharply accelerated by the presence of certain contaminations, even in low quantities, such as light metals like boron, titanium, and aluminum. (See section “Processing Basics and Safety”). It is recommended to consult Solvay Specialty Polymers before adding any fillers or pigments to PVDF.

Surface Properties

Angle of Contact and Surface Tension

The angle of contact θ of a drop of liquid on a material and the wetting surface tension γ_s give an indication about the wettability of this material.

If the angle θ is small and the surface tension γ_s is high, it means that the material is easily wettable. If the liquid is water, the surface is called “hydrophilic”. If the angle θ is large and the surface tension γ_s is low, the material is hard to wet and, in the case of water, is called “hydrophobic”. Since the adherence to a material is linked to the value of its surface tension γ_s , if this value is low the material presents anti-adhesive characteristics. Table 11 gives the values of the angle of contact θ for water and the surface tension of various polymers compared with those for PVDF.

Angle θ for PVDF is higher than 65–70°, which classes it in the category of hydrophobic materials. The moderate surface tension explains (among other things) its anti-fouling and anti-staining characteristics.

Table 11: Angle of contact and surface tension of PVDF and other thermoplastics (20 °C/68 °F)

Polymer	Angle of Contact θ (water) [Degrees]	Surface Tension γ_s [mJ/m ²]	Surface Tension γ_c^* [mJ/m ²]
PTFE	108	19	18
PCTFE	84	31	31
PVDF	80	34	25
HD – PE	88	33	31
PET	76	47	43
PA 6.6	72	47	46

Method for measuring γ_s : measurement of the static angle θ for liquids with various dispersive and polar interactions; * Critical surface tension γ_c (Zisman method): values taken from the technical literature

Hardness Shore hardness (ISO 868, ASTM D2240)

Table 12 gives the Shore D hardness of various Solef® PVDF grades.

Table 12: Shore D hardness of Solef® PVDF

Grades	Shore D Hardness
Solef® PVDF resins	
1008, 6008, 9009 and 460	78
6010	77
11010	72
31508/0003	53
60512	70
Solef® PVDF compounds	
3208/0150	78
3108/0903 and 8808/0902	82

Ball Hardness

Ball hardness was measured on compression molded plates according to the DIN 53456 standard for Solef® 1010 and 11008 grades (see Table 13).

Table 13: Ball hardness of Solef® PVDF

Grades	Hardness [N/mm ²] (F = 132 N, after 30 s)
1010	
as molded	58
annealed	59
11008	
as molded	33
annealed	37

Rockwell Hardness (ASTM D785)

Table 14 presents the Rockwell M and R hardness of Solef® 1010 and 11008, measured on compression molded plates.

Table 14: Rockwell hardness of Solef® PVDF

Grades	Rockwell Hardness	
	M	R
1010		
as molded	68	109
annealed	69	110
11008		
as molded	11	94
annealed	18	96

Roughness

Surface quality strongly depends on processing conditions. By optimizing the manufacturing process it is possible to produce Solef® PVDF sheets and pipes having extremely low roughness.

Examples of R_a values (average of the distance of peaks and valleys from the average surface level) measured on various Solef® PVDF items are reported in Table 15.

These roughness values match the very demanding specifications of semiconductor producers who require perfectly smooth surfaces in their installations for transporting ultra-pure water and chemicals.

Even lower roughness values can be reached after careful optimization of extrusion conditions, as shown below in the Atomic Force Microscopy (AFM) pictures. By numerical elaboration of the AFM scans roughness values as 0.032 μm for the 50 μm \times 50 μm scan and 0.018 μm for the 5 μm \times 5 μm scan were calculated (average on 8 measurements).

Table 15: Average roughness of internal walls of extruded Solef® 1010 pipes and sheets

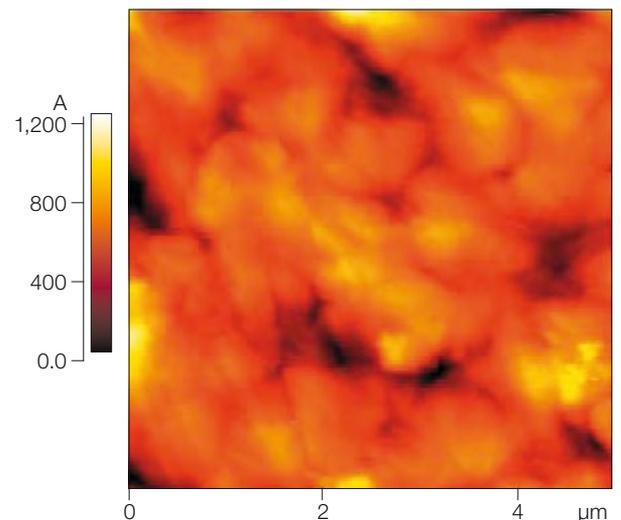
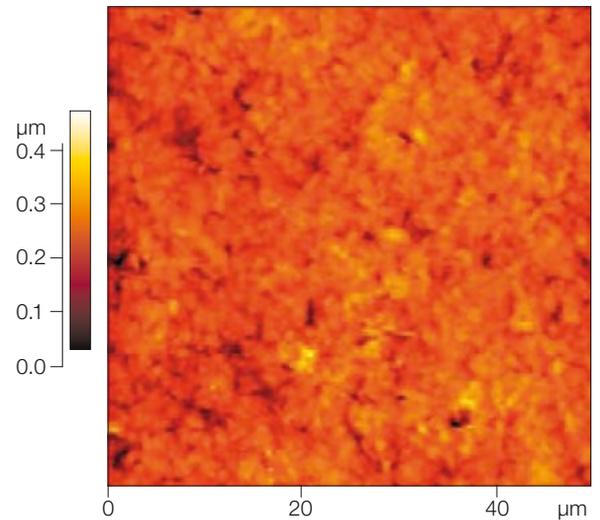
Type of Object	Roughness R_a [μm]	
	M*	T*
Pipe \varnothing = 63 mm (2.48 in)	0.08	0.06
Pipe \varnothing = 110 mm (4.33 in)	0.09	0.10
Extruded sheet		
Thickness = 3 mm (0.12 in)	0.04	0.04
Extruded sheet		
Thickness = 10 mm (0.39 in)	0.08	0.19

* M: machine direction; T: transversal direction

Atomic Force Microscopy Topographic Images of Solef® PVDF Pipes

D = 63 mm pipes.

Scanned surfaces: 50 μm \times 50 μm and 5 μm \times 5 μm .



Coefficient of Friction (ASTM D1984)

The coefficient of friction is strongly influenced by parameters such as surface roughness, sliding rate, contact pressure, lubrication, etc.

According to the ASTM D1984 method, the coefficients μ_0 (static) and μ (dynamic) are evaluated under a load of 2 N (0.45 lbf) and a displacement rate of 150 mm/min.

The values appear in Table 16. Given the importance of the surface condition of the samples, variable according to their mode of production and their form (films, sheets, plates), these values are given in the form of a variation range.

The Solef® 3208/0150 grade was specially developed to lower the coefficient of friction and ensure a significantly lower variability of its value with respect to the surface condition (see Table 17). It is particularly well-suited for the production of ball valve housings.

Table 16: Coefficients of friction of Solef® PVDF

Surfaces in Contact	Friction Coefficient	
	μ_0 static	μ dynamic
PVDF homopolymer	0.20–0.40	0.20–0.35

Tests on itself, on glass, on low carbon steel of roughness $R_a = 0.06 \mu\text{m}$, on rigid PVC

Table 17: Coefficient of friction of Solef® 3208/0150 grade

Surfaces in Contact	μ_0 static	μ dynamic
Solef® 3208/0150	< 0.20	< 0.20

Tests on itself, on glass, on low carbon steel of roughness $R_a = 0.06 \mu\text{m}$, on rigid PVC

Abrasion Resistance

The abrasion resistance was determined using a TABER abrasion test, which measures the wear of a material by friction on an abrasive substance. The specimen is fixed to a turning plate and in contact with an abrasive disk loaded with a weight of 9.81 N (2.21 lbf). The abrasion resistance is given by the weight lost of the specimen after a certain number of revolutions.

Table 18 presents the results with PVDF in comparison with other materials. The tests were done after 1,000 revolutions, using “Calibrase CS-17 and CS-10” grinding wheels. According to the TABER test, PVDF behaves like an abrasion-resistant material comparable to polyamide 6.

In addition, Table 19 presents the AKRON abrasion test, in accordance with the BS 903 standard, performed on Solef® PVDF in comparison with other materials.

Table 18: Abrasion resistance of PVDF (AKRON test)

Materials	Abrasion [% vol]
Solef® PVDF	0.18
NBR rubber	0.19
Rigid PVC	0.24
PP	0.51

Table 19: Abrasion resistance of PVDF (TABER test)

Materials	Abrasive Disk	Weight Loss [mg/1000 rev.]
Solef® PVDF homopolymers	CS-10	5–10
	CS-17	7–10
Solef® 21508 and 31508	CS-10	5–8
PA 6	CS-10	5
	CS-17	4–8
ECTFE	CS-10	13
	CS-17	25
PP (homopolymers)	CS-10	15–20
	CS-17	18–28
304 stainless steel	CS-10	50
PTFE	CS-10	500–1,000

Solubility

Homopolymer PVDF swells in strongly polar solvents such as acetone and ethyl acetate, and is soluble in aprotic polar solvents such as dimethylformamide and dimethylacetamide.

Table 20 presents several solubility results in various solvents. The reported values are the maximum quantity of resin that can be introduced into the solution without formation of gel at 23 °C (73,4 °F).

Table 20: Solubility of Solef® PVDF homo- and copolymer resins in various solvents at 23 °C (73.4 °F)

Solvent	Solubility [g/kg of solvent]		
	Solef® 1010	Solef® 11010	Solef® 21508
Acetone	~ 0	15	520
Methyl ethyl ketone	< 10	< 10	430
Cyclohexanone	< 10	< 10	< 10
Ethyl acetate	< 10	< 10	< 10
γ butyrolactone	< 10	< 10	< 10
Dichloromethane	< 10	< 10	–
Dimethylformamide	200	220	440
Dimethylacetamide	200	210	350
Tetrahydrofuran	< 10	–	500
N-methylpyrrolidone	240	–	370
Acetone + Tetrahydrofuran (1/1 vol)	< 10	–	480
Tetrahydrofuran + Dimethylformamide (1/1 vol)	230	–	–
Dimethylformamide + Methyl ethyl ketone (38/62 vol)	260	270	–

Optical Properties – Appearance

Solef® PVDF are milky white, translucent polymers. In thicknesses of less than 100 µm, they become transparent when the crystallinity is lowered by water quenching after melting.

Refractive Index

The refractive index of Solef® PVDF at 23 °C for 589 nm light is:

$n = 1.42$ for the homopolymer resins

$n = 1.41$ for the copolymer resins

UV, Visible and IR Absorption Spectra

Figure 21 presents the incident light extinction coefficient as a function of wavelength (according to the Lambert-Beer law) between 200 and 900 nm, in the case of compression molded Solef® 1010 plates from 1 to 4 mm of thickness.

In addition, the absorption spectra in the visible, UV and IR ranges, evaluated on films, are given in Figures 22 through 24.

Transparency, Haze, Gloss (ASTM D1746, ASTM D1003 and ASTM D2457)

The optical properties in white light are measured under various aspects:

- Total light transmission through the object
- Transparency or fraction of the transmitted light deflected by more than 0.1° of solid angle
- Haze or fraction of the transmitted light deflected by more than 5° of solid angle
- Gloss or luminosity according to a given angle of reflection

Solef® PVDF films have good optical properties, as shown by Table 21. These characteristics depend on the processing conditions, surface quality, etc., as well as the film thickness.

Fig. 21: Extinction coefficient vs. wavelength for Solef® 1010

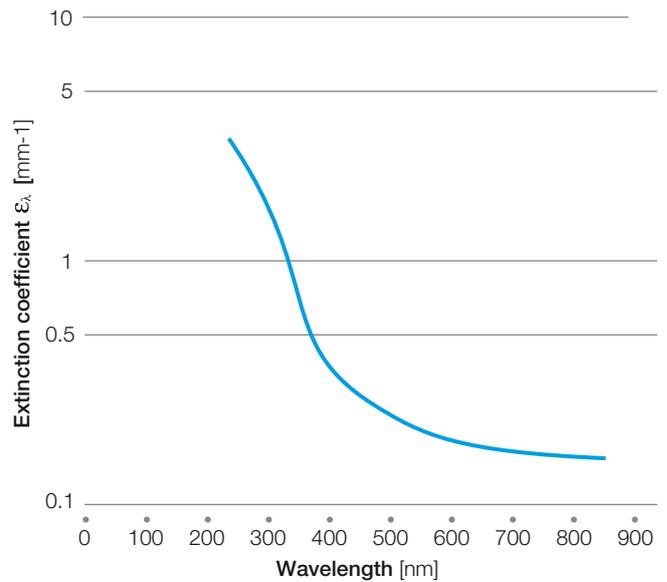


Fig. 22: Absorption spectra of Solef® 1008 in UV and visible ranges – influence of thickness

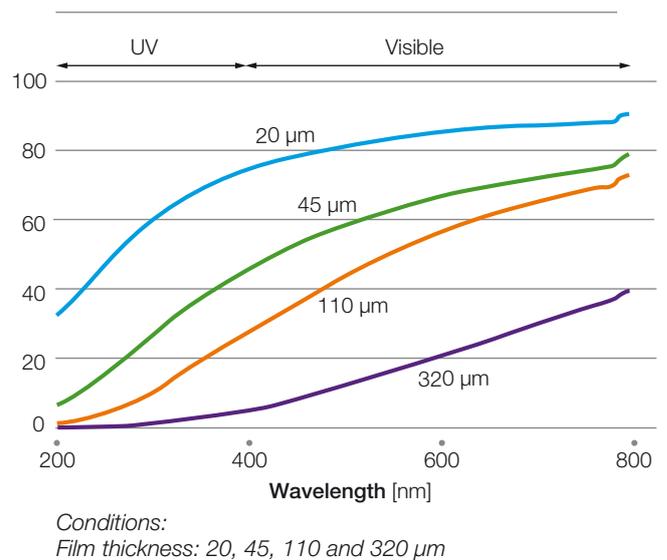


Fig. 23: IR-ATR spectrum of Solef® 1008 homopolymer film (transmission)

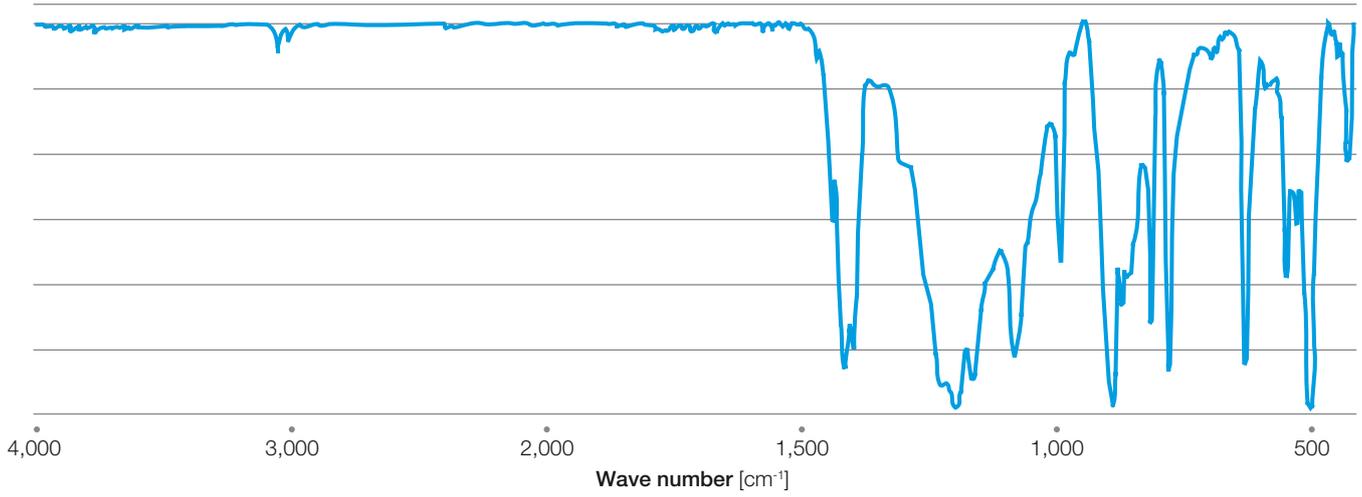


Fig. 24: IR-ATR spectrum of Solef® 11008 copolymer film (transmission)

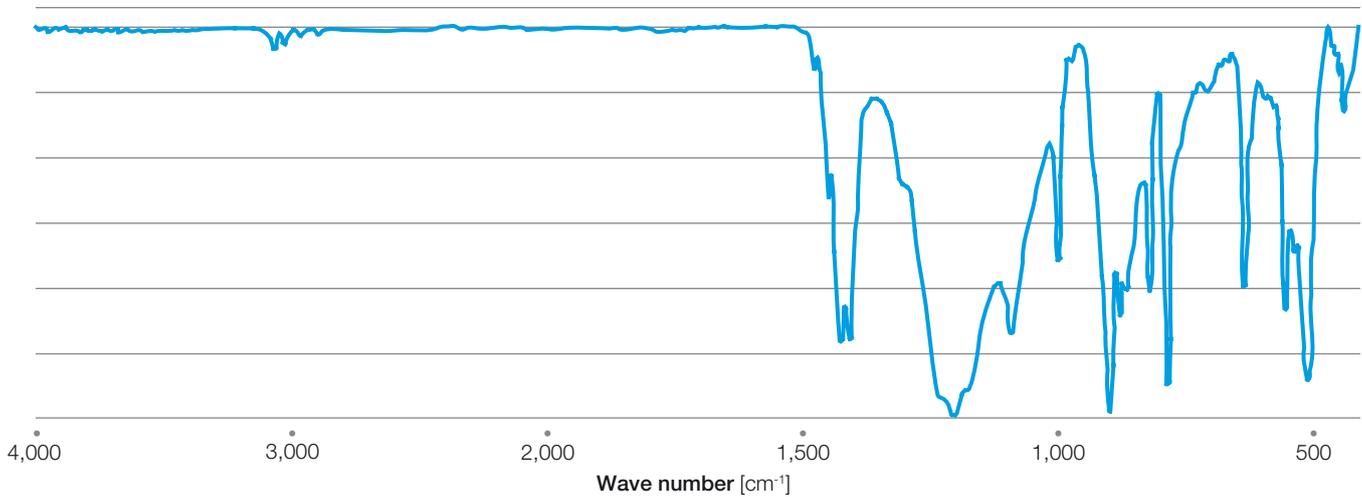


Table 21: Optical properties of Solef® PVDF films vs. thickness

Thickness [μm]	Total Light Transmission [%] (in the Air)	Transparency [%] (in the Air)	Haze [%]	Gloss at 45° [%]
Solef® 1008				
12 ^(a)	97	79	1.3	59
20 ^(b)	97	80	10	41
45 ^(b)	96	29	23	30
110 ^(b)	95	40	36	35
320 ^(b)	91	6	64	20
Solef® 1010				
10 ^(c)	93	–	7	–
Solef® 21510				
50 ^(c)	96	40	17	17
100 ^(c)	96	35	19	17

(a) Biaxially drawn film; (b) Uniaxially drawn film; (c) Extruded blown film

Short-Term Stresses

Tensile Properties

(ASTM D638, DIN 53448)

Tensile properties are determined by clamping a test specimen into the jaws of a testing machine and separating the jaws at a specified rate. The force required to separate the jaws divided by the minimum cross-sectional area is defined as the tensile stress. The test specimen will elongate as a result of the stress, and the amount of elongation divided by the original length is the strain. If the applied stress is plotted against the resulting strain, a curve similar to that shown for instance in Figure 25 is obtained for ductile polymers like PVDF.

The tensile tests make possible to measure the following characteristics:

- Modulus of elasticity E (Young's modulus)
- Stress (or strength) and elongation at yield
- Stress (or strength) and elongation at break

The thermal history and processing technique influence the tensile characteristics.

Apart from the characteristics cited above, the tensile test also makes it possible to measure the Poisson's ratio. Poisson's ratio is the ratio of lateral strain to longitudinal strain within the proportional limit. The following values were obtained for Solef® 1010 grade:

- At 23 °C (73.4 °F) $\nu = 0.35$
- At 100 °C (212 °F) $\nu = 0.50$

As an example, Figure 25 gives the overlay of the tensile curves recorded at various temperatures (between -40 °C (-40 °F) and 140 °C (284 °F) on Solef® 1008 specimens.

Notes: Between approximately 40 and 100 °C (104 and 212 °F), the strength at break can be superior to the yield stress. This increasing of mechanical resistance results from the orientation of molecular chains.

Figures 26 and 27 present several tensile characteristics for Solef® 1010 as a function of temperature.

Notes: Tensile yield strength decreases steadily with the increase of temperature. Elongation at yield increases gradually with the increase of temperature and Elongation at break rises slightly until room temperature then rises sharply above 30 °C (86 °F)

Fig. 25: Tensile curves for Solef® 1008 at various temperatures

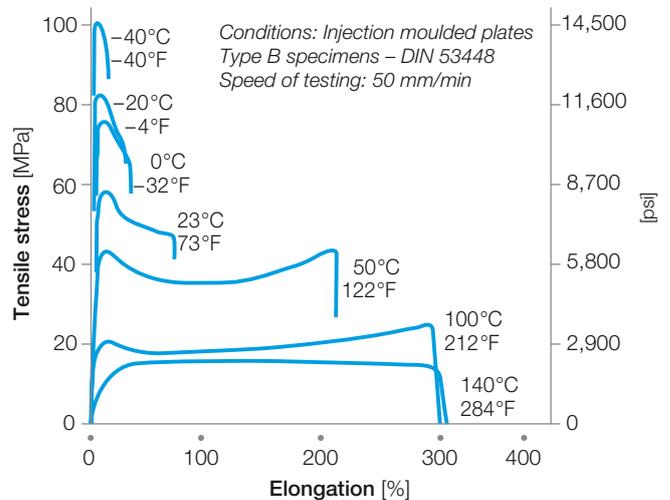


Fig. 26: Tensile yield strength of Solef® PVDF vs. temp.

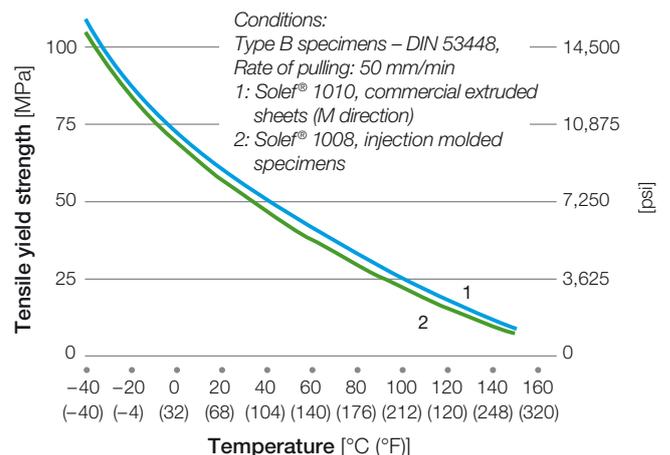


Fig. 27: Elongation at yield and at break of Solef® PVDF vs. temperature

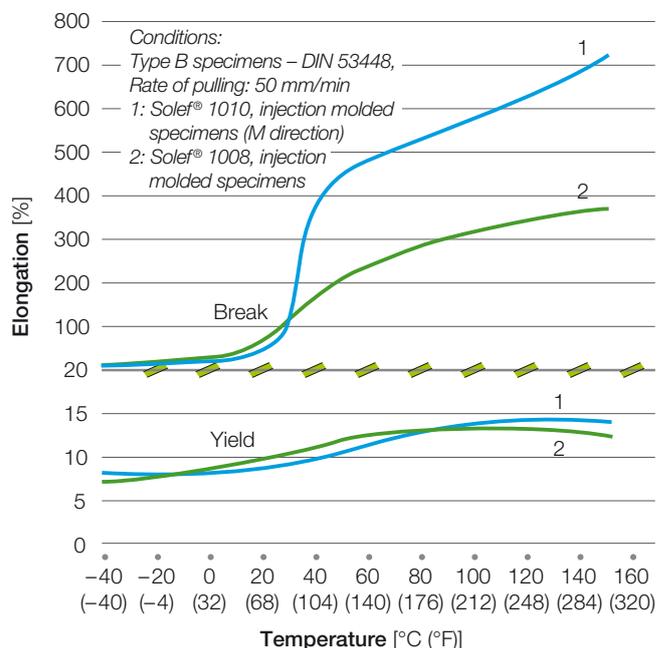


Figure 28 gives the tensile yield strength for Solef® 1010, 11010, 60512 and 460 grades, and the strength at break (no yield point) of Solef® 8808/0902 compound in a temperature range of 20 to 150 °C (68 to 302 °F).

Figure 29 illustrates the variation of the Young's modulus as a function of the temperature for Solef® 1010, 11010, 60512 460 resins, and for Solef® 8808/0902 compound.

Table 22 presents the tensile properties of extruded films made of Solef® 1010 and 11010 resins.

Fig. 28: Tensile strength at yield or at break of PVDF vs. temperature

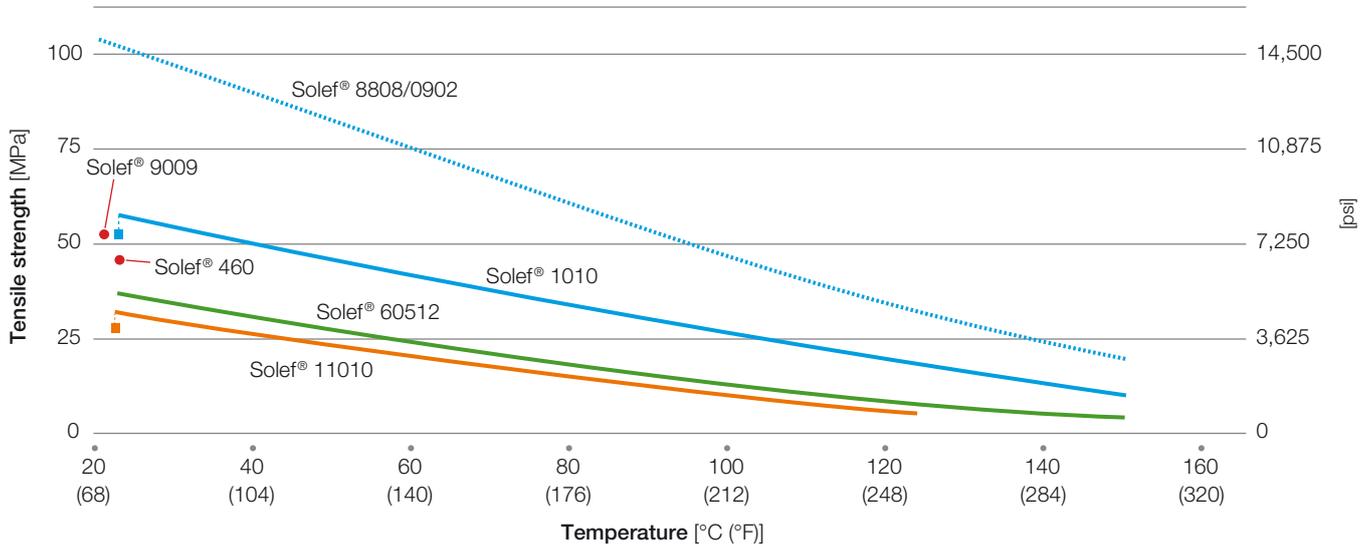


Fig. 29: Young's modulus of PVDF vs. temperature

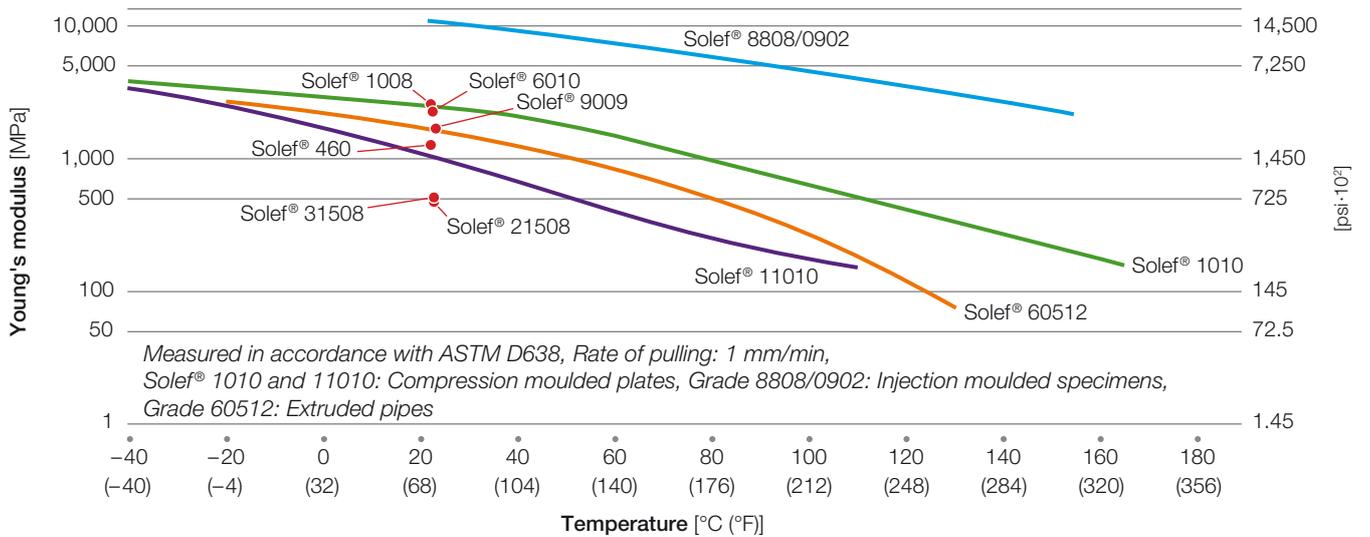


Table 22: Tensile properties of Solef® PVDF films

Grades	Thickness of Film [µm]	Stress at Yield [MPa (psi)]		Stress at Break [MPa (psi)]		Elongation at Break [%]	
		M	T	M	T	M	T
1010	50	50.0 (7,265)	52.0 (7,540)	70.6 (10,237)	44.2 (6,409)	285	230
	100	52.9 (7,671)	56.4 (8,178)	70.2 (10,179)	56.4 (7,410)	380	265
	200	52.3 (7,584)	58.1 (8,425)	43.4 (6,279)	51.1 (5,858)	465	590
11010	50	32.8 (4,756)	29.7 (4,307)	66.9 (9,701)	46.7 (6,772)	435	535
	100	31.6 (4,582)	32.2 (4,669)	63.2 (9,164)	49.4 (7,163)	610	560
	200	32.2 (4,669)	34.4 (4,988)	56.9 (8,251)	44.0 (6,380)	675	580

Conditions: Films produced by extrusion with flat die and chill roll, Tensile measurement according to the ASTM D882 standard at 23 °C (73,4 °F), Rate of pulling: 500 mm/min, M: machine direction; T: transversal direction

Flexural Properties (ASTM D790, DIN 53432)

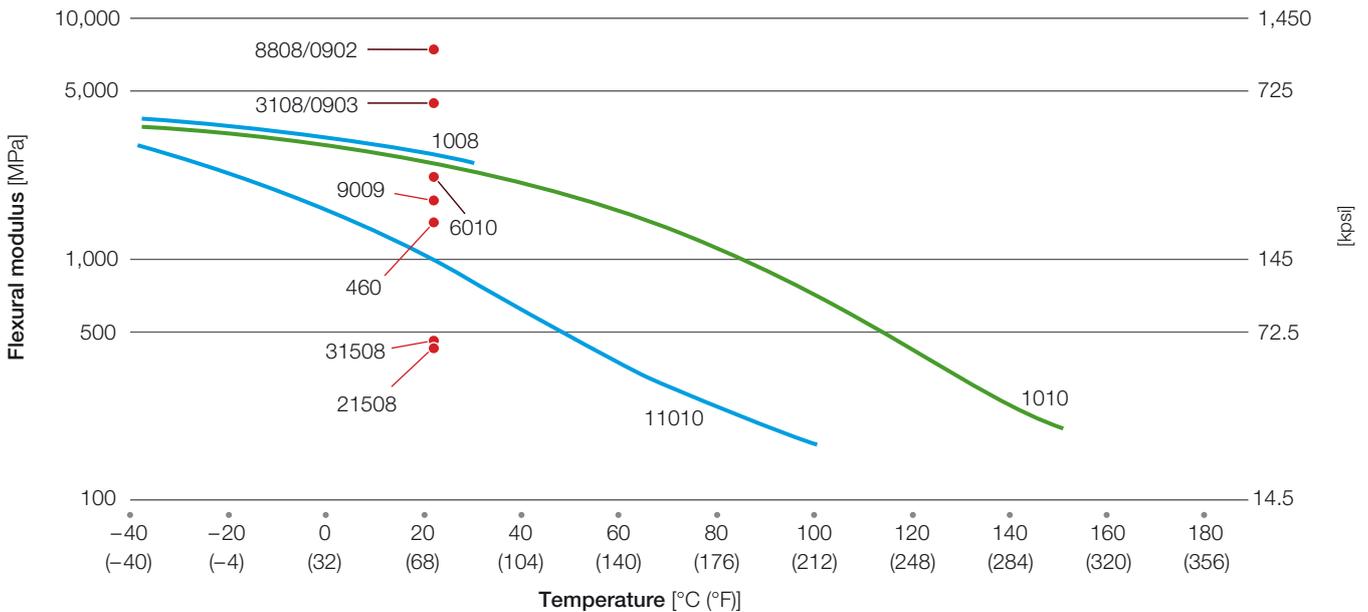
Flexural properties were determined using the three-point loading method. In this method, the test specimen is supported on two points, while the load is applied to the center. The specimen is deflected until rupture occurs or the fiber strain reaches five percent.

Flexural testing provides information about a material's behavior in bending. In this test, the bar is simultaneously subjected to tension and compression.

The mechanical flexural characteristics of various Solef® PVDF grades are presented in Figures 30 and 31.

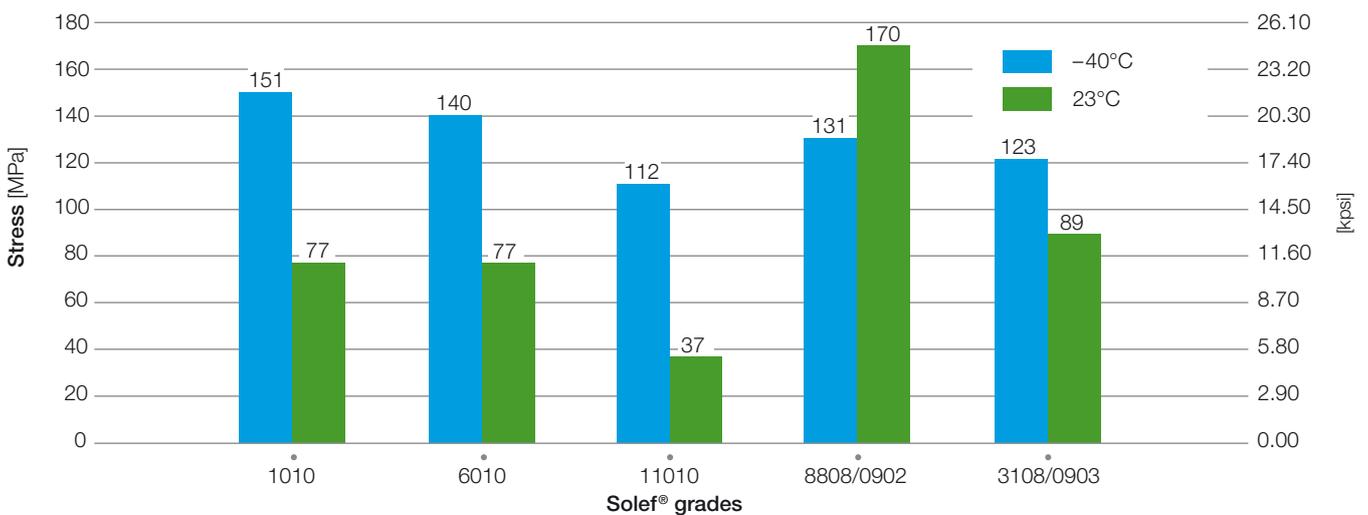
Figure 31 presents ultimate flexural strength of various Solef® PVDF resins grades at temperatures of -40°C (-40°F) and 23°C (73.4°F). Tests performed on annealed compression molded plates, except for Solef® 8808/0902: injection molded specimens.

Fig. 30: Flexural modulus of PVDF vs. temperature



Conditions:
 Measured in accordance with ASTM D790 – Rate of bending: 1 mm/min
 Solef® 1008, 3108/0903, 11010, 31508/0003: Compression moulded plates
 Solef® 1010 and Solef® 460: extruded sheets

Fig. 31: Ultimate flexural strength of various Solef® PVDF grades



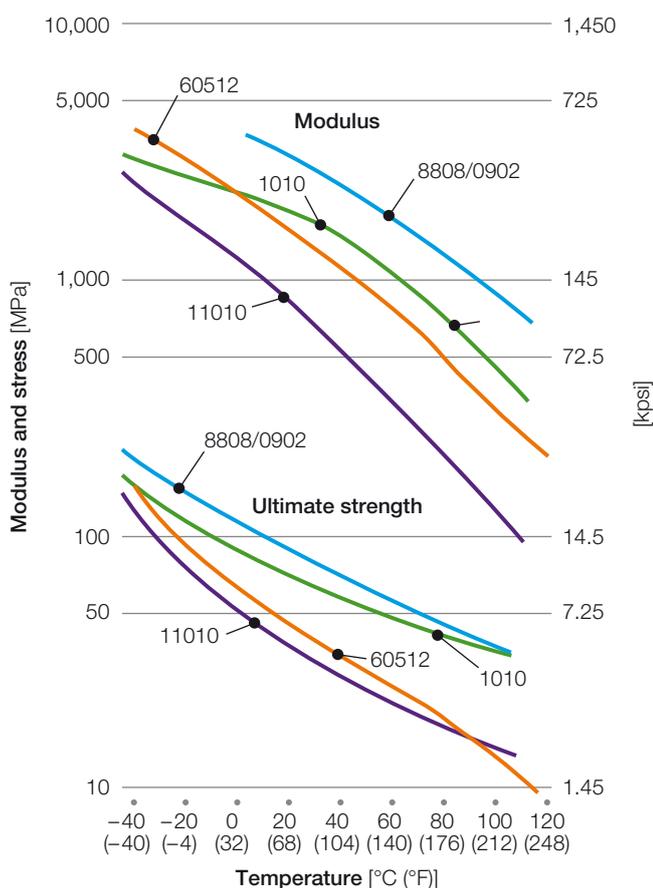
Compressive Properties (ASTM D695)

Compressive strength and modulus were measured on a test specimen placed between parallel plates. The distance between the plates is reduced while the load required for pushing the plates together and the plate-to-plate distance is monitored. The maximum stress endured by the specimen (this will usually be the load at rupture) is the compressive strength, and the slope of the stress/strain curve is the compressive modulus.

In compression the ultimate strength and elasticity modulus of Solef® 1010 at 20°C (68°F) are 75 MPa (10.9 kpsi) and 2,150 MPa (311 kpsi), respectively.

Figure 32 gives the compression modulus and the ultimate compressive strength of Solef® 1010, 11010, 60512 resins as well as Solef® 8808/0902 compound in temperature range between -40°C and 125°C (-40 and 257°F).

Fig. 32: Compression modulus and ultimate compressive strength of Solef® PVDF vs. temperature



Conditions: Measured in accordance with ASTM D 695 standard. Rate of compression: 1.3 mm/min. Solef® 1010, 11010, 8808/0902: compression (molded plates) Solef® 60512: extruded sheets

Long Term Static Stress – Creep

Creep Under Tensile Stress (ASTM D2990)

When a bar made of a polymeric material is continuously exposed to a constant stress, its dimensions will change in response to the stress. This phenomenon is commonly called “creep”. In the simplest case, the tensile mode, the test bar will elongate as a function of time under stress. The term “strain” is used for the amount of length increase or elongation divided by the initial length.

During characterization tests, models are used which are based on shorter term tests. The model developed by Solvay makes it possible to evaluate the stress-elongation behavior in the area of very low strain rates and then generate long term creep curves (strain vs. time) for different stress levels (Figures 33 through 37). These curves demonstrate that PVDF offers excellent creep resistance, even at high temperatures.

Tests on Pipe – Direct Bursting Resistance to Maximum Rising Pressure (Short Term)

The internal pressure of liquids transported through piping generates a biaxial stress against the wall of these pipes (when the pipe walls are thin). The theory of elasticity demonstrates that, on the internal wall, the hoop (or tangential) stress σ_t is equal to twice the axial (or longitudinal) stress. The bursting of a pipe thus generally occurs by axial cracking.

The stress σ_t is linked to the characteristics of the pipe and the pressure, in accordance with the relation (theory of elasticity applied to the pipes with low e/D ratio):

$$\sigma_t = p \cdot \frac{D - e}{2e}$$

p: internal pressure,
D: external diameter, e: wall thickness

The resistance to direct bursting (very short term: a few minutes) of Solef® PVDF pipes was carried out by submitting them to increasing pressure until they burst. The tests were carried out on pipes with $\varnothing = 8$ and 12 mm and thicknesses of 0.5 to 1.1 mm under two distinct conditions:

- at room temperature (23°C/73.4°F) with an increase of pressure of 60 bar (870 psi) in 1 minute, and then of 30 bar/min (435 psi/min) until bursting
- at increasing temperature in an oven starting at 140°C (284°F) for homopolymers or 120°C (248°F) for copolymers at a rate of 0.3°C/min (0.5°F/min) on sealed pipes 3/4^{ths} filled with water. The bursting pressure is equivalent to vapor pressure of the water added to the air expansion, at the temperature at which the pipe bursts.

The summary results of these tests are given in Table 23. Under these test conditions, these values are applicable only to tubes of small diameters and thin walls ($\varnothing < 12$ mm; thickness ≤ 1.1 mm) and not to pipes of greater diameter and thick walls, for which the state of stresses is not biaxial but triaxial.

Fig. 33: Modeled isochrones at 23 °C (73.4 °F) of Solef® 1010 (extruded sheets)

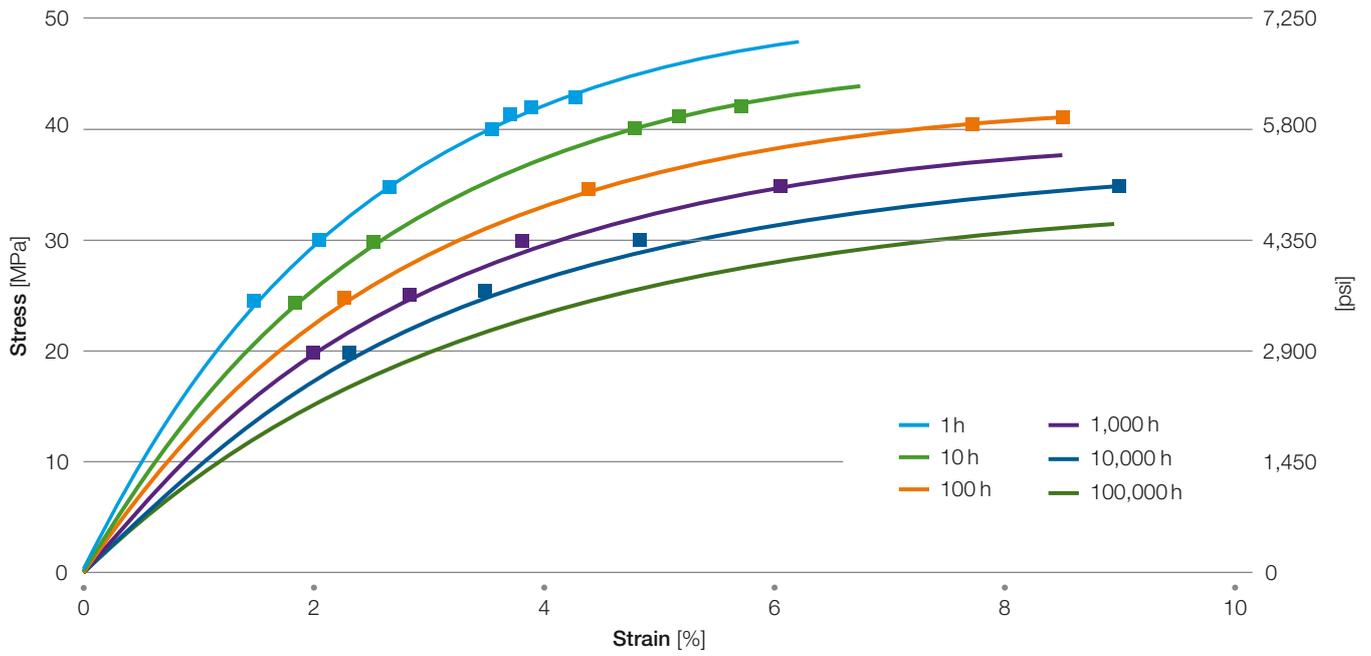


Fig. 34: Experimental values for creep under tensile stress at 23 °C (73.4 °F) of Solef® 1010 (extruded sheets)

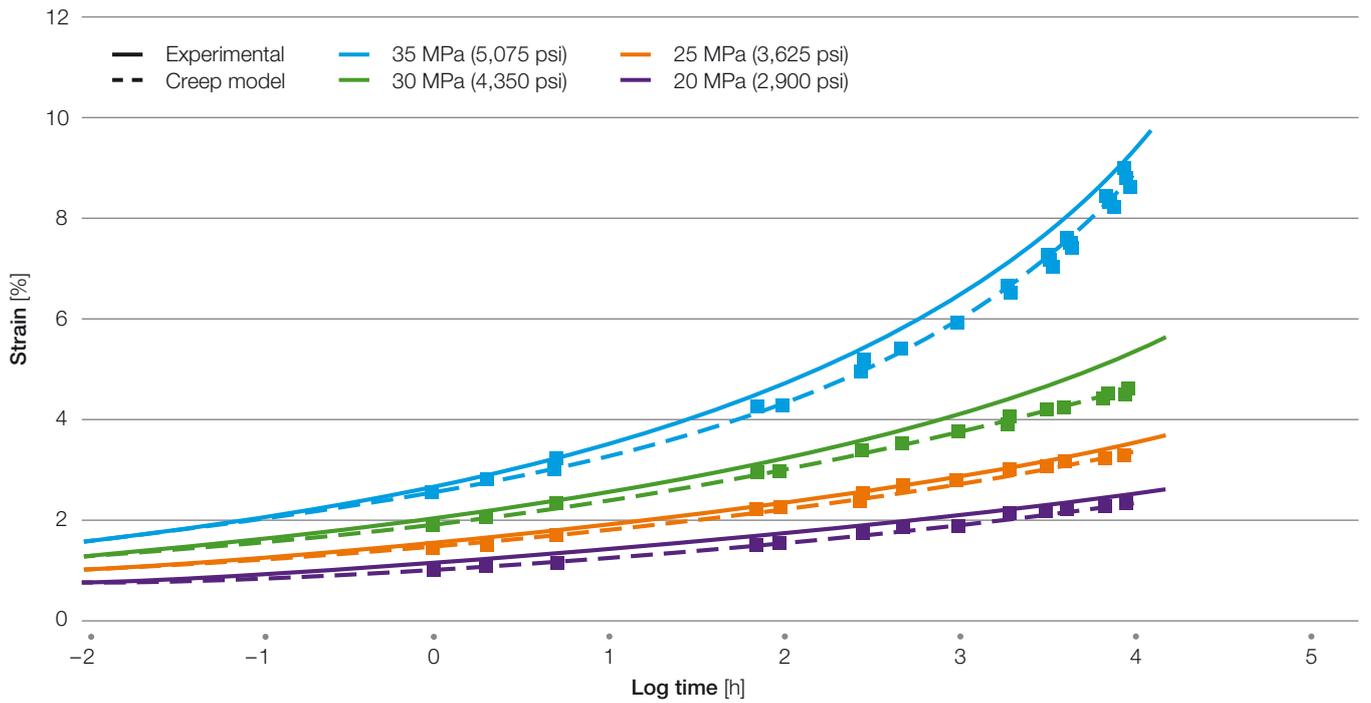


Fig. 35: Creep under tensile stress at 140 °C (284 °F) of Solef® 1010 (extruded sheets)

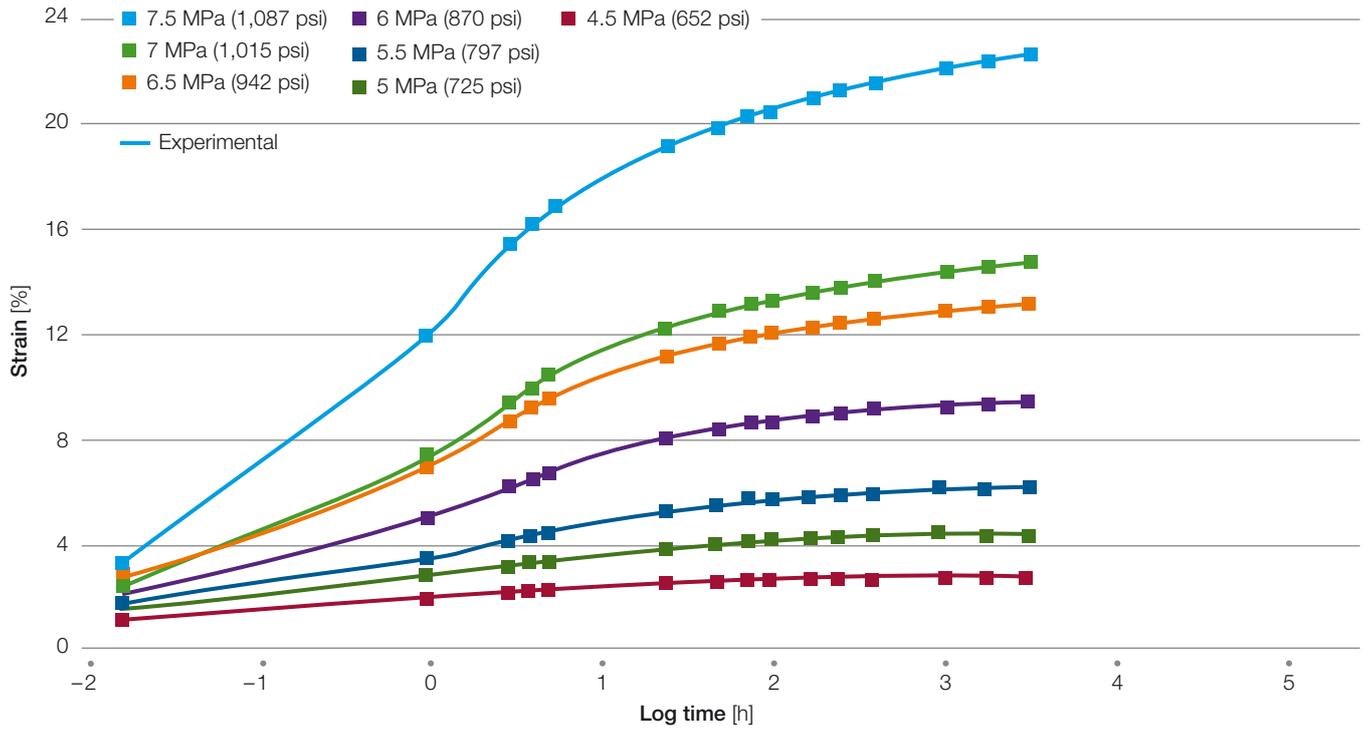


Fig. 36: Creep under tensile stress at 120 °C (248 °F) of Solef® 1010 and 60512

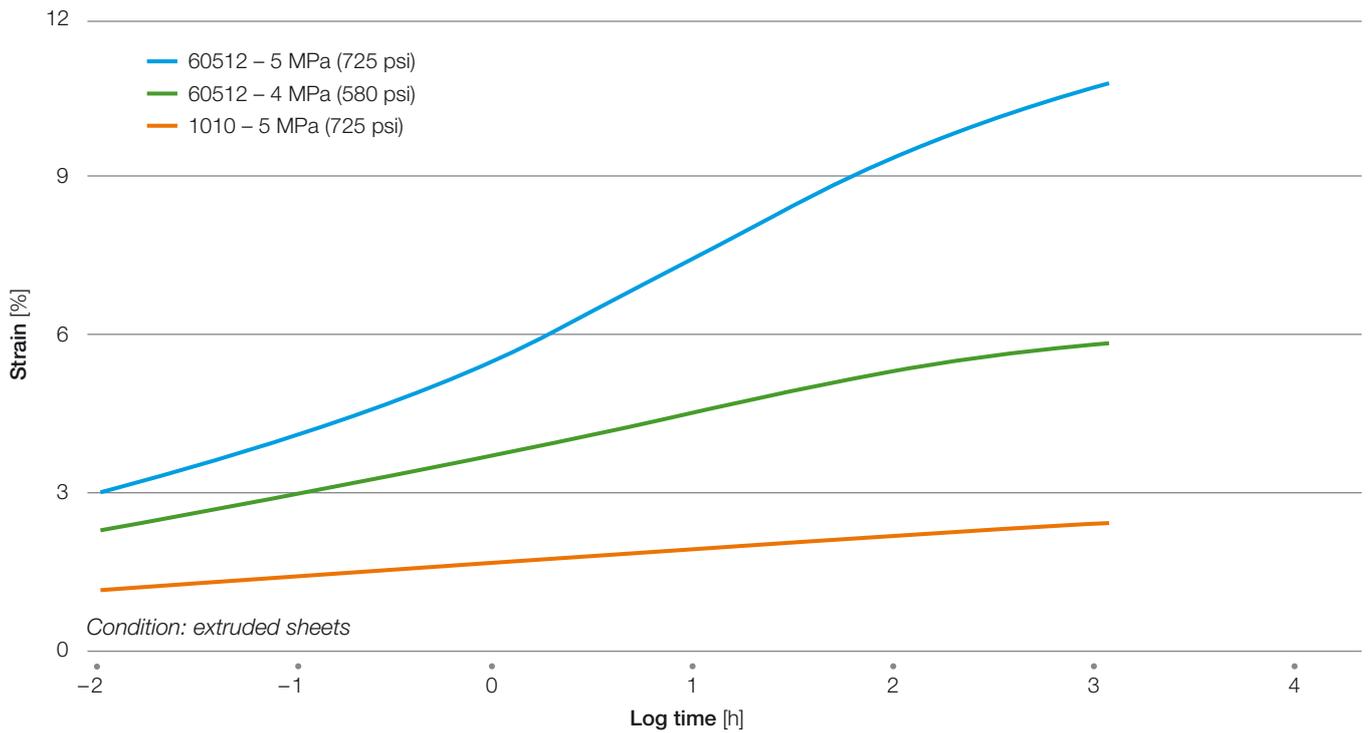


Fig. 37: Creep under tensile stress of Solef® 8808/0902 compound at 120 °C (248 °F)

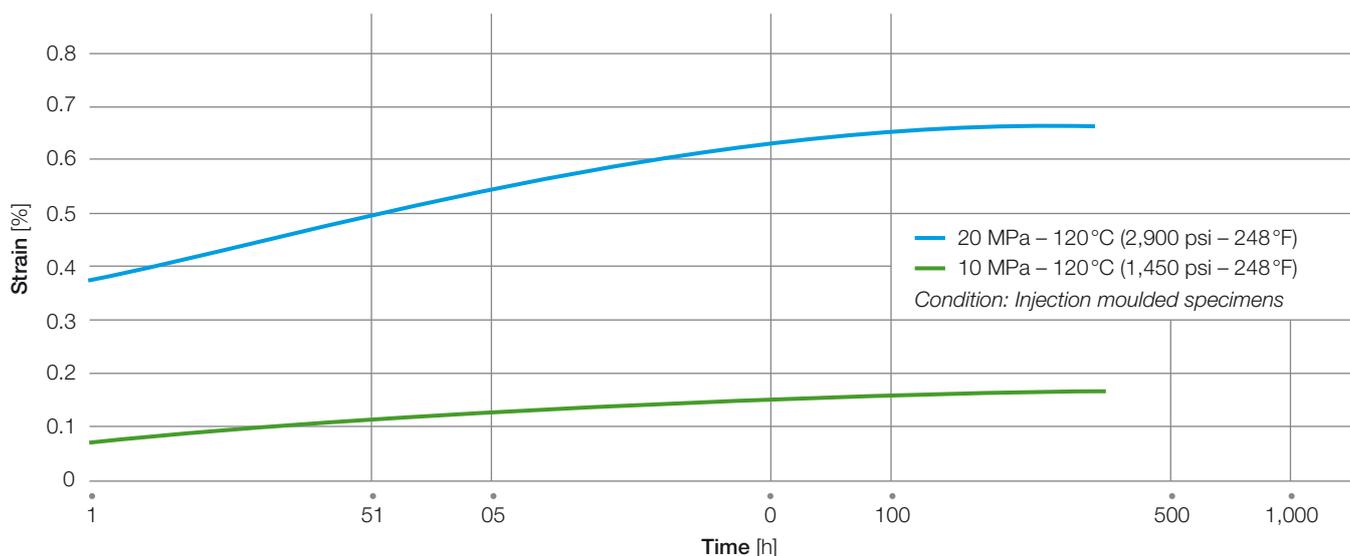


Table 23: Very short term bursting resistance of Solef® PVDF pipe

Grades	Bursting Temperature [°C (°F)]	Bursting Pressure [bar (psi)]	Hoop Stress [MPa (psi)]
1010*	23 (73.4)	94 – 139 (1,364 – 2,017)	55 – 61 (8,000 – 8,800)
1010*	156 (313)	5.8 – 6.4 (84 – 93)	2.5 – 3.5 (362 – 508)
11010**	134 (273)	3.4 – 3.5 (49 – 51)	1.5 – 1.6 (218 – 232)

* pipes Ø 8 mm and 12 mm. D/e = 9 to 13

** pipes Ø 12 mm. D/e = 10

Tests on Pipe – Bursting Resistance to Long Term Static Pressure

First of all, it should be noted that the long term behavior of Solef® PVDF pipes subjected to internal pressure has been the topic of studies, still in progress, for over 20 years. The tests are conducted using DECHEMA test equipment for measuring bursting pressures of small diameter (exterior diameter D = 8 to 12 mm), thin walled pipes in a neutral environment (water), and in aggressive environments as part of the assessment of the chemical resistance of PVDF (on this subject, see the chapter “Chemical resistance”).

In a neutral environment, the pipes are each arranged in a double stainless steel envelope plunged into an oil-bath thermostat. Each pipe is filled with water and connected to a compressed nitrogen tank which ensures pressurization. An electrical contact manometer measures the pressure and trips the circuit of a timer when the pipe bursts. The temperature is measured by thermocouple in an identical pipe not subjected to pressure. Figure 38 presents the bursting hoop stress of Solef® PVDF pipes subjected to constant pressure versus time until rupture (DECHEMA test equipment) as a function of the time necessary for rupture (logarithmic scales). Pipes manufactured with Solef® X10N resin of the first generation, very close to the current 1010 grade, have resisted for more than 20 years at 100 °C (212 °F) and 120 °C (248 °F).

Figure 39 shows the long term hoop stress (LT HS) extrapolated to 50 years in a neutral environment as a function of temperature, from data of Figure 38 and according to linear extrapolation method described in ISO/TR 9080. This curve relates to bursting pressures without any safety factor.

The maximum acceptable operating pressures are below these values, and are obtained by incorporating an adequate safety factor. This is defined in ISO/10931: “Plastics piping systems for industrial applications – Polyvinylidene fluoride PVDF”.

Solef® 1010 received in 1991 the approval from the Plastics Pipe Institute (PPI, USA) as a material for manufacture of pipes whose wall thickness is calculated on the basis of hydrostatic pressure values at various temperatures.

Figure 40 shows the design stresses for water extrapolated to 50 years of PVDF pipes, according to ISO/10931-2, for a minimum required strength (MRS) of 25 MPa (3,625 psi) and safety coefficient (Cmin) of 1.6.

Fig. 38: Hoop stress of Solef® 1010 pipes vs. time until rupture

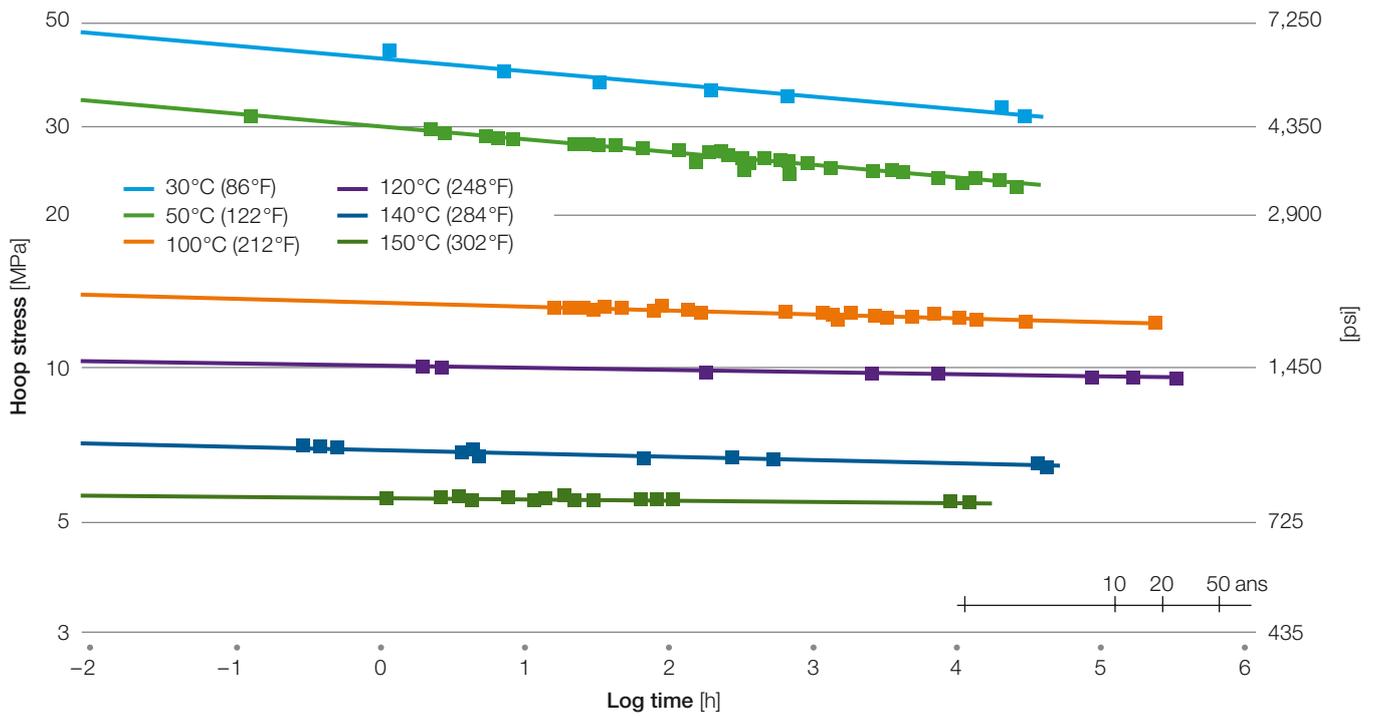
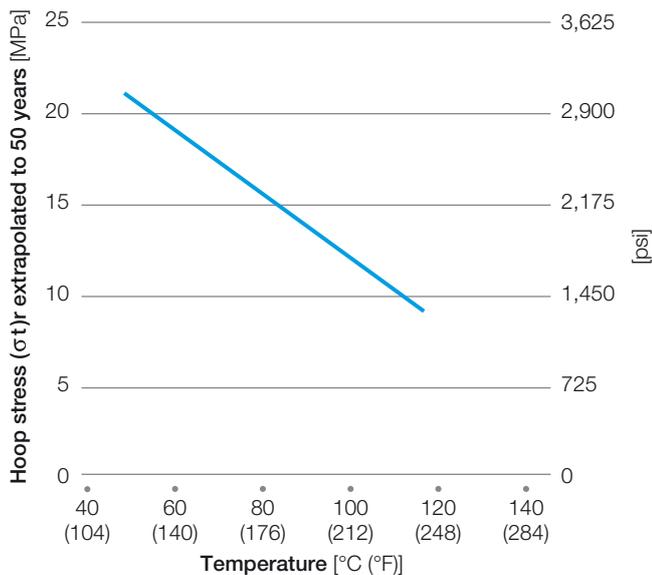
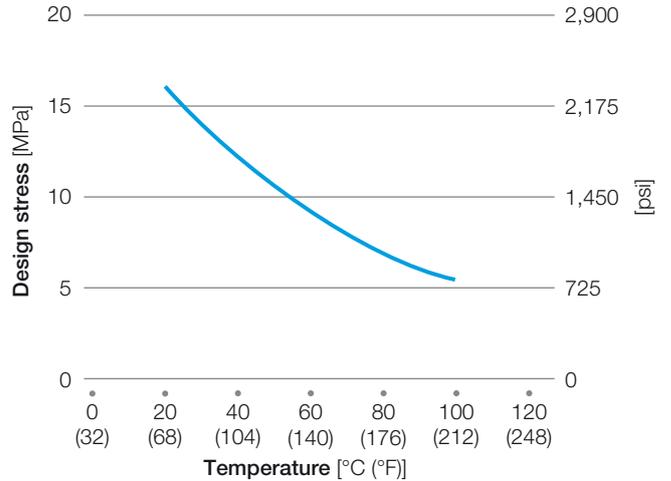


Fig. 39: Long term hoop stress of Solef® 1010 pipes extrapolated to 50 years (ISO/TR 9080)



Conditions: Solef® 1010 DECHEMA equipment for testing pipes with small diameters and thin walls, subjected to adjustable constant internal pressure in a neutral environment (water) - Exterior diameter: 8 – 10 – 12 mm. Thickness: 0.8 – 1 mm, Length: 300 mm, Temperature measured inside the pipes. Linear correlation between 50°C (122°F) and 120°C (248°F): $Y = 28.86 - 0.164 X$ $R^2 = 0.997$

Fig. 40: PVDF pipes in presence of water – Design stress extrapolated to 50 years (ISO 10931-2)



Tests on Pipe – Long Term Hoop Stress Using IPT Equipment

The long term behavior of Solef® PVDF pipes subjected to internal pressure has been studied lately using the IPT test equipment (IPT Service GmbH, Germany). The IPT tests are generally conducted on medium diameter pipes (D = 32 mm or more), in a neutral environment (water).

The pipes are maintained at test temperature with a forced hot air circulation. A regulation device maintains the temperature and internal pressure constant. Any loss of water due to permeation is compensated automatically from a pressurized tank.

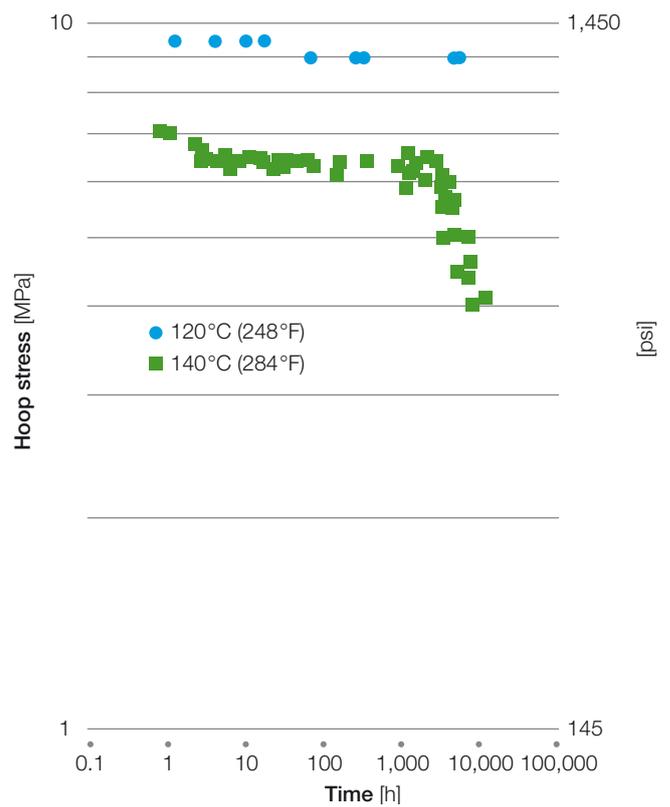
Each test station, comprising several pipes under pressure, is equipped with a timer which is automatically cut out at each pipe failure.

Figure 41 below shows the bursting hoop stress of Solef® 1010 pipes vs. time in the IPT test equipment.

As can be seen the test method based on IPT equipment generates regression curves with an inflexion point (“knee”) after 3,000 h tests at 140°C (284 °F). This phenomenon has not been observed in the tests conducted for more than 20 years, using DECHEMA test equipment described above.

As the IPT test method will become the international standard (ISO 10931-2), Solvay will refer to it in future, in preference to the DECHEMA one.

Fig. 41: Long term hoop stress of Solef® 1010 pipes using IPT test equipment (ISO 10931-2)



Dynamic Loading

Alternating Low Amplitude, Short Term Stresses – DMTA (Dynamic Modulus) (ASTM D4065)

PVDF, like all thermoplastics, behaves as a viscoelastic material. Under the effect of a stress, the response (deformation) includes an elastic component and a viscous component.

Under a forced harmonic stress system, one measures the amplitude and the phase displacement δ of the resulting deformation. When it is performed over a wide range of temperatures, this method of evaluation makes it possible to identify the thermomechanical spectrum of the material at a given frequency, characterized by:

- the temperature variation of the elastic modulus E' (real or purely elastic component of the complex modulus E^* , where $E^* = E' + iE''$)
- the variation of the mechanical damping (or loss) $\text{tg } \delta$ as a function of the temperature. $\text{tg } \delta$ is the ratio of the viscous (E'') and elastic (E') components:

$$\text{tg } \delta = \frac{E''}{E'}$$

The curve of $\text{tg } \delta$ displays peaks which correspond mainly to the second-order transitions, the most important of which is the glass transition (due to the amorphous phase).

These transitions are the result of progressive liberations of movements of molecular segments (greater or smaller depending on the transition) when the temperature rises (thermal agitation).

The DMTA (dynamic mechanical thermo-analysis) technique was used to characterize the Solef® PVDFs, in torsion rectangular geometry with a frequency of 1 Hz.

Figures 42 and 43 show the curves of E' and $\text{tg } \delta$ of some Solef® PVDF homopolymers and copolymers, respectively.

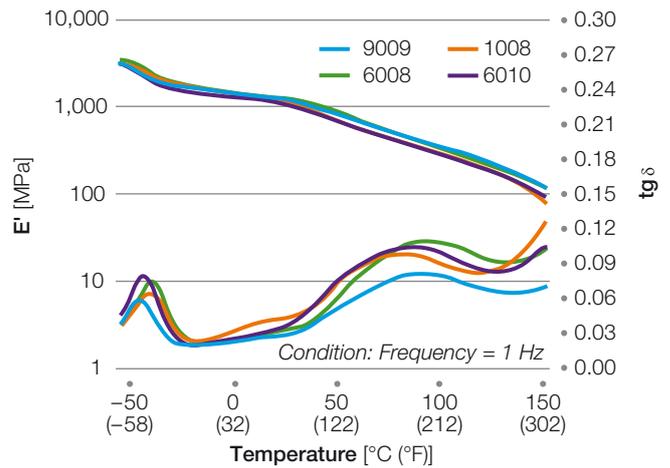
In particular, for the Solef® 9009 resin, one observes primarily:

- A $\text{tg } \delta$ curve with a maximum at -36°C (-32.8°F), main glass transition, also called T_{g_L}
- A modulus E' curve displaying a clearly visible inflection point (T_{g_L}) at -36°C (-32.8°F).

For copolymers Solef® 11010 and 31508/0003, the glass transitions are respectively -30°C (-22°F) and -28°C (-18.4°F).

It is to recall that the temperatures of these transitions reduce as the stress frequency declines (the reverse is also true). They can also be identified by other physical techniques such as dilatometry, dielectric measures, etc.

Fig. 42: Modulus E' and $\text{tg } \delta$ of Solef® PVDF homopolymers vs. temperature (DMTA)



Alternating Long Term Stresses – Fatigue Tests (ASTM D671, DIN 53 442, NF T 51-120)

The fatigue tests, performed under alternating or cyclic stress, make it possible to determine the Wöhler curve of the material which represents the variation of the maximum stress amplitude as a function of the number of cycles-to-failure. The fatigue or endurance limit of the material generally corresponds to the maximum stress achieved after 106 or 107 cycles.

Figure 44: Wöhler curve for Solef® 1008 tested at 20°C (68°F) under cyclical tension at a frequency of 0.5 Hz between an adjustable maximum value σ and a zero value.

On this graph we have overlaid the tensile yield strength level σ_e recorded during a static tensile test. With Solef® PVDF, fatigue breaks are obtained only at very high stress levels, close to σ_e . All the ruptures are of a ductile nature.

Fig. 43: Modulus E' and $\text{tg } \delta$ of Solef® PVDF copolymers vs. temperature (DMTA)

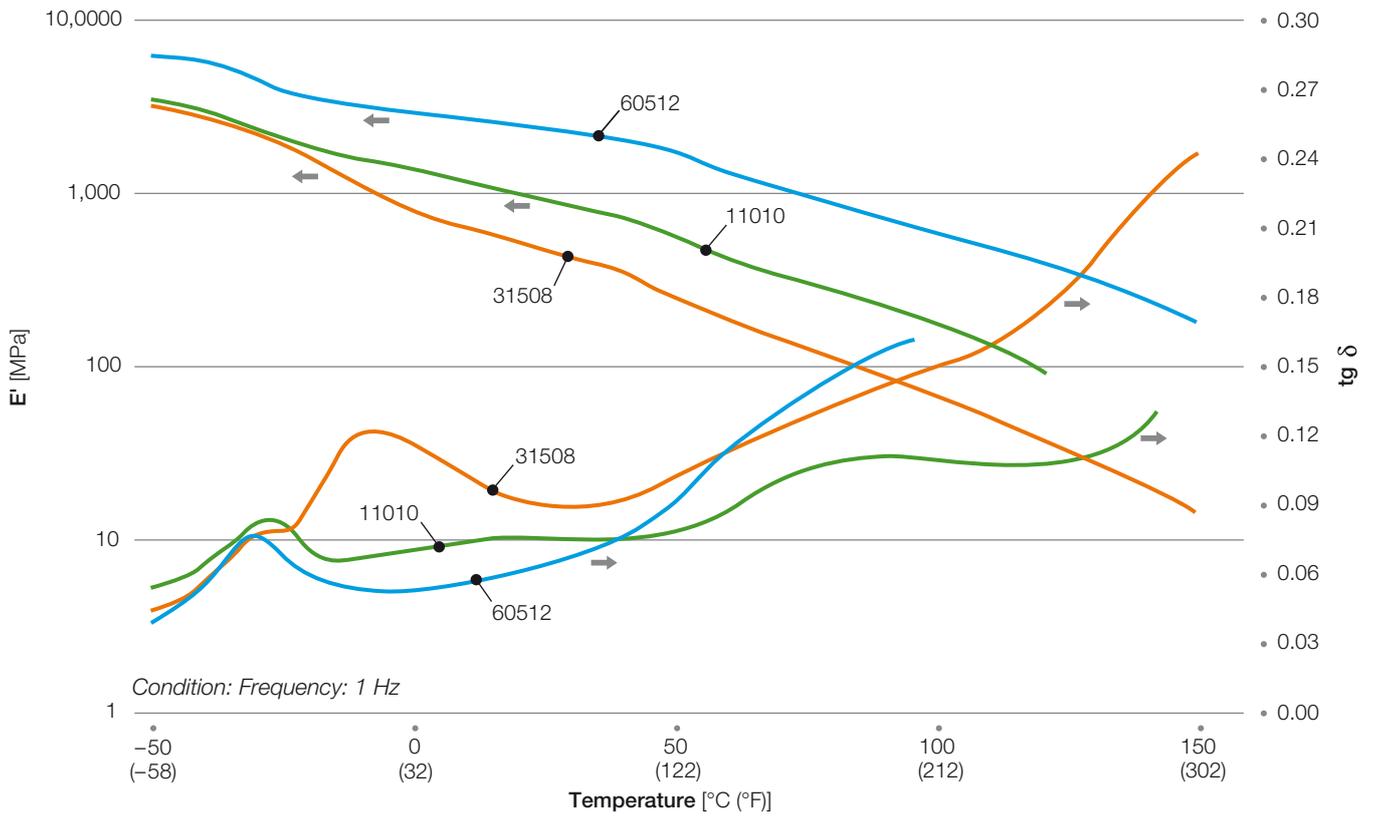
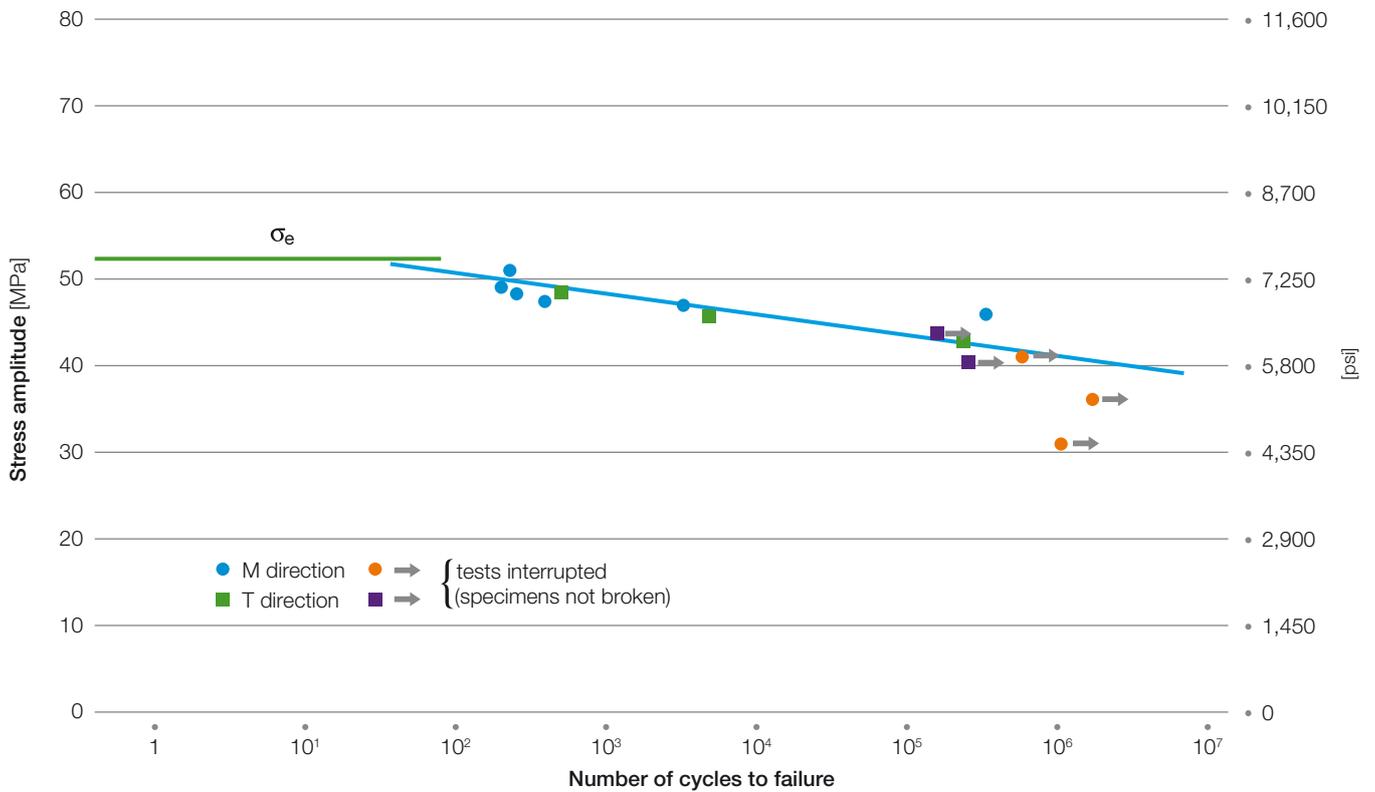


Fig. 44: Fatigue under cyclical tensile stress for Solef® 1008 at 20°C (68°F)



Conditions:
 σ_e : tensile yield strength in accordance with ASTM D638, Specimen type 1, rate of pulling: 5 mm/min
 Fatigue test: Specimens taken from injection moulded plates (unnotched), source: RAPRA

Figure 45: Wöhler curves for the Solef® 1010 grade at 20, 60 and 100 °C (68, 140 and 212 °F). The fatigue tests were limited to the oligocyclic range (< 10⁴ cycles). The fatigue is evaluated under alternating uniaxial tensile stress, between a maximum adjustable value σ and a low residual value (2.5 MPa/362.5 psi), at the frequency of 0.5 Hz. Two thicknesses – 1 and 4 mm – were tested in order to evaluate the influence of this parameter on the fatigue limit.

Like in the preceding case, the fatigue failures of a ductile nature are only obtained under stresses close to σ_e (> 0.8 σ_e). In the absence of notches, Solef® PVDF is so characterized by a very high endurance limit, far above that of a large number of thermoplastics.

Fatigue on Notched Specimens – Critical Stress Intensity Factor K_{IC}

Fracture mechanics studies of the materials made it possible to discover the crack growth laws so as to predict their conditions of instability on the basis of the geometry of the system (form, type of stress application), characteristics of the material and environment (temperature, medium).

At the tips of a central crack of a specimen under tension there are very high stresses which can far exceed the tensile yield strength σ_e . Following the Dugdale model, the opening of the lips of a crack δ (crack opening displacement = COD) by plastic deformation is expressed by the relationship:

$$\delta = \frac{\sigma^2 \Pi c}{\sigma_y E} = \frac{(K_I)^2}{\sigma_y E}$$

where σ : nominal stress applied to the specimen

σ_y : real stress along the crack

c : half-length of the crack

E : modulus of elasticity

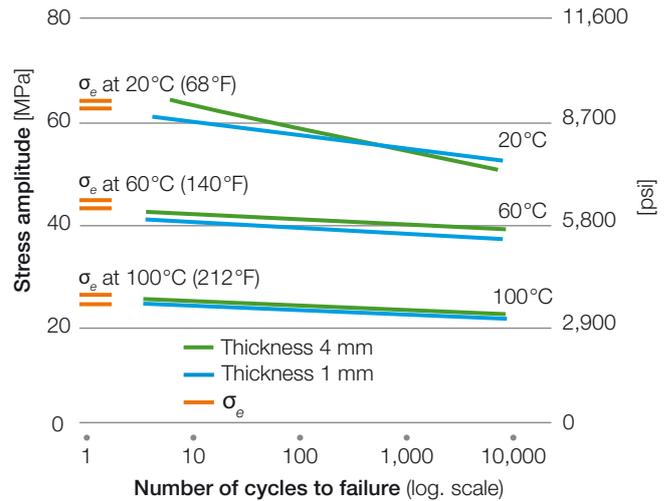
K_I : stress intensity factor at the tip of the crack

The K_{IC} factor corresponds to the maximum value of K_I , beyond which failure occurs by sudden propagation of the crack. It expresses the toughness of the material, i.e. the energy necessary for the creation of two break surfaces. This includes on the one hand the specific surface energy S and on the other the plastic deformation energy in the zone adjacent to the crack line in the case of ductile materials.

Fatigue tests on notched Solef® 1010 specimens were performed at several temperatures under cyclical tensile stress at a frequency of 5 Hz.

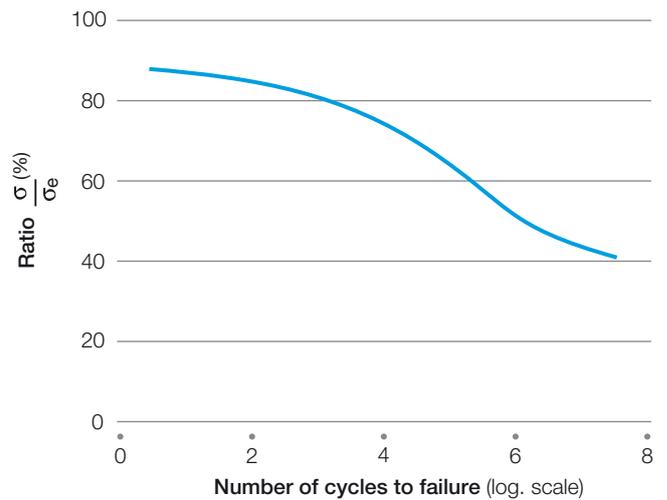
Figure 46 shows the fatigue breaking stress as related to σ_e in percent as a function of the number of cycles to failure, at a temperature of 25 °C (77 °F).

Fig. 45: Oligocyclic fatigue of Solef® 1010 at various temperatures



Conditions: Solef® 1010, Specimens taken from compression moulded plates. Tests: Cyclical tensile fatigue on unnotched specimens: $f = 0.5$ Hz
 σ_e : Tensile yield strength at the rate of 250 mm/min (for 1 and 4 mm thickness)

Fig. 46: Fatigue tests on notched specimens – Wöhler curve of Solef® 1010 at 25 °C (77 °F)



Conditions: Cyclical tensile fatigue tests
 σ_e : maximum stress amplitude per cycle
 σ_e : tensile yield strength
 Length of initial notch: 0.4 mm (on each side), thickness: 2 mm

Impact Strength

Several methods are used to measure the impact resistance of plastics, such as Izod and Charpy tests presented below. These impact tests allow designers to compare the relative impact resistance under controlled laboratory conditions and, consequently, are often used for material selection or quality control.

Izod Flexural Impact Strength

The notched Izod test (ASTM D256) is one of the most widely employed methods for comparing polymeric materials. In this test, a notched specimen is clamped at one end (“cantilever-beam”) and then struck at the other end by a swinging pendulum. At the point of impact, the striker has a known amount of kinetic energy. The impact energy is calculated from the excess energy remaining in the pendulum after breaking the specimen.

Figure 47 shows the flexural impact strength between -40°C (-40°F) and 100°C (212°F) of various Solef® PVDF grades (notched Izod).

Charpy Flexural Impact Strength (ASTM D256)

Like the Izod test, the Charpy flexural impact test involves striking a test specimen piece with a striker, mounted at the end of a pendulum. In the Charpy test the specimen is supported at both ends (“simple-beam”) and the striker impacts the test piece immediately behind a machined notch. Again, the impact energy is calculated from the excess energy remaining in the pendulum after breaking the specimen.

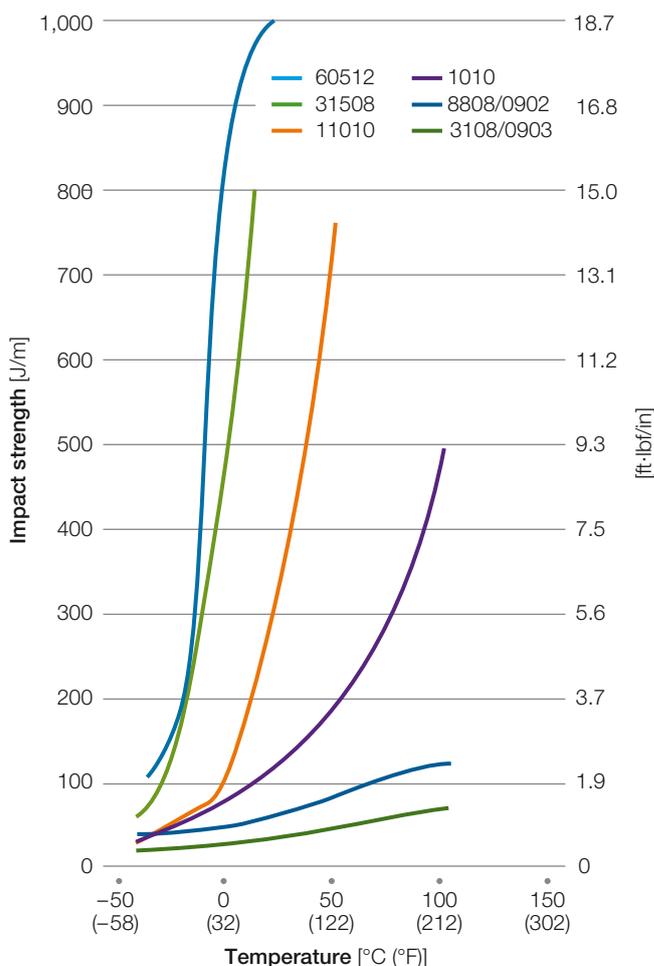
Flexural impact strength of Solef® 1010 and 1012 was evaluated using the Charpy method (see Table 24)

Table 24: Charpy flexural impact strength

Specimens	Impact Strength [kJ/m ² (ft·lbf/in ²)]
Solef® 1010 – extruded sheet (propagation in M direction*)	17.2 (8.2)
Solef® 1010 – extruded sheet (propagation in T direction*)	17.8 (8.5)
Solef® 1010 – compression molded plate	18.1 (8.6)
Solef® 1012 – compression molded plate	24.5 (11.6)

* M: machine direction; T: transversal direction.

Fig. 47: Izod impact resistance of various Solef® PVDF grades vs. temperature



Conditions: IZOD flexural impact test on notched specimens (ASTM D256), Specimens taken from compression moulded plates (except for Solef® 60512: extruded sheets)

Brittleness Temperature

This test method covers the determination of the temperature at which plastics exhibit brittle failure under impact conditions specified in the ASTM D746 standard. To determine the brittleness temperature, specimens secured to a specimen holder are immersed in a bath containing a heat transfer medium that is cooled. The specimens are struck at various temperatures at a specified linear speed and then examined. The brittleness temperature is defined as the temperature at which 50% of the specimens fail.

The brittleness temperatures of various Solef® PVDF grades are presented in Table 25.

Comment: The test method based on the statistical distribution of failures as a function of the temperature is very sensitive to the processing method and thermal treatments.

As shown with the homopolymers series, the brittleness temperature decreases as the molecular weight is higher.

The copolymers have brittleness temperatures which are significantly below those of the homopolymers. The 30000 and 60000 series copolymers (VF2 – CTFE copolymers) have a brittleness temperature $\leq -30^{\circ}\text{C}$ ($< -22^{\circ}\text{F}$)

Multiaxial Impact Tests

– Instrumented Dart Impact

(ISO 6603, ASTM D3763, DIN 53443-2)

The behavior under multiaxial impact stresses of plastic materials is evaluated by the perforation method using an instrumented falling weight. The dart is equipped with a cell to measure the force of impact, making it possible to record the force-deformation diagram and deduce from it the energy absorbed during the puncture of the specimen.

Table 26 gives the results obtained on various Solef® grades, and on several engineering thermoplastics.

The Solef® PVDF copolymers, because they are more deformable than the homopolymers, have greater impact strength at room temperature.

Table 25: Brittleness temperature of Solef® PVDF according to ASTM D746. Compression molded plate

Grades	Brittleness Temperature [°C (°F)]
PVDF homopolymers	
1010	0–10 (32–50)
6010	–5–5 (23–41)
1012	0–10 (32–50)
1015	–12 (10.4)
PVDF copolymers	
11010	–18 (–0.4)
11008	–17 (1.4)
21508	–22 (–8)
31508	–37 (–35)
60512	–31 (–24)

Table 26: Impact tests by instrumented falling weight of Solef® PVDF and thermoplastics

Specimens	Temperature [°C (°F)]	Impact Strength (absorbed energy per unit of thickness) [J/mm (ft·lbf/in)]
Solef® 1010	23 (73)	4.0 (75)
	–40 (–40)	0.4 (7.5)
Solef® 11010	23 (73)	9.5* (178)
	–40 (–40)	0.5 (9.4)
Solef® 31508	23 (73)	7.0* (131)
	–40 (–40)	1.2 (22.5)
PET (indicative values)	23 (73)	0.15 (2.8)
POM (indicative values)	23 (73)	0.6 (11.2)
PP (homopolymer/indicative values)	23 (73)	0.15 (2.8)

Test conditions: Aperture diameter of the specimen support: 40 mm, Diameter of the dart: 6.4 mm, Height of fall: 1 m, Weight of the dart: 1.11 kg, Thickness of the specimens: 2 mm, * Weight of dart: 2.22 kg

Resistance to Impact and Tearing on Films

The brittleness temperature of Solef® 1008 films, determined by impact in accordance with the DIN 53372 standard, is –40°C (–40°F). In addition, the impact resistance of Solef® PVDF films was evaluated in accordance with the ASTM D1709 method (free falling dart impact test) and the ISO 6383/2 method, also known as the Elmendorf tear test. The results are presented in Table 27.

Table 27: Tests of impact and tearing on Solef® PVDF films

Type of Film	Thickness [μm]	Dart Drop Test [g for 50 % break- age] (ASTM D1709)	Elmendorf Tearing Force per Unit of Thickness [mN/μm] (ISO 6383/2)	
			M**	T**
Solef® 1008	45 (30)	50	(10)	(132)
	130	170	16	25
	320	–	25	27
Solef® 1008 biaxially drawn	30	800	12	11
Solef® 11010	75	60	40	230
Solef® 21510*	100	–	162	156
	20	–	160	650
Solef® 31508	100	–	45	35
Solef® 31508*	100	–	86	84

* Manufactured by blow molding

** M: machine direction; T: transversal direction

Reprocessing Effects on Mechanical Properties

Tests have been performed on the Solef® 1010 grade as a function of the number of complete reprocessings (extrusion-pelletizing). Table 28 gives the mechanical properties recorded before and after reprocessing (up to 30 times).

This table show that, after 30 reprocessing steps:

- the melt flow index is only slightly modified
- the mechanical properties are virtually unmodified

Table 28: Reprocessing effects on mechanical properties of Solef® 1010 grade

Properties	Units	Number of Complete Reprocessings						
		0	5	10	15	20	25	30
MFI at 230 °C (ASTM D1238)	g/10 min (5 kg)	6.34	6.42	6.64	6.83	6.96	7.06	7.20
Mechanical properties (on compression molded plates), Tension* (ASTM D638)								
Yield strength	MPa (psi)	52.6 (7,642)		54.1 (7,845)		54.3 (7,874)		53.9 (7,816)
Elongation at yield	%	7		9		10		9
Stress at break	MPa (psi)	32.3 (4,684)		36.9 (5,351)		43.9 (6,366)		44.3 (6,424)
Elongation at break	%	29		24		30		25
Modulus (secant)	MPa (kpsi)	2,430 (352)		2,430 (352)		2,350 (341)		2,590 (376)

(*) Measurement at 5 mm/min except for modulus (1 mm/min)

Electrical Properties

General Characteristics

Solef® PVDF are prime materials for use in jacketing copper plenum cables applications. They are particularly well suited for use in hostile environments as jacketing material for non-plenum cable applications where flexibility, toughness, thermal and chemical resistance are a must.

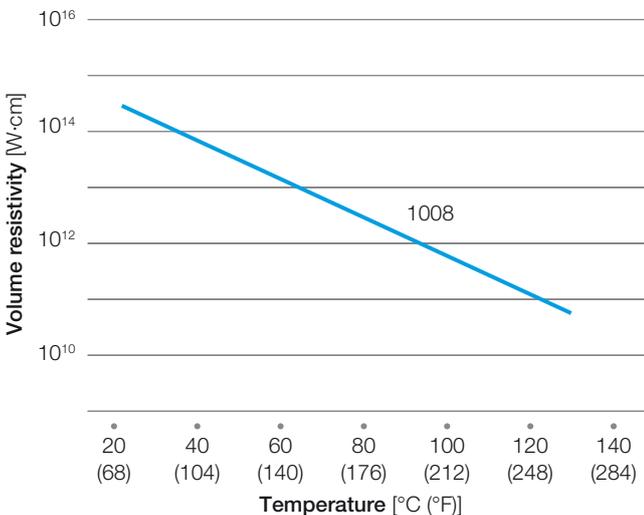
Volume and Surface Resistivities

(ASTM D257, DIN 53482)

The volume resistivity gives the insulating power in the direction of the thickness, while the surface resistivity indicates primarily the insulating power on the surface. Figure 48 shows the variation of the volume resistivity (W-cm) vs. temperature for Solef® 1008 grade.

The surface resistivity under 500 V of this grade at 23 °C (73.4 °F) is $\geq 1 \cdot 10^{14}$ W/sq. The PVDF resin is a good electrical insulator. Solef® 3108/0903 and 3110/0907 grades, filled with carbon black, were developed for antistatic applications. In these cases, the surface resistivity is lower than 1,000 W (500 V, 23 °C/73.4 °F).

Fig. 48: Volume resistivity of Solef® PVDF vs. temperature



Conditions: Compression moulded plates (1 mm), measured in accordance with DIN 53482 after 1 and 2 min

Dielectric Strength

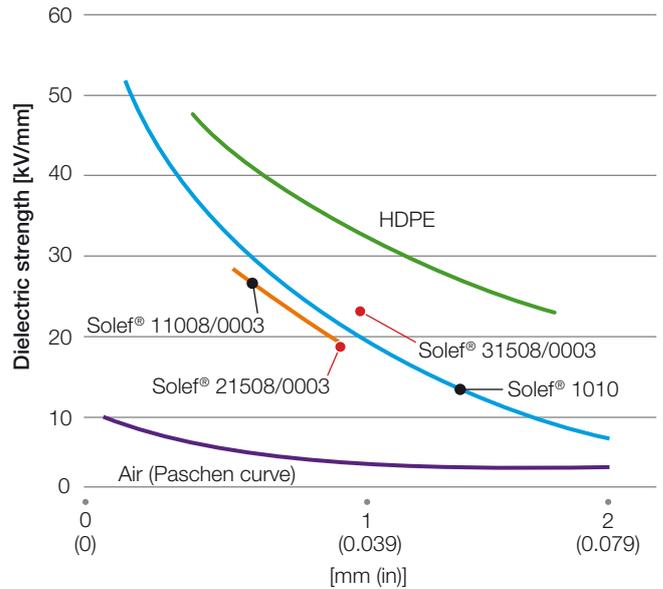
(ASTM D149, DIN 53481)

Dielectric strength is a measure of a material's ability to resist high voltage without dielectric breakdown. It is measured by placing a specimen between electrodes and increasing the applied voltage through a series of steps until dielectric breakdown occurs. Although the results have units of kV/mm, they are not independent of sample thickness. Therefore, data on different materials are comparable only for equivalent sample thicknesses.

Figure 49: dielectric strength of Solef® PVDF compression molded plates as a function of thickness. The values are within the range of those recorded for polyolefins.

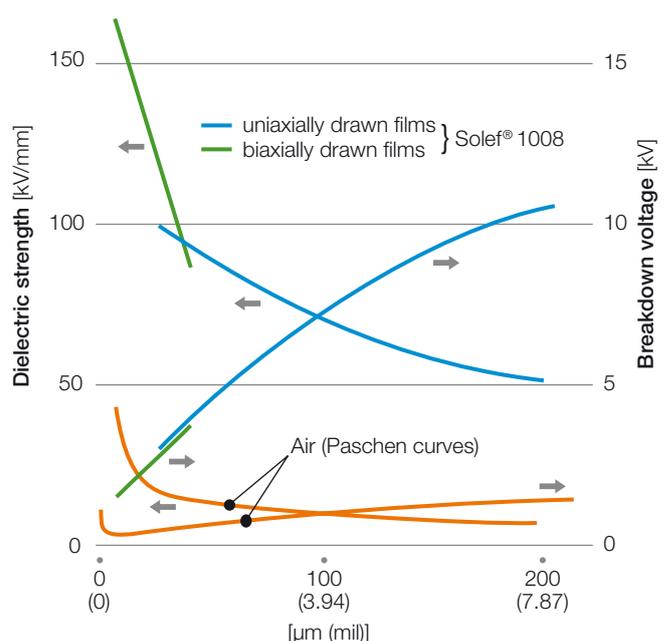
Figure 50: variation of dielectric strength and breakdown voltage of films as a function of thickness.

Fig. 49: Dielectric strength of Solef® PVDF vs. plate thickness



Conditions: Measurements in accordance with ASTM D149, environment: oil, rate: 1kV/s, temperature: 23 °C/73.4 °F

Fig. 50: Dielectric strength and breakdown voltage of Solef® 1008 films vs. thickness



Conditions: Measured in accordance with ASTM D149, Temperature: 23 °C/73 °C

Dielectric Constant and Tangent of Loss Angle

(IEC 250, ASTM D150, DIN 53483)

Dielectric constant ϵ_r is defined as the ratio of the capacitance of a condenser using the test material as dielectric to the capacitance of the same condenser with a vacuum replacing the dielectric. Insulating materials are used in two very distinct ways: (1) to support and insulate components from each other and ground, and (2) to function as a capacitor dielectric. In the first case, it is desirable to have a low dielectric constant. In the second case, a high dielectric constant allows the capacitor to be physically smaller.

Tangent of loss angle (also referred to as dissipation factor or $\text{tg } \delta$) is a measure of the dielectric loss (energy dissipated) of alternating current to heat. In general, low dissipation factors are desirable.

- Figures 51 and 52: dielectric constant and $\text{tg } \delta$ of Solef® 1010 as a function of temperature measured at different frequencies (Compression molded plates – thickness: 2 mm)
- Figures 53 and 54: same characteristics for Solef® 11008/0003 grade,

Figure 55: variation of ϵ_r and of $\text{tg } \delta$ of Solef® 11008/0003 and 31508/0003 grades (for wire and cable market) vs. frequency up to 10 MHz

Like the dynamic mechanical stresses, the electrical characteristics are influenced by glass and crystalline phase transitions. The maximum values observed at low frequency are moved towards higher temperatures when the frequency increases.

Fig. 51: Dielectric constant of Solef® 1010 at low frequency vs. temperature

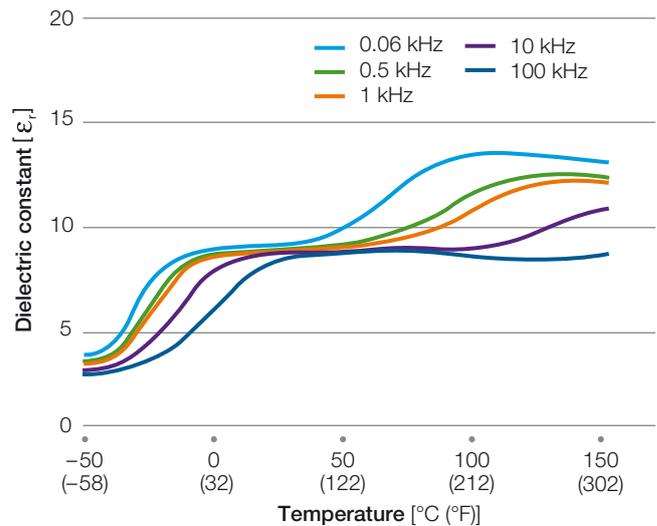


Fig. 52: Tangent of dielectric loss angle of Solef® 1010 at low frequency vs. temperature

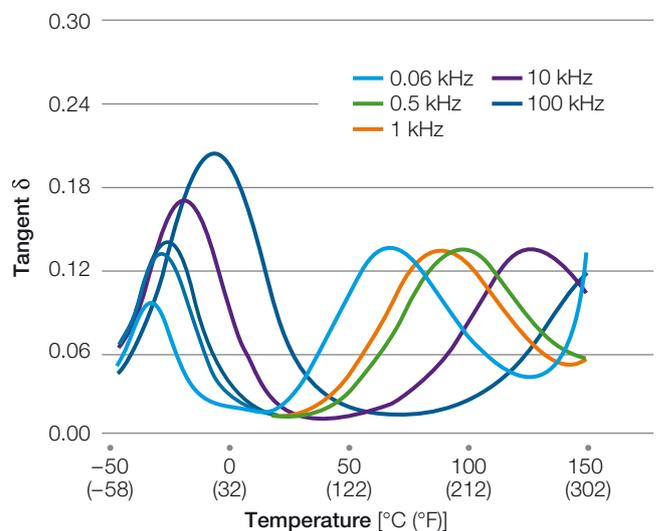


Fig. 53: Dielectric constant of Solef® 11008/0003 at low frequency vs. temperature

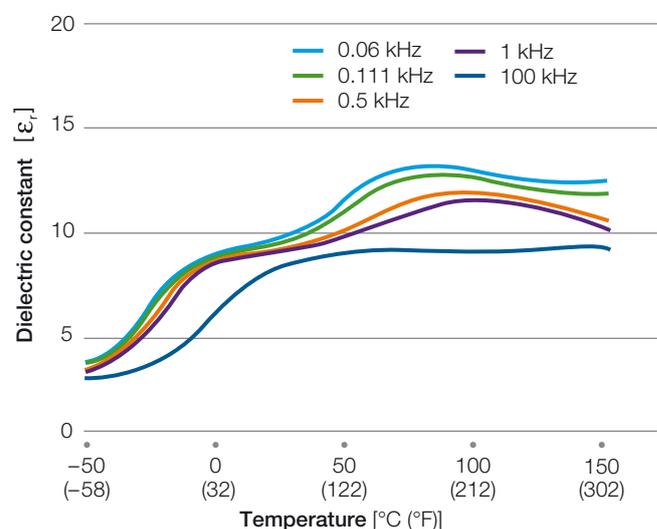


Fig. 54: Tangent of dielectric loss angle of Solef® 11008/0003 at low frequency vs. temperature

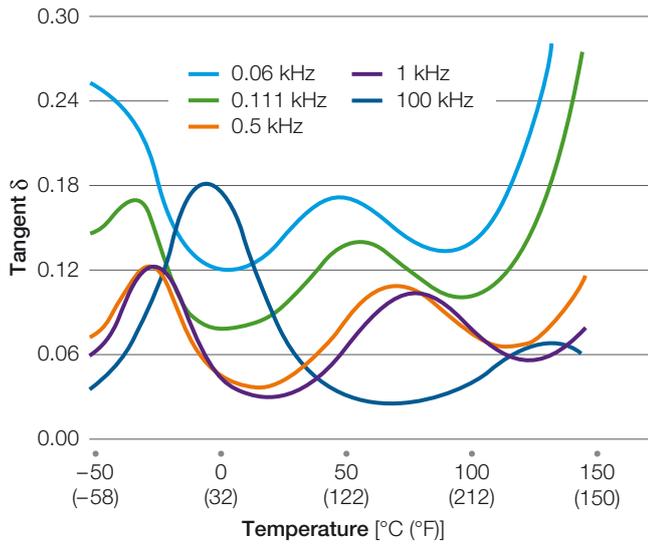
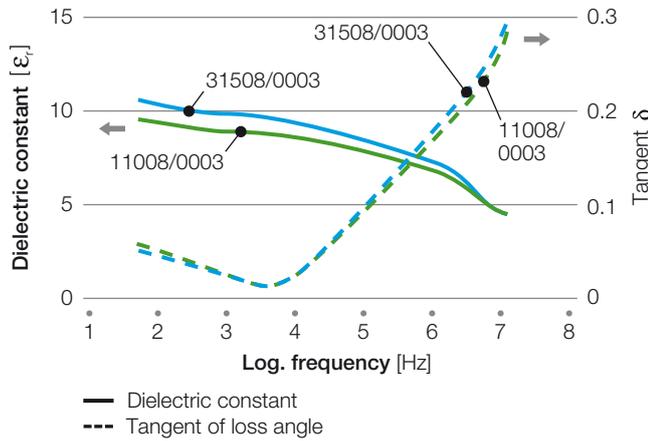


Fig. 55: Dielectric constant and tg δ of Solef® 11008/0003 and 31508/0003 vs. frequency



Conditions: Measured in accordance with ASTM D 150 at 23°C (73.4°F), 2 mm compression moulded plates

Comparative Tracking Index (IEC 112, ASTM D3638, NF C 26-220)

The comparative tracking index (CTI) is designed to characterize the resistance of an insulating material to surface tracking when it is subject to electrical voltage in a moist environment.

The CTI index is the maximum voltage for which one can allow to fall, between two electrodes applied to the surface of the material, 50 drops of an electrolyte (NH₄Cl: 0.1 % – rate: 1 drop every 30 seconds) without forming a conducting path between these electrodes.

Table 29 shows the values measured for various PVDF grades. Solef® PVDF resins have a CTI value greater than 600 volts.

Table 29: Comparative Tracking Index CTI in accordance with the IEC 112 standard

Grades	CTI [V]
Solef® PVDF resins	
1010	600+
6010	600+
460	600+
11010/0003	600+
21508/0003	600+
31508/0003	600+
Solef® PVDF compounds	
8808/0902	< 100

Piezo- and Pyroelectricity

When certain materials are subjected to mechanical stress, electrical charges proportional to the stress appear on their surface. Conversely, if they are subjected to a difference of potential, they undergo mechanical deformation. This phenomenon is called piezoelectricity. Likewise, when the temperature of the material varies, an electrical voltage is generated at its edges: this is the pyroelectric effect.

Solef® PVDF possesses these two qualities, which are sharply accentuated by the orientation of its molecular dipoles by polarization under the effect of an intense electrical field at high temperature.

Solef® PVDF is particularly well-suited for the manufacture of polarized films and sheets, because of its molecular structure, its purity (which makes it possible to obtain thin and regular films), and its suitability for crystallizing by drawing under the crystalline form β , which favors maximum polarizability.

The piezoelectric activity of films is defined by the coefficients of proportionality d between the mechanical causes and the electrical effects.

The d coefficients (coulomb/newton) are obtained by measuring the charge density (coulomb/m²) which appears on the surfaces of the film when a mechanical stress of 1 newton/m² is applied in accordance with:

- Thickness: d_{33} (or d_T if the film cannot be deformed)
- Plane of the film and in machine direction: d_{31}
- Plane of the film and in cross direction: d_{32} .

If one measures the variation of the electrical field per stress unit, one obtains the coefficients g , related to the d coefficients by the equation $g = d/\epsilon_r$, where ϵ_r is the dielectric constant.

The constants d and g are most often used for designing electromechanical transducers. The pyroelectric constant p is the surface charge density (C/m²) which appears when the film temperature is raised by 1 Kelvin; p is given in C/m² K. This coefficient is employed in the design of thermal sensors.

Table 30 brings together the piezo- and pyroelectric characteristics of Solef® PVDF homopolymer films.

Table 30: Piezo- and pyroelectricity of Solef® PVDF films and sheets of various thicknesses (23 °C/73.4 °F)

Properties	Biaxially Drawn Films				Uniaxially Drawn Sheets	
	9 μ m 0.35 mil	25 μ m 0.98 mil	40 μ m 1.6 mil	130 μ m 5.1 mil	0.5 mm 0.020 in	1 mm 0.040 in
d_{33} [pC/N]	-17.5	-16.5	-19.5	-33	-30	-30
d_{31} [pC/N]	6.5	8.5	9.5	23	18	18
d_{32} [pC/N]	6.5	8.5	9.5	3	3	3
g_{33} at 1 kHz [V·m/N]	-0.17	-0.16	-0.19	-0.3	-0.3	-0.3
p_{33} [μ C/m ² ·K]	-27	-26	-32	-	-	-
Diel. constant ϵ_r at 1 kHz	11.5	11.5	11.5	12	12	12
tg δ at 1 kHz	$15 \cdot 10^{-3}$	$15 \cdot 10^{-3}$	$15 \cdot 10^{-3}$	$15 \cdot 10^{-3}$	$18 \cdot 10^{-3}$	$18 \cdot 10^{-3}$
DC breakdown voltage [V/ μ m]	750	585	540	-	-	-

Environmental Resistance

Chemical Resistance

In general, Solef® PVDF has excellent resistance to a wide range of chemicals. The chemical resistance of PVDF homopolymers can be considered as very similar regardless of the polymerization process used.

PVDF polymer is remarkably resistant against:

- Most inorganic acids and salts
- Organic acids
- Aliphatic and aromatic hydrocarbons
- Crude oil and fuels
- Alcohols and ethers
- Halogens, with the exception of fluorine

However, there are some limitations regarding use of Solef® PVDF in certain chemical environments. The polymer, in fact, can suffer swelling from short polar solvents that are able to form hydrogen bonds as well as chemical attack from strong bases and free radicals. In particular, PVDF is not suitable for use in the following media:

- Basic environments having pH \geq 12 and amines
- Chemicals that can generate free radicals, such as chlorine in the presence of UV light
- Fuming sulphuric acid (oleum)
- A strongly polar solvent that can form hydrogen bonds (dimethylformamide, dimethylacetamide and N-methylpyrrolidone, for example, are well known solvents for PVDF even at room temperature)
- Melted alkali metals or their amalgams.

Table 31 presents an overview of the chemical resistance of PVDF to the most common chemicals. This is notably an excerpt of the more detailed Tables of Chemical Resistance of Solef® PVDF.

Table 31: Overview of the chemical resistance of Solef® PVDF

Chemical	Formula	Concentration [%]	Maximum Temperature [°C (°F)]
Inorganic Acids			
Hydrochloric	HCl	37	140 (284)
Hydrofluoric	HF	50	110 (230)
Nitric	HNO ₃	50	100 (212)
		65	75 (167)
Phosphoric	H ₃ PO ₄	85	140 (284)
Sulphuric	H ₂ SO ₄	up to 70	140 (284)
		80	125 (257)
		85	100 (212)
		93	50 (122)
		97	23 (73)
		oleum	not resistant
Bases			
Ammonium hydroxide	NH ₄ (OH)	30	23 (73)
Potassium hydroxide	KOH	30	not resistant
Sodium hydroxide	NaOH	50	not resistant
Sodium hypochlorite	NaClO	5 – stabilized at pH 12	50 (122)
Hydrocarbons			
n-Hexane	CH ₃ (CH ₂) ₄ CH ₃	100	140 (284)
Toluene	C ₆ H ₅ CH ₃	100	100 (212)
Alcohols			
Methanol	CH ₃ OH	100	50 (122)
Ethanol	CH ₃ CH ₂ OH	100	100 (212)

continued on next page

Chemical	Formula	Concentration [%]	Maximum Temperature [°C (°F)]
Organic acids, esters and ketones			
Acetic acid	CH ₃ COOH	100 50	50 (122) 75 (167)
Acetone	CH ₃ COCH ₃	100 5	not resistant 75 (167)
Acetophenone	C ₆ H ₅ COCH ₃	100	25 (77)
Ethyl Acetate	CH ₃ COOCH ₂ CH ₃	100	25 (77)
Classic polymer solvents			
Dimethylformamide	CH ₃ CON(CH ₃) ₂	100	not resistant
Dimethylsulphoxide	CH ₃ SOCH ₃	100	not resistant
N-Methylpyrrolidone	\square N(CH ₃)CO(CH ₂) ₃ \square	100	not resistant
Halogenated Solvents			
Chlorobenzene	C ₆ H ₅ Cl	100	50 (122)
Chloroform	CHCl ₃	100	50 (122)
Amines and nitriles			
Acetonitrile	CH ₃ CN	100	not resistant
Aniline	C ₆ H ₅ NH ₂	100	50 (122)
Dimethylamine	(CH ₃) ₂ NH	100	25 (77)
Peroxides			
Hydrogen peroxide	H ₂ O ₂	30	50 (122)
Fluids used in the automotive industry			
Crude oil		100	140 (284)
Dexron II (gear oil)		100	140 (284)
Gasoline		100	140 (284)
Mineral oil		100	140 (284)

Comparison with Other Plastics

Table 32 shows the performances of Solef® homopolymer resins in comparison to those of other hydrogenated plastics used in the chemical industry.

Table 32: Performance of Solef® PVDF homopolymers compared to other plastics

Environment	PVDF			PP			PVC			FRP		
	30°C 68°F	60°C 140°F	90°C 194°F									
H ₂ SO ₄ , 90%	+	+	○	○	○	-	+	○	-	-	-	-
HCl, conc.	+	+	+	+	○	-	+	+	○	+	○	-
HNO ₃ , 50%	+	+	+	-	-	-	+	○	-	-	-	-
HF, 40%	+	+	+	+	+		+	○	-	-	-	-
NaOH, 50%	-	-	-	+	+	+	+	+		+	+	
NaOCl, 15%	○	○	○	○	-		+	+		+	○	
Cl ₂ , dry gas	+	+	+	-	-	-	○	○		○	○	○
Cl ₂ , moist gas	○	○	○	-	-	-	○	○		○	○	○
Ketones, esters	○	-	-	+	-	-	-	-	-	-	-	-
Aromatic hydrocarbons	+	+	○	○	-	-	-	-	-	-	-	-
Chlorinated solvents	○	○	+	-	-	-	-	-	-	-	-	-

+: No significant change of properties

○: Modifications of properties, but may be used under mild conditions

-: Considerable alteration in material properties

Chemical Resistance of New Solef® Copolymer Developed for the Oil and Gas Applications

Solef® PVDF shows excellent resistance to hydrocarbon solvents (aliphatic, cyclic, and aromatic) that are present in the crude oil. Typically some swelling could be observed which can lead to a lowering of the modulus. However, the fluoropolymers are generally inert to these types of solvents and no chemical attack would be expected, even at high temperatures.

In order to achieve a good flexibility without appreciable loss in chemical resistance, VDF-based copolymers were developed. In particular, Solef® 60512 allows very good flexibility and good mechanical properties at low temperature combined with a chemical resistance close to the homopolymer. These features led to a wide use of Solef® 60512 copolymer in the Oil and Gas Applications.

Table 33 below presents swelling data of Solef® 60512 copolymer in contact with various hydrocarbon solvents that are present in crude oil.

Table 33: Chemical resistance of Solef® 60512 copolymer to hydrocarbon solvents* present in crude oil

Chemical	Weight increase Solef® 60512	Solef® PVDF homopolymer
Toluene 100 °C (212 °F)	+ 6.3 %	+ 3.7 %
Xylene 100 °C (212 °F)	+ 5.2 %	+ 3.0 %
Crude oil 135 °C (275 °F)	+ 0.9 %	+ 0.7 % (at 125 °C)
Benzene 80 °C (176 °F)	+ 6.6 %	–
Methanol 130 °C (266 °F)	+ 11.4 % *	+ 6.3 %

* slight dissolution

Permeability

Water Absorption

(ISO 62, ASTM D570, DIN 53495, NF T 51-166, BS 430 A)

- Homo- and copolymer resins: after 24 h at 23 °C (73.4 °F), absorption lower than 0.04 % by weight
- After 30 min and 30 days at 100 °C (212 °F), the Solef® 1010 grade led to absorption of 0.08 % and 0.19 % by weight, respectively. Expressed by surface unit of the sample, this absorption has the value of 1.9 g/m² after 30 min
- 4.5 g/m² at saturation

Note: The presence of fillers in the compounds modifies the behavior, and in some cases the water uptake can be significantly higher: consult Solvay Specialty Polymers.

Permeability

Permeability is determined by a dynamic method consisting of circulating the permeating gas, or storing the permeating liquid, on one side of the membrane to be evaluated while the other side is swept by an inert gas. The permeating gas once diffused, is continually drawn and dosed by chromatography.

The permeability P is given by the equation:

$$P = \frac{Q \cdot e}{S \cdot \Delta p \cdot t}$$

- where: Q: quantity of permeating gas having diffused
 e: thickness of the membrane
 S: exposed surface of the membrane
 t: time
 Δp: difference of permeating gas pressure between the 2 sides of the membrane.

P is expressed in:

- cm³ N·mm/m²·d·bar: for the gases
- g·mm/m²·d: for the liquids (we consider Δp ~ 1 bar)

P varies with the temperature T according to a law of Arrhenius in the form:

$$P = P_0 \cdot e^{-E/RT}$$

Although it involves an intrinsic characteristic of the material, independent of the thickness, P depends on the condition of the material in relation with its processing: type and degree of crystallinity, molecular orientation, surface condition, etc.

Note: As a general rule, the copolymers are more permeable than the homopolymers.

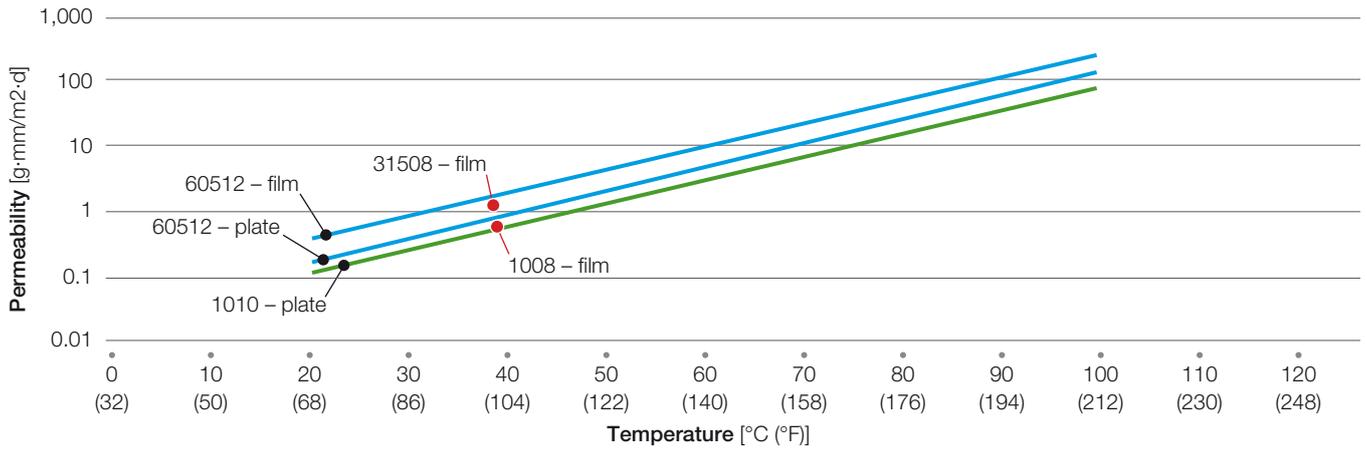
Water Permeability

Table 34: Water permeability of Solef® 1010

Type of Sample	Temperature [°C (°F)]	Permeability [g·mm/m ² ·d]
Film of 100 μm	23 (73)	0.2
	38 (100.4)	0.9
Sheet of 0.5 mm	23 (73)	0.2
	38 (100.4)	0.6
	100 (212)	1.5 30
Plate of 2 mm	23 (73)	0.2
	50 (122)	1.4
	100 (212)	26
	120 (248)	80

Water Vapor Permeability

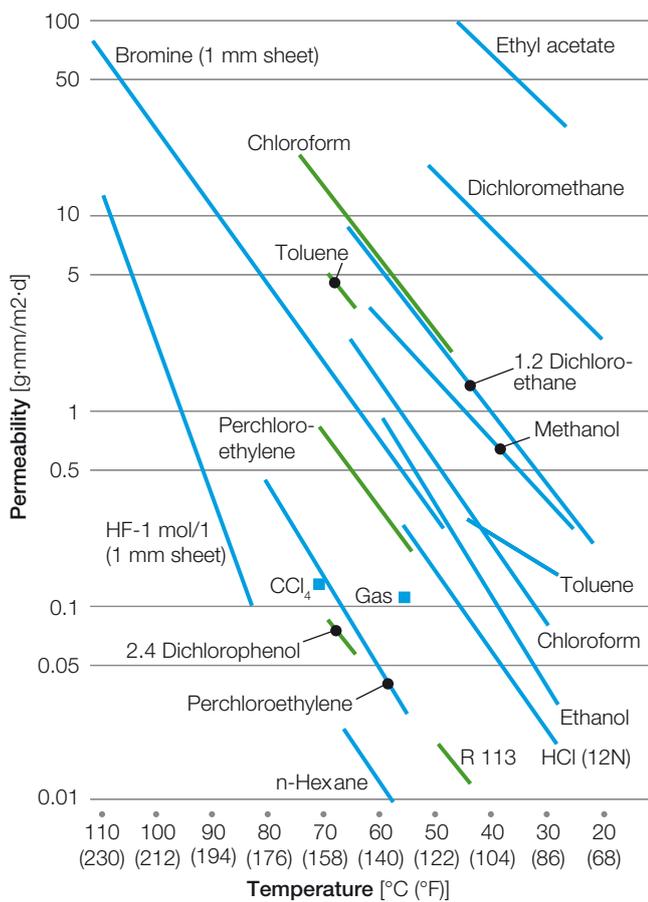
Fig. 56: Water vapor permeability of Solef® PVDF vs. temperature



Conditions: ASTM F1249-89 standard, Films: 100 μm, Extruded plates: 2 mm

Permeability to Liquids and Gases

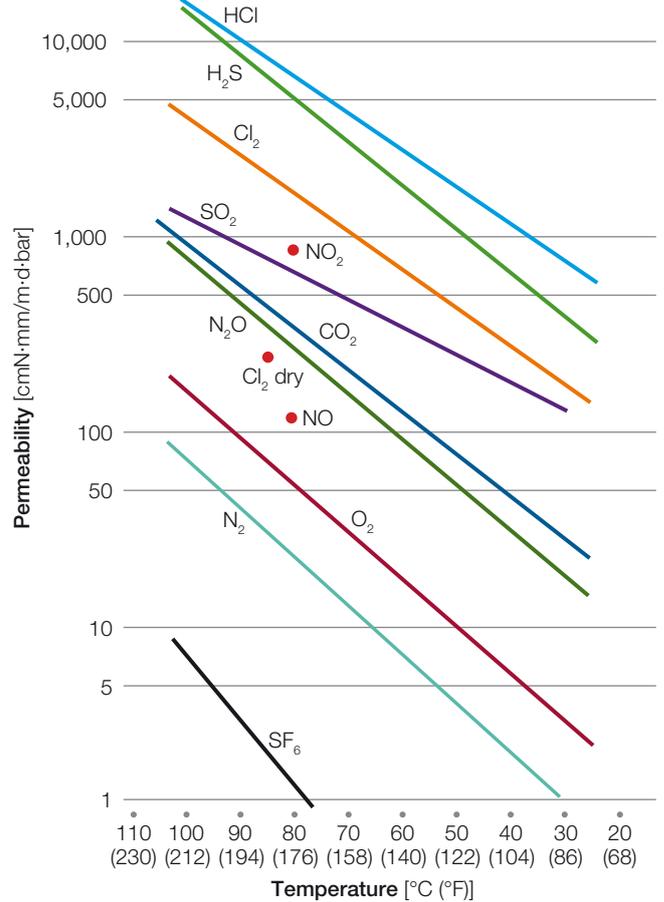
Fig. 57: Permeability to liquids of Solef® PVDF homo- and copolymers vs. temperature



— Solef® 1008 or 1010 homopolymer
— Solef® 11010 copolymer

Conditions: Measures performed on extruded films of ~100 μm by chromatography

Fig. 58: Permeability to gases of Solef® PVDF homopolymers vs. temperature



Conditions: Measured by gas chromatography: O₂, N₂, SF₆, N₂O, CO₂, Cl₂ dry, Measured according to ASTM D1434: NO, NO₂, SO₂, Cl₂, H₂S, HCl, Extruded films of ~100 μm

Thermal Aging Tests

Fluoropolymers generally have greater thermal stability than their hydrocarbon counterparts. This stability is due to the high electronegativity of the fluorine atom and thus to the high dissociation energy of the C-F bond.

In particular, PVDF has an excellent resistance to long term thermal aging (up to a temperature of 150 °C/302 °F), dependent on grades.

Tensile tests were performed on Solef® 1008 injection molded specimens after 2 years aging at 20 °C (68 °F), 120 °C (248 °F) and 150 °C (302 °F). See Table 35.

The mechanical characteristics remain constant and within the range of the measurement variations.

In the case of Solef® 11010 copolymer, aging tests up to 1,000 hours at 150 °C (302 °F) on compression molded sheets produced the same results, i.e. an excellent preservation of mechanical properties (see Table 36). The possible occurrence of a certain yellowing on aging has no effect on PVDF properties.

Table 35: Thermal aging tests at various temperatures on Solef® 1008

Aging Period [Days]	Tensile Yield Strength [MPa (psi)]			Secant Modulus at 1 % Deformation [MPa (kpsi)]			Elongation at Break [%]		
	20 °C 68 °F	120 °C 248 °F	150 °C 302 °F	20 °C 68 °F	120 °C 248 °F	150 °C 302 °F	20 °C 68 °F	120 °C 248 °F	150 °C 302 °F
1	50 (7,250)	53 (7,685)	51 (7,395)	1,900 (275)	1,700 (246)	1,600 (232)	9.5	10.5	11.8
11	49 (7,105)	54 (7,830)	51 (7,395)	2,000 (290)	1,900 (275)	1,800 (261)	8.5	10.0	13.0
160	53 (7,685)	54 (7,830)	51 (7,395)	2,300 (333)	2,100 (304)	1,800 (261)	7.0	9.0	11.5
358	54 (7,830)	55 (7,975)	53 (7,685)	2,300 (333)	2,300 (333)	2,200 (319)	7.0	10.0	> 11.0
730	52 (7,540)	54 (7,830)	–	2,300 (333)	1,800 (261)	–	6.6	10.4	–

Source: RAPRA – Injection molded specimens

Table 36: Thermal aging tests at 150 °C (302 °F) of Solef® 11010 grade

Properties	Units	Aging Period [h]			
		0	8	100	1000
Tensile properties					
Yield stress	MPa psi	28 4,060	28 4,060	29 4,205	28 4,060
Strength at break	MPa psi	41 5,945	34 4,930	34 4,930	40 5,800
Elongation at break	%	> 500	> 480	> 480	> 500
Modulus	MPa kpsi	1,020 148	1,070 155	1,020 148	870 126
Thermal properties					
HDT under 0.46 MPa (66.7 psi)	°C °F	113 235	122 252	132 270	149 300

Compression molded plates, thickness 2 mm
Rate of pulling: 10 mm/min (Modulus: 1 mm/min)

Maximum Continuous Use Temperature

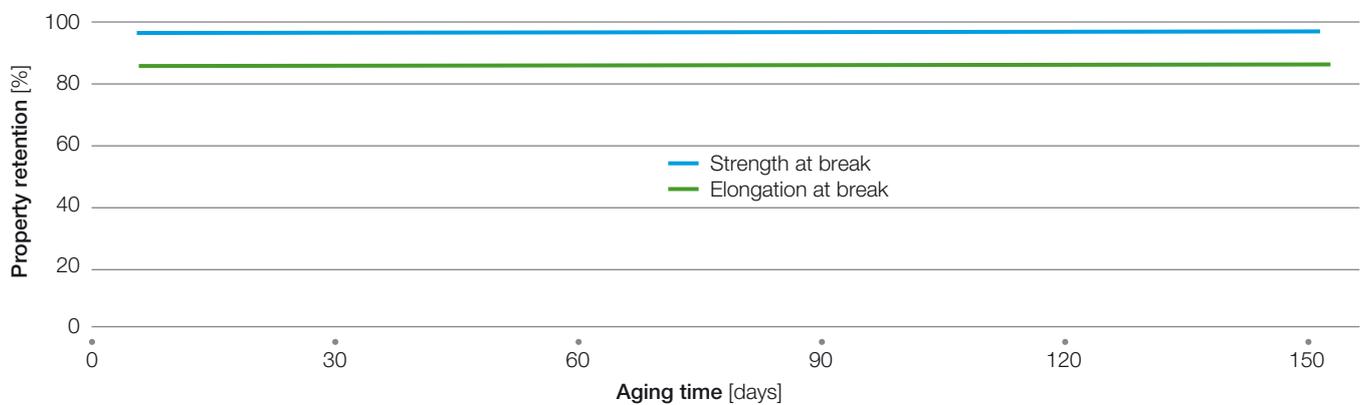
The maximum continuous service temperature of Solef® PVDF pipes subjected to hydrostatic pressure is 150 °C (302 °F). See also section “Bursting resistance to long term static pressure”.

Various institutes have approved the flexible linings made of Solef® PVDF for use in contact with gases at 160 °C (320 °F) in the combustion gas circuit at the outlet of high-performance boilers. These gases, when condensing, are aggressive (presence of sulfuric acid) and may corrode metal materials.

In the wire and cable industry, on the basis of tests performed by Underwriters Laboratories on finished communications cables, Solef® 11010/0003 and 31508/0003 grades received the “UL rating 150 °C (302 °F)”, while the 21508/0003 grade received the “UL rating 125 °C (257 °F)”.

For instance Figure 59 illustrates the results of tests performed by UL on 24 AWG (25 pair) cables jacketed with Solef® 31508/0003 copolymer, in accordance with the UL 444 procedure, making it possible to define the continuous use temperature (UL rating 150 °C/302 °F).

Fig. 59: Mechanical properties of cables jacketed with Solef® 31508/0003 copolymer vs. aging at 158 °C (316 °F)



Conditions: 24 AWG (25 pair) cables insulated and jacketed with Solef® 31508/0003, tests performed by UL in accordance with UL procedure 444
* Source: UL File E 76532

Weathering Resistance

Solef® PVDF offer excellent intrinsic resistance to natural aging and do not require anti-UV additives.

Artificial Aging Using Weather-O-Meter Equipment

Solef® 1008 film at 60 °C (140 °F) was irradiated with a carbon arc lamp with a maximum emission of 390 nm, and whose spectrum is rich in wavelengths between 330 and 430 nm. After 7,200 hours exposure (which is enough to affect most plastics), no measurable modification was identified with regard to the mechanical properties (tensile and impact strength).

Artificial Aging Using Xenon-Arc Weather-O-Meter and Water Exposure in Accordance with the UL 746C Procedure

Solef® 6008 considered stable for outdoor use (1,000 hours of Xenon-arc Weather-O-Meter conditioning and water exposure and immersion for 7 days at 70 °C/158 °F): very good retention of tensile impact and tensile strength, no variation inflammability test (see Table 37).

Table 37: Artificial aging using Xenon-arc Weather-O-Meter and water exposure (UL 746C)

Properties	Units	Percent Retention After Conditioning		
		Initial Properties	1,000 h UV	7 days water at 70 °C (158 °F)
UL 94 Flame test	Class	V-0	V-0	V-0
Tensile impact test	kJ/m ² ft-lbf/in ²	81 38.5	99 %	100 %
Tensile strength	MPa psi	45 6,525	100 %	95 %

Test conditions: Solef® 6008 plates – 1 mm thick, Tensile impact test measured in accordance with ASTM D1822, Tensile strength measured in accordance with ASTM D638

Accelerated Tests, Using Q-U-V Equipment

Solef® 1008: 5000 hours of cycles composed of 4 hours exposure to UV at 60 °C (140 °F) followed by 4 hours of condensation at 40 °C (104 °F) on 2 mm thick sheets: tensile modulus of 2,600 MPa (377 kpsi) unchanged.

Solef® 31508: 3000 hours of cycles composed of 6 hours exposure to UV at 45 °C (113 °F) followed by 2 hours of condensation at 45 °C (113 °F) on 100 µm films: aspect unchanged (color, gloss).

Accelerated Natural Aging Test

EMMAQUA method (ASTM D838 standard) on 80 µm thick films made of Solef® 1008: no alteration after 1 year weathering (see Table 38).

Table 38: Accelerated natural aging of Solef® 1008 films EMMAQUA tests, DSET Lab. Inc.

Properties	Unit	Aging Period [Months]			
		0	4	8	12
Yellowing index (ASTM 1925)	–	1,7	2,9	2,9	3
Melting temperature (DSC)	°C	174	174	172	173
	°F	345	345	342	343
Tensile test at 50 mm/min:					
Tensile yield stress	MPa	40	40	43	42
	psi	5,800	5,800	6,235	6,090
Strength at break	MPa	63	44	47	45
	psi	9,135	6,380	6,815	6,525
Elongation at break	%	520	440	320	460
Modulus*	MPa	1,280	1,490	–	1,310
	kpsi	86	216	–	190
Tensile impact strength (DIN 53448)	kJ/m ²	450	430	600	380
	ft·lbf/in ²	214	205	285	181

80 µm thick films produced by flat die extrusion on chill roll, Mechanical properties measured in the machine direction

* Rate = 1 mm/min

Natural Aging in Arizona

Aging of 80 µm films made of Solef® 1008 and 11010: no property alteration was found after several years, as shown by tests performed after 9 years aging (see Table 39).

Table 39: Natural aging tests performed in Arizona on Solef® PVDF films, DSET Lab. Inc. – New River

Properties of Solef® 1008 (I) and 11010 (II) Grades	Units	Aging [Years]									
		0		0,5		1		6		9	
		I	II	I	II	I	II	I	II	I	II
Yellowing index (ASTM 1925)		1,7	1,9	3,3	4,1	4,2	3,4	0,9	1,2	1,8	4,7
Melting temperature (DSC)	°C	174	159	174	158	174	159	173	158	175	160
	°F	345	318	345	318	345	318	343	316	347	320
Tensile test at 50 mm/min:											
Tensile yield stress	MPa	40	22	41	23	39	25	42	24	44	25
	psi	5,800	3,190	5,945	3,335	5,655	3,625	6,090	3,480	6,380	3,625
Strength at break	MPa	63	54	48	44	35	49	60	56	59	54
	psi	9,135	7,830	6,960	6,380	5,075	7,105	8,700	8,120	8,555	7,830
Elongation at break	%	520	470	440	370	320	380	450	410	425	420
Modulus*	MPa	1,280	590	1,350	670	1,150	660	1,350	700	1,370	670
	kpsi	186	86	196	97	167	96	196	102	199	97
Tensile impact strength (DIN 53448)	kJ/m ²	450	3,400	450	2,800	250	2,300	400	2,700	–	–
	ft-lbf/in ²	214	1,618	214	1,332	119	1,094	190	1,285	–	–
Resistance to Elmendorf tearing (ASTM 1922)	N	1,9	2,5	1,4	1,5	1,5	1,5	2,8	3,2	2,6	3,1
	lbf	0,43	0,56	0,32	0,34	0,34	0,34	0,63	0,72	0,59	0,70

80 m thick films manufactured by flat die extrusion on chill roll, Mechanical properties measured in the machine direction

* Rate of pulling = 1 mm/min

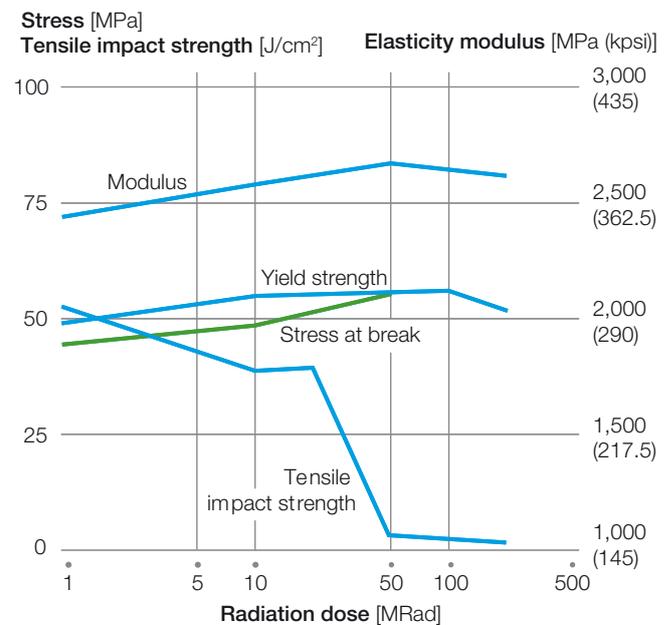
Resistance to High Energy Radiation

Solef® PVDF undergoes cross-linking when it is subjected to γ radiation, which modifies its mechanical characteristics. Depending on the conditions of service, the maximum tolerable dose can reach 20 to 40 MRad (This depends particularly on the thickness and the presence or absence of oxygen).

Radiation exposure tests using a Co⁶⁰ source were performed on injection molded specimens of Solef® 1010. The mechanical properties were measured after different doses of radiation. The results are presented in Figure 60. We observe a progressive increase of the modulus, the yield strength and stress at break, while the tensile impact strength diminishes gradually until a dose of 20 MRad, then more sharply for higher doses. The insolubility of PVDF in dimethylformamide (DMF) varies from 0 to 20% when the dose increases from 0 to 1 MRad. The insoluble portion increases to 72% at 10 MRad. Subjected to an accelerated electron bombardment of 3 MeV (β radiation), Solef® PVDF undergoes the same effects: crosslinking is virtually complete at the dose of 10 MRad.

In sterilization under a γ radiation dose of 2.5 and 5 MRad, Solef® PVDF preserves virtually all its properties, despite a discoloration which gradually appears with the radiation dose increase.

Fig. 60: Mechanical properties of Solef® 1010 vs. doses of γ radiation



Conditions: Injection moulded specimens

Temperature: 23°C (74.3°F)

γ-ray rate: 1 Gray/s

Resistance to Fire

Solef® PVDF display excellent intrinsic fire behavior. Nevertheless, PVDF is combustible like all organic materials. The gross calorific value (GCV) measured on Solef® homopolymer in powder form is 14.7 MJ/kg ($6.32 \cdot 10^3$ Btu/lb), in accordance with the calorimetric bomb test DIN 51 900 Part 3.

In addition, the lower flammability limit for the Solef® PVDF homopolymer powder fluidized in the air (concentration above which an explosion can occur in presence of a spark) was measured using a Hartmann pipe. It is 80 g/m³ ($5.0 \cdot 10^{-3}$ lb/ft³) for an average particle diameter (dp) ~ 60 µm (class St1 following VDI 3673: slightly explosive).

UL-94 Flammability Test (Underwriters Laboratories)

Table 40 lists the PVDF resins that have received the highest classification UL-94 V-0 according to the UL 94 procedure.

Table 40: Solef® PVDF grades certified UL-94 V-0

Grades

Solef® 1006/0001	Solef® 6008/0000
Solef® 1008/0001	Solef® 6010/0000
Solef® 1009/0001	Solef® 460
Solef® 1010/0001	Solef® 11008/0003
Solef® 1012/0001	Solef® 21508/0003
Solef® 6008/0001	Solef® 31508/0003

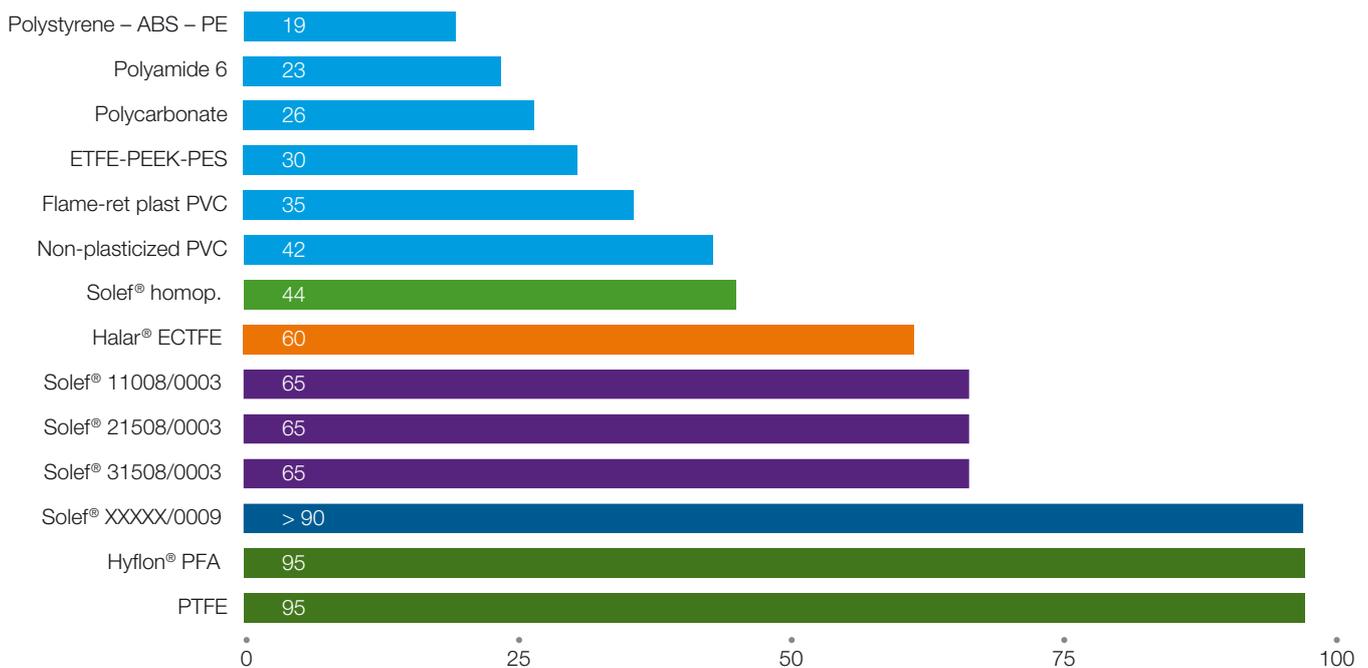
Limiting Oxygen Index – LOI

The oxygen index is defined by ASTM D2863 as the minimum concentration of oxygen, in a mixture of oxygen and nitrogen that will support flaming combustion of a test material.

Since ordinary air contains roughly 21 % oxygen, a material whose oxygen index is appreciably higher than 21 is considered flame resistant because it will only burn in an oxygen-enriched atmosphere.

Figure 61 presents the LOI at 23 °C (73.4 °F) of Solef® PVDF resins in comparison with other thermoplastics. It includes Solef® PVDF copolymers specially developed for wire and cable applications and offered with patented fire retardant formulations. There are in particular Solef® PVDF copolymers with a LOI of > 90% which are available on request. Those grades are identified as follows: XXXXX/0009.

Fig. 61: Limiting oxygen index (LOI) of Solef® PVDF resins and various thermoplastics (thickness: 3 mm)



Flame Spread in UL 723

“Steiner Tunnel Test” (ASTM E84, UL 723)

The test ASTM E84 (or UL 723) is designed to evaluate the flame spread on the surface of a material and the density of smoke released by the combustion.

This test is carried out in a horizontal tunnel 25 feet long with forced ventilation. The ceiling of the tunnel is covered with 4 contiguous sheets of Solef® 1010 with dimensions of 6 ft x 2 ft and a thickness of 3 mm (0.12 in). Two gas burners with a heating power of 5.3 MJ/min (5.0 kBtu/min), located at the entrance of the tunnel under the material to be tested constitute the flame source. The maximum propagation distance and smoke density are normally assessed in comparison to wood (red oak) whose flame propagation index and optical density index are both 100. Class 1 corresponds to materials which have flame propagation indices between 0 and 25 and smoke density indices below 450.

As for example the results for Solef® 1010 are:

- Propagation distance: 1.5 ft
- Flame propagation index: 5
- Smoke density: 90
- Classification: class 1

UL 910 Modified Steiner Tunnel Test

In addition, similar tunnel tests were performed by the Underwriters Laboratories (UL 910 or NFPA-262 on finished products) for telephone cables insulated with Solef® PVDF copolymer, with jacketing of wire bundles using same Solef® PVDF grade. The results of the flame propagation tests appear in Table 41.

The Solef® PVDF copolymers specially developed for the wire and cable market are thus classified by UL suitable for communication cables and plenum cables applications.

Epiradiator Test (NF P 92-501)

The French epiradiator test consists of exposing a specimen to a radiant heat source of 3 W/cm² (2.59 Btu/s·ft²), in presence of a pilot flame which is supposed to burn any gases which are released. Materials are classified from M1 (the best for combustible materials) to M4. Virgin PVDF resins were classed as M2 (difficult to burn).

Smoke Emission – NBS Chamber Test

The NBS chamber test consists of exposing a specimen (76 × 76 × th. mm) to a radiant heat source of 2.5 W/cm² (2.16 Btu/s·ft²) in the presence (or not) of flames, and to measure the opacity of the smoke emitted by the specimen. The results obtained with Solef® PVDF appear in Table 42 in comparison to other thermoplastics.

Table 41: UL 910 test on electrical cables jacketed with Solef® PVDF

Types of Cables	Specification	100 Pairs of Twisted Telephone Cables (24 AWG)	25 Pairs of Twisted Telephone Cables (24 AWG)	
		11010/0003	21508/0003	31508/0003
Solef® PVDF grade		11010/0003	21508/0003	31508/0003
Temperature rating [°C (°F)]	–	150 (302)	125 (257)	150 (302)
Max. flame spread [ft]	≤ 5	3	2.5	2
Average optical density	≤ 0.15	0.01	0.02	0.06
Maximal optical density	≤ 0.5	0.06	0.1	0.1

Table 42: Smoke production of Solef® PVDF (NBS chamber). Comparison with other thermoplastics

Material	Thickness [mm (in)]	Max. Specific Optical Density [Dm]		Optical Density VOF4	
		w/o flame	with flame	w/o flame	with flame
1010	2 (0.079)	25	270	–	–
11010	2 (0.079)	45	145	–	–
11008/0003	5 (0.20)	120	150	4	55
31508/0003	5 (0.20)	75	85	0	40
PMMA*	3 (0.12)	63	117	–	–
Polypropylene*	3 (0.12)	550	162	–	–
Flame-retardant polypropylene*	3 (0.12)	820	600	–	–
Polystyrene*	3 (0.12)	476	960	–	–

Safety, Hygiene, Health Effects

Fluoropolymer resins, like Solef® PVDF, are known for their high chemical stability and low reactivity.

Where toxicological studies have been conducted on fluoropolymers, no findings of significance for human health hazard assessment have been reported. None of the fluoropolymers are known to be a skin irritant or sensitizer in humans.

Following massive exposure to fluoropolymer resin dust by inhalation, increases in urinary fluoride were produced; however, no toxic effects were observed.

Some Solef® PVDF resins are formulated with additives such as fillers, pigments, stabilizers, etc, to provide favourable processing, or other characteristics. These additives may present other hazards in the use of the resins.

The Safety Data Sheet available for each of the commercial grades should be consulted for specific health information and to follow all the necessary safety instructions.

For further details, please consult the official texts relating to the national laws on Workplace Protection and the brochure “Guide for the Safe Handling of Fluoropolymer Resins”.

Toxicity of Decomposition Products

The main Solef® PVDF grades must be processed at temperatures between 200 °C and 250 °C (392 and 482 °F).

Under these conditions, there is no risk of decomposition of the PVDF (except in the presence of contaminants – See Section “Processing Basics and Safety”).

Nevertheless fumes can be generated even at the temperatures reached during the normal hot processing of fluoropolymers and it is necessary to assume that the resulting fumes can present a potential health hazard. It is essential that adequate ventilation is provided to prevent exposure in the workplace. (See Section “Processing Basics and Safety”).

The consequence of over-exposure to the fumes from fluoropolymers decomposing under these conditions is termed “Polymer Fume Fever”. This is a temporary, influenza like illness with fever, chills and sometimes a cough which lasts approximately 24 to 48 hours. The illness is also associated with exposure to the decomposition products produced by smoking tobacco products, such as cigarettes, which have become contaminated by fluoropolymer resins, even by trace quantities. It is essential that smoking and tobacco products be banned in work areas where fluoropolymer resins are handled.

The main types of products formed in the decomposition of fluoropolymers are oxidation products, mainly hydrogen fluoride and carbonyl fluoride; at higher temperatures, low molecular weight fluoropolymer particulates are released.

As an indication with respect to HF, the ACGIH TLV Ceiling value (the concentration that should not to be exceeded during any part of the working exposure) is 2 ppm (1.7 mg/cm³), the indicative occupational exposure limit values established by Directive 2000/39/EC is 3 ppm (2.5 mg/m³) for short-term (15-minutes) exposure period and the IDLH (Immediately Dangerous to Life or Health Concentrations) value set by NIOSH is 30 ppm.

In the event of fire, it is preferable to extinguish it with sand or extinguishing powder; use of water may lead to the formation of acid solutions.

The odour threshold of hydrogen fluoride is significantly less than the occupational exposure limits. Inhalation of hydrogen fluoride at higher concentration will give rise to symptoms of choking, coughing and severe eye, nose and throat irritation. In severe cases, and possibly following a symptom free period, fever, chills, difficulty in breathing, cyanosis, and pulmonary oedema may develop which may lead to death. Acute overexposure to hydrogen fluoride can result in injury to the liver and kidneys.

Approvals

Food Contact

The inertness of sintered fluoropolymers and their resistance to high temperatures have made them a good candidate material for articles to be used in contact with foodstuffs.

At present, in Europe, plastic materials coming into contact with food are regulated by the EU Commission Regulation No. 10/2011 and its amendments. Under this directive plastic articles intended to come into contact with food shall have all their monomers or starting substances listed in the above mentioned directive and are required to comply with an overall migration limit and specific migration limits for the monomers used in the production of the polymer. It is the responsibility of the supplier of the finished article to ensure compliance with these limits.

The fluorinated monomers used in Solef® PVDF homopolymers (vinylidene fluoride) and copolymers (vinylidene fluoride, hexafluoropropylene, chlorotrifluoroethylene) meet the requirements of the above mentioned Directive.

Solef® homopolymers comply with the specifications of the United States Food and Drug Administration (FDA) 21CFR 177.2510; Solef® VDF/HFP and VDF/CTFE copolymers comply with the specifications of 21CFR 177.2600.

The compliance with these regulations depends on the Solef® PVDF polymer family and on the grade used; consequently, users should contact the Solvay Specialty Polymers representative to obtain information on current listings.

National Water Contact Standards

Several States operate national acceptance schemes (NASs) for products and/or materials used in contact with drinking water. These schemes involve testing of materials and products and/or the assessment of evidence for product acceptability. The objective of all NASs is to ensure that products used in contact with drinking water do not cause a significant risk to consumers' health, or cause unacceptable effects on drinking water quality, such as tastes and odours. The test requirements, acceptance criteria and acceptance levels vary among the NASs.

Listings expire periodically and depending on market demand they may or may not be recertified. Contact your Solvay Specialty Polymers representative for the latest listing.

Germany

Table 43 lists the resins that have been tested and comply with:

- the KTW recommendations of the German Federal Health Office at temperature up to 90 °C (194 °F); the plastic materials are tested in respect of its influence on the appearance quality of the water, the release of its constituents into the water and its disinfectants demand
- DVGW W270; the plastic materials are tested for the microbial resistance

Table 43: Solef® PVDF grades in compliance with KTW and DVGW W270

Grades Tested by KTW	Grades Tested by DVGW W270
Solef® 1008/0001	Solef® 1008/0001
Solef® 1010/0001	Solef® 1010/0001
Solef® 1010/0901	Solef® 1010/0901 (black master batch)

United Kingdom

Table 44 lists the Solef® PVDF grades that have met the requirements of the Water Regulations Advisory Scheme (WRAS) Tests of Effects on Water Quality – BS 6920, Hot and Cold Water Use and are suitable for use in contact with potable water

Table 44: Solef® PVDF grades in compliance with BS 6920

Solef® 1008/0001	Solef® 1010/0901
Solef® 1010/0001	

National Sanitation Foundation (NSF International)

NSF International is a non-governmental organization that develops standards for public health and safety. It also provides lists of materials that conform to their standards.

NSF Standard 51 – Food Equipment Materials

Table 45 lists the Solef® PVDF polymers certified to this standard at the maximum temperature of 126 °C (259 °F). The listed materials are certified for all food types (dry solids, aqueous, acidic, dairy products, oil and alcoholic beverages).

Table 45: Solef® PVDF grades in compliance with NSF Standard 51

Solef® 1008/0001	Solef® 6020/1001
Solef® 1010/0001	Solef® 11008/1001
Solef® 1015/1001	Solef® 21216/1001
Solef® 6008/0001	Solef® 21508/1001
Solef® 6010/1001	

NSF Standard 61 – Drinking Water System Components – Health Effects

Table 46 lists the Solef® PVDF polymers certified to meet NSF Standard 61 at 85 °C (185 °F)

Table 46: Solef® PVDF grades in compliance with NSF Standard 61

Solef® 1008/0001	Solef® 6020/1001
Solef® 1010/0001	Solef® 11008/0001
Solef® 1015/1001	Solef® 11008/1001
Solef® 6008/0001	Solef® 11010/1001
Solef® 6010/0001	Solef® 21216/1001
Solef® 6010/0000	Solef® 21508/1001

Medical Applications

Solef® 1008 has been tested according to USP chapter 88 “Biological reactivity tests, in vivo” and has demonstrated its compliance with the requirements of USP Plastic Class VI.

Although USP Class VI testing is widely used and accepted in the medical products industry, it does not fully meet any category of ISO 10993-1 testing guidelines for medical device approval.

Each specific type of medical product must be submitted to appropriate regulatory authorities for approval. Manufacturers of such articles or devices should carefully research medical literature, test and determine whether the fluoropolymer is suitable for the intended use. They must obtain all necessary regulatory agency approvals for the medical product including all raw material components.

Solvay Specialty Polymers does not allow nor support the use of any of our products in any permanent implant applications. For any questions regarding our implant policy, please contact your Solvay Specialty Polymers representative.

Processing Basics and Safety

Solef® PVDF grades are melt processable fluoropolymers which can be processed using techniques applicable to standard thermoplastics like polyolefins. However, some peculiarities have to be taken into account. Here below a general description of the main aspects of processing is detailed.

Safety

PVDF resins are relatively non-toxic resins which are not hazardous under typical handling or processing conditions. But, as with all polymer materials exposed to high temperatures, good safety practice requires the use of adequate ventilation when processing. Ventilation should be provided to prevent exposure to any fumes and gases which could be generated. Excessive heating may produce fumes and gases which are irritating or toxic.

Certain additives such as mica, glass fibers, light metal such as titanium, boron, aluminum, may catalyze thermal decomposition rates and need to be avoided.

Since the standard melt temperatures of PVDF do generally not exceed 250 °C (482 °F) during extrusion and since decomposition does not take place below 350 °C (662 °F), a safety margin of roughly 100 °C (212 °F) is observed for homopolymer. This safety margin is slightly reduced with VF2-CTFE copolymers. Nevertheless, these products are processed without problems at temperatures lower than 250 °C (482 °F).

General Considerations

Handling and Storage

Drying is unnecessary as the resin does not absorb water. The low water absorption inhibits the dissipation of frictional static charges. Consequently, the resin container should be covered at all times to prevent the deposition of contaminants on the pellets or powder. When bringing the resin from a colder room, the closed packing should not be opened until the resin has gained the temperature of the processing room. This avoids condensing atmospheric moisture on the pellets or powder.

Extruder Type

A single screw extruder of the type used to process polyolefin is preferred. The barrel can be polished or machined with very small grooves. The barrel-screw tolerance should be about 200 microns. Typical design considerations are listed in the following Table.

Feeding zone	15–20 D
Compression zone	0.5–3 D
Metering zone	5–7 D
Total Length	25 D (e. g. 15 D + 3 D + 7 D or 18.5 D + 0.5 D + 6 D – short compression section for long feeding section)
Compression ratio	2.5 – 3
Pitch	= diameter
Front angle of screw	60°

In general, stagnation zones and excessive shear should be avoided (the latter can induce the formation of a gamma phase, a crystalline PVDF phase with lower thermal stability).

For industrial production, the screw and barrel material should resist both corrosion and abrasion. If different materials are used for the screw and barrel, the screw hardness should be lower than the barrel hardness. As Solef® PVDF resins are processed at temperatures varying from 200 to 240 °C (392 to 464 °F), equipment with material of similar construction to those used for processing PVC and polyolefins is adequate. For intensive processing of PVDF, the use of more corrosion resistant materials is more appropriate.

For more detailed information it is recommended that the fabricator consults with the local Solvay Specialty Polymers representative.

Head – Die

A pressure gauge and temperature gauge should be preferably installed in the head. Screen packs and a breaker plate can be used for additional backpressure and filtering (40/80/40 mesh/breaker plate).

In general, rounded angles are recommended for the die and any associated equipment. For the die and core material, corrosion resistant materials such as hard chromium plating or nickel plating, Duranickel (301), Hastelloy (276 °C), are recommended for the parts in contact with the polymer. The use of low iron tooling is especially useful with VF2-CTFE copolymers (Solef® 30000 series), which show more sticking on the tooling.

Operating the Extruder

Set-Up

Always use a clean extruder to avoid contamination.

Temperature Profile

A typical temperature profile for set up is shown in the following Table:

Zone 1	180–200 °C (356–392 °F)
Zone 2	200–220 °C (392–428 °F)
Zone 3	210–230 °C (410–446 °F)
Zone 4	210–230 °C (410–446 °F)
Breaker	220–240 °C (428–464 °F)
Head	220–240 °C (428–464 °F)
Die	220–240 °C (428–464 °F)

Melt temperatures should be 200–240 °C (392–464 °F). If the extrudate exhibits a yellow or brown coloration, it means that the melt temperature is too hot. It is generally advised to keep the melt temperature as low as possible to avoid degradation.

Stopping – Restarting

When the extrusion of Solef® PVDF is stopped, the following recommendations should be observed depending on the duration of the stoppage:

0–0.5 hours:	Maintain the set temperatures
0.5–2 hours:	Decrease the set temperatures to 180 °C (356 °F)
> 2 hours:	Stop the heating

Before restarting, reset the set temperatures to normal. Start extrusion again when the melt temperature is > 200 °C (392 °F). Please consider that VF2-CTFE copolymers (Solef® 30000 series) have a lower thermal stability, and hence should be purged with homopolymer before stopping the extruder.

Contact us for more detailed information.

Cleaning

At the end of an extrusion program (or if problems of degradation occurs), purge with a thermo-stable, highly viscous, pure polymer whose processing is compatible with PVDF (e.g. PE, PP). Never burn PVDF wastes.

Do not clean pieces in a salt bath. Physical cleaning of screw and barrel has to be done (it is advisable to use brass tooling). Physically cleaned screw, die and core can be put into an ultrasonic bath, filled with dimethylacetamide and heated up to 60 °C (140 °F) (immersion time: 1 hour) under sufficient venting (due to toxicity of solvent).

Recommendations for Tube Extrusion

Solef® PVDF pipes are widely used in semiconductors and CPI. For more information about optimal extrusion conditions, contact your Solvay Specialty Polymers representative.

General Recommendations for Other Types of Extrusion

Films, Sheets, Plates

Solef® PVDF can be extruded using a flat die to make films, sheets and plates from 10–20 µm up to about 1 cm.

Thin films are extruded onto a standard chill roll. The rapid chilling gives very small dimension crystallites and a high proportion of amorphous polymer phase, so the film is remarkably transparent.

During production, the film has a tendency to accumulate static electricity. The usual precautions are enough to ensure its removal. Non-oriented films can also be blow extruded.

For sheets regularity of thickness is ensured by calendering and keeping a small bank at the entrance of the first two rolls which must be heated to between 110 and 120 °C (230 and 248 °F).

For sheet lining applications, PVDF sheets can be backed during extrusion – calendering using cloth of glass fiber or synthetic fibers, which are selected for adhesion and heat forming.

Typical temperature profiles for film extrusion are here below reported in Table 47.

The manufacture of wire coating is carried out with conventional techniques. The melt temperature can be in the range 220 – 250 °C (428 – 482 °F) depending on the speed of the process.

The head must be profiled with care, avoiding any stagnant areas or sudden changes of direction. The method used should be by drawing a pipe onto the wire and the conventional draw down ratio can be defined as the ratio between the exit section of the die and the final section of the insulation on the wire.

The material should be drawn and cooled immediately, usually in a water bath.

Filaments

Solef® PVDF can also be extruded to produce mono- and multi-filaments. Draw down ratios are generally quite low and the melt temperature range can be between 200 and 250 °C (392 and 482 °F).

Table 47: Typical temperature profiles for film extrusion

Processing Conditions	Units	Homopolymers		Copolymers		
		Solef® 1008 and 6008	Solef® 1010 and 6010	Solef® 21508	Solef® 31508	
Extruder temperature profile	Zone 1	°C (°F)	190 (374)	190 (374)	160 (320)	190 (374)
	Zone 2	°C (°F)	210 (410)	230 (446)	180 (356)	210 (410)
	Zone 3	°C (°F)	220 (428)	230 (446)	200 (392)	220 (428)
	Zone 4	°C (°F)	230 (446)	230 (446)	210 (410)	230 (446)
	Die	°C (°F)	230 (446)	230 (446)	210 (410)	230 (446)
Chill-roll temperature		°C (°F)	95 (203)	95 (203)	70 (158)	25 (77)

Recommendations for Injection Molding

Equipment Plasticizing Unit

A conventional polyolefin screw extruder type can be employed.

Nozzle

An open nozzle should be used.

Mold

Hot channels can lead to stagnation at high temperature, which could induce degradation problems. For this reason Solvay Specialty Polymers would not recommend the use of hot channels. Nevertheless they are used in the industry.

The shrinkage of PVDF injected parts is 2–3%. The mold has to be designed in order to account for that shrinkage. It is recommended to heat the mold and let PVDF pieces cool slowly, while applying a sufficient hold pressure. This assures a complete filling and strong weld line (almost 100% of properties achievable on the weld line). The optimum mold temperature is 60–90°C (140–194°F). Also higher temperatures are possible. The holding pressure should be close to the injection pressure. If lower shrinkage than 2–3% is required, a reinforced grade should be used.

Processing Parameters

Temperature profile:

Feeding zone	190°C (374°F)
Compression zone	200–220°C (392–428°F)
Metering zone	200–240°C (392–464°F)
Nozzle zone	200–240°C (392–464°F)
Melt temperature	200–240°C (392–464°F)
Screw rotation speed	3–10 m/min (tangent speed)
Back pressure (plastification)	5–20 bar (72–290 psi)
Injection pressure	600–1,500 bar (8,700–21,000 psi)
Hold-on pressure	600–1,500 bar (8700–21,000 psi)

Injection speed: low (to avoid shear), but quick enough to fill the mold before crystallization occurs.

General Recommendations Temperature

Verify the temperature of the mold cavities using a temperature probe.

Check the melt temperature using a temperature probe in a volume of melt, shot on an insulator (a glove, cardboard, etc.).

Shot Volume

Set the initial cooling time and a zero holding time and pressure.

Inject incomplete parts by gradually increasing the shot volume using an average to high injection speed. When the mold is almost filled (90 to 95%), set the initial holding pressure and gradually increase the holding time.

In this way, the end of the filling is done under constant pressure and part over-packing is avoided.

Holding Phase

Adjust the holding phase parameters to obtain a constant part weight and the required dimensional stability.

Cooling

The cooling time depends on the part geometry. Gradually adjust the cooling time until the optimal cycle time is obtained.

Shrinkage

Shrinkage governs a large range of final properties or defects: size tolerances, internal stresses, voids, sinks marks, etc.

The linear shrinkage is 2–3%, but the real value is the volumetric shrinkage. It depends on mold geometry, filling characteristics and rheological properties.

Annealing

In order to release internal stresses, the parts can be annealed at 150°C (302°F) with slow heating and cooling. A good starting base for annealing time at 150°C is 1/2 h for 1 cm thickness (1 h for 2 cm, etc.).

Safety

Stopping – Restarting: if the material remained a long time at high temperature, make the first injection outside the mold, in order to check that the resin has not turned yellow.

Recommendations for Compression and Transfer Molding

In every field where Solef® PVDF are used (chemical industry, electronic industry, ...) thick parts may be needed to build complete installations. Such thick items can be machined from thick semifinished rod or block. These can be either extruded or compression molded from pellets. This last method is quite easy but experience has shown that a carefully designed procedure is needed.

General Considerations

An adequate viscosity of the employed grade has to be chosen so that flowing out of the mold (flashing) is minimized during compression. For this reason, high viscosity resins are used.

The process has to be carried out in a way to obtain color homogeneity and no voids in the final semifinished item.

Process Description

Basically, compression molding comprises three steps:

- Heating and melting the granules
- Molten cake compression
- Cooling

Two methods are usually proposed in the first step: melting of granules inside the mold or outside the mold.

First Step: Heating and Melting the Granules

Melting inside the mold (usually up to 4 cm thickness)

The required amount of PVDF granules can be melted directly in the preheated mold. Preheating temperature of the mold should be 210°C (410°F). Make sure that preheating period is long enough to obtain adequate and stable temperature all over the mold surfaces.

Preheat the granules to 150°C (302°F) before filling the mold.

The melting time in the mold must be sufficient to melt all the granules, even in the middle of the layer, before any compression. Sheets up to 4 cm thick can be produced by this way. Above 4 cm, melting time would be too long and the color could be too dark. The second method is then preferred: melting outside the mold in order to reduce the melting time.

Melting outside the mold (for all thicknesses)

The granules can be melted in a ventilated oven at about 210°C (410°F). The molten cake is then transferred in the preheated mold. Make sure that the granules are completely molten before being transferred and pressed.

Melting of the resin is also possible by using an extruder. The melt is then transferred in the preheated mold as previously described.

This way is indicated to obtain the best semi-finished items.

Second Step: Molten Cake Compression

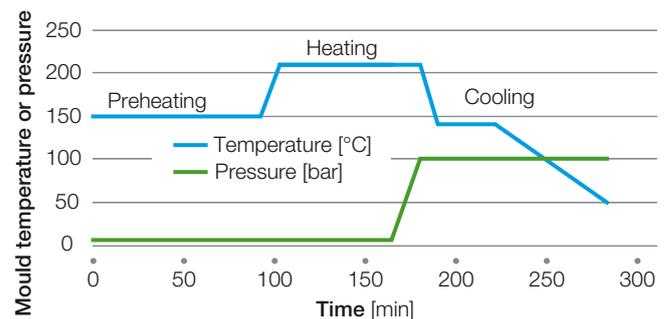
Melting inside the mold

In this case, the mold temperature is maintained at 210°C (410°F) throughout the compression period.

An example of cycle is reported hereafter (see also Fig. 62).

1. Granules preheating	At 150°C (302°F) 90 min in 2 cm layers in a ventilated oven
2. Mold preheating	At 210°C (410°F) 60 min
3. Granules melted	30 min/cm thickness at 210°C (410°F) with no pressure (minimum 60 min)
4. Stepwise pressure increase	Molten cake pressing lasting 15 min for every cm thickness at 210°C (410°F)
5. Quick cooling down	Quick cooling down to 140°C (284°F) and plateau maintained 30 min/cm thickness at 140°C (284°F), under maximum pressure
6. Slow cooling down	From 140° (284°F) to 50°C (122°F) 60 min/cm thickness under maximum pressure.

Fig. 62: Example of sheet compression molding – Sheet thickness of 1 cm



Melting outside the mold

In this case, the mold should be preheated at 150°C (302°F) and maintained at that temperature throughout the compression period. The way of setting up the pressure is the same as with the first method.

Note: If the mold clearance is not small enough, some molten resin may flow out of the mold when the pressure is too high. In this case, the maximum pressure applied during compression step should be reduced. Higher pressure should then be applied afterwards, after a few minutes, when a thin skin is cooled down the surface sealing the openings.

Third Step: Cooling

The cooling step is the same for both methods (melting of granules inside the mold or outside the mold).

Pressure: Pressure must be maintained at the maximum value throughout the cooling period (at least 100 bar/1,451 psi, ideally 150 bar/2,176 psi), down to about 50 °C (122 °F). The top force must be deep enough to take up the shrinkage during cooling and to prevent void formation.

Temperature: Decrease the mold temperature down to 140 °C (284 °F) and keep it constant for a certain time. By maintaining this plateau, excessive internal stresses can be avoided. The duration of the plateau is a compromise between internal stress minimization and yellowing. It should be at least 30 minutes per cm thickness.

The further cooling time from 140 to 50 °C (284 to 122 °F) is again the same compromise as too quick cooling would generate high temperature gradients and, as a consequence, high internal stresses.

Do not forget that when the sheet skin is at 50 °C (122 °F), the core may still be very hot, that is why pressure must be maintained for several hours. With such a long cooling time, annealing should not be necessary.

Equipment Required – Mold

The mold should have adequate size and sufficiently fine clearance to prevent excessive flowing out of the mold during the molten resin compression.

It should have top, bottom and side heating and cooling devices. These should be separately monitored to allow the top and bottom temperatures to be kept equal and to allow a slower cooling rate for the sides, the top and bottom surfaces. The mold should also be equipped to control the temperature of each face of the mold.

PTFE, PET or FEP film may be useful to prevent PVDF resin sticking on the mold inside walls.

Equipment Required – Press

The press should be able to reach at least 50 bar (725 psi), ideally up to 150 bar (2,176 psi).

Equipment Required – Oven

The oven should be ventilated to prevent temperature gradients. Temperature must be precisely controlled.

Machining

Semi-finished articles in Solef® PVDF can be machined without any special problem, employing the same techniques and equipment which are used with polyamides.

Welding

Items produced from all non-reinforced grades of Solef® PVDF can be easily assembled using standard welding methods, such as:

- Hot air welding with welding rod
- Butt welding
- Heat-sealing
- Ultrasonic
- IR welding

Hot air welding

The parts to be welded are profiled. After cleaning, they are clamped in place. The air is heated in the hot air gun. The air temperature taken at 5 mm from the end of the nozzle can be around 350 °C (662 °F). The melting rod is inserted into the bevel maintaining a continuous vertical pressure of 0.2–0.4 bar (2.9–5.8 psi).

The welding factor, which is generally defined as the ratio between the strength of the weld and the strength outside the welded zones, gives values between 0.8 and 0.9.

Butt welding

The melting parts are heated by pressing onto a metal heater which is held at 250–270 °C (482–518 °F) and which has been surface treated (usually with PTFE) to minimize adhesion. The ideal pressure on the hot surface is between 0.5–0.6 bar (7–8 psi) and the time should be sufficient for the fusion of the material to a depth of 4–5 mm at the contact surface. The heating unit is then removed and contact is made under a pressure of ideally 0.6–0.8 bar (8–11 psi).

Welding factors obtained by this technique are generally between 0.9 and 1.

NOTE: All the information given in these pages can only be considered as examples for processing of Solef® PVDF. Please contact Solvay Specialty Polymers for detailed information.



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