

Solef[®] & Hylar[®] PVDF

Polyvinylidene fluoride
Design and Processing Guide

Solvay
Solexis



TABLE OF CONTENTS

INTRODUCTION	5
The company	5
Solef® and Hylar® PVDF	5
CHEMISTRY	6
1. Composition and principle of polymerization	6
2. Copolymers	6
3. Purity of the resin	6
4. Comparison to other fluoropolymers	7
TYPICAL APPLICATIONS	9
PRODUCT RANGE	11
1. Material Selection	11
2. Packaging and storage	12
PHYSICAL PROPERTIES	13
1. Structural properties	13
2. Thermophysical properties	16
3. Short term thermal stability - Thermogravimetric analysis (TGA)	23
4. Surface properties	23
5. Solubility	27
6. Optical properties – Appearance	27
MECHANICAL PROPERTIES	30
1. Short-term stresses	30
2. Long term static stress - Creep	34
3. Dynamic loading	39
4. Impact strength	44
5. Reprocessing effects on mechanical properties	46
ELECTRICAL PROPERTIES	47
1. General characteristics	47
2. Volume and surface resistivities	47
3. Dielectric strength	47
4. Dielectric constant and tangent of loss angle	48
5. Comparative Tracking Index	49
6. Piezo- and pyroelectricity	49
ENVIRONMENTAL RESISTANCE	51
1. Chemical resistance	51
2. Permeability	53
3. Thermal aging tests	55
4. Maximum continuous use temperature	56
5. Weathering resistance	56
6. Resistance to high energy radiation	59
7. Resistance to fire	59
SAFETY, HYGIENE, HEALTH EFFECTS	62
1. Toxicity of decomposition products	62
2. Approvals	62
PROCESSING BASICS AND SAFETY	65
1. Safety	65
2. General considerations	65
3. Operating the extruder	66
4. Recommendations for tube extrusion	66
5. General recommendations for other types of extrusion	66
6. Recommendations for injection moulding	67
7. Recommendations for compression and transfer moulding	68
8. Machining	70
9. Welding	70

LIST OF TABLES

Table 1: Characteristics of PVDFs on the market according to ASTM D 3222 standard	6
Table 2: Ultra-pure water extraction data from Solef® PVDF pellets	7
Table 3: PVDF and the other fluorinated polymers	7
Table 4: Comparison of tensile creep characteristics of fluoropolymers Temperature = 23°C (73.4°F)	8
Table 5: Molecular weights of Solef® resins measured by Gel Permeation Chromatography.....	13
Table 6: Average MFIs at 230°C (446°F) under different loads	14
Table 7: Thermophysical data recorded by DSC	17
Table 8: Thermal conductivity of Solef® and Hylar® PVDF	19
Table 9: Coefficient of linear thermal expansion for Solef® and Hylar® PVDF	21
Table 10: Density at 23°C (73.4°F) of Solef® compounds	22
Table 11: Angle of contact and surface tension of PVDF and other thermoplastics (20°C/68°F)	25
Table 12: Shore D hardness of Solef® and Hylar® PVDF	25
Table 13: Ball hardness of Solef® PVDF.....	25
Table 14: Rockwell hardness of Solef® PVDF	25
Table 15: Average roughness of internal walls of extruded Solef® PVDF 1010 pipes and sheets	25
Table 16: Coefficients of friction of Solef® and Hylar® PVDF	26
Table 17: Coefficient of friction of Solef® 3208/0150 grade.....	26
Table 18: Abrasion resistance of PVDF (TABER test)	26
Table 19: Abrasion resistance of PVDF (AKRON test).....	26
Table 20: Solubility of Solef® homo- and copolymer resins in various solvents at 23°C (73.4°F).....	27
Table 21: Optical properties of Solef® PVDF films vs. thickness	29
Table 22a: Tensile properties of Solef® PVDF films (SI Units).....	32
Table 22b: Tensile properties of Solef® PVDF films (US Customary Units).....	32
Table 23: Very short term bursting resistance of Solef® PVDF pipe	37
Table 24: Charpy flexural impact strength.....	44
Table 25: Brittleness temperature of Solef® PVDF according to ASTM D 746. Compression moulded plate ...	45
Table 26: Impact tests by instrumented falling weight of Solef® PVDF and thermoplastics.....	45
Table 27: Tests of impact and tearing on Solef® PVDF films.....	46
Table 28a: Reprocessing effects on mechanical properties of Solef® 1010 grade (SI Units)	46
Table 28b: Reprocessing effects on mechanical properties of Solef® 1010 grade (US Customary Units).....	46
Table 29: Comparative Tracking Index CTI in accordance with the IEC 112 standard.....	49
Table 30: Piezo- and pyroelectricity of Solef® PVDF films and sheets of various thicknesses (23°C/73.4°F) ...	50
Table 31: Overview of the chemical resistance of Solef® and Hylar® PVDF	51
Table 32: Performance of Solef® and Hylar® homopolymers compared to other plastics.....	52
Table 33: Chemical resistance of Solef® 60512 copolymer to hydrocarbon solvents* present in crude oil.....	53
Table 34: Water permeability of Solef® PVDF 1010	53
Table 35a: Thermal aging tests at various temperatures on Solef® PVDF 1008 (SI Units)	55
Table 35b: Thermal aging tests at various temperatures on Solef® PVDF 1008 (US Customary Units).....	55
Table 36: Thermal aging tests at 150°C (302°F) of Solef® 11010 grade	55
Table 37: Artificial aging using Xenon-arc Weather-O-Meter and water exposure (UL 746C)	57
Table 38a: Accelerated natural aging of Solef® PVDF 1008 films (SI Units) EMMAQUA tests – DSET Lab. Inc.	57
Table 38b: Accelerated natural aging of Solef® PVDF 1008 films (US Customary Units) EMMAQUA tests – DSET Lab. Inc.	57
Table 39a: Natural aging tests performed in Arizona on Solef® PVDF films (SI Units) DSET Lab. Inc. – New River.....	58
Table 39b: Natural aging tests performed in Arizona on Solef® PVDF films (US Customary Units) DSET Lab. Inc. – New River.....	58
Table 40: Solef® and Hylar® PVDF grades certified UL-94 V-0	60
Table 41: UL 910 test on electrical cables jacketed with Solef® PVDF.....	61
Table 42: Smoke production of Solef® PVDF (NBS chamber) Comparison with other thermoplastics	61
Table 43: Solef® PVDF grades in compliance with KTW and DVGW W270	63
Table 44: Solef® PVDF grades in compliance with BS 6920.....	63
Table 45: Solef® grades in compliance with NSF Standard 51	63
Table 46: Solef® grades in compliance with NSF Standard 61.....	63
Table 47: Typical temperature profiles for film extrusion	67

LIST OF FIGURES

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).....	8
Fig. 2: Various crystalline phases and modes of crystallization of PVDF (A. Lovinger)	13
Fig. 3: Relation between MFIs at 5 and 2.16 kg and between MFIs at 10 and 5 kg	14
Fig. 4: Melt viscosity at 220°C (428°F) of various Solef® copolymers grades.....	15
Fig. 5: Melt viscosity at 200°C (392°F) of the 1000 series Solef® PVDFs	15
Fig. 6: Melt viscosity of Solef® PVDF 1010 at various temperatures	15
Fig. 7: Melt viscosity of Solef® PVDF 11008/0003 at various temperatures.....	15
Fig. 8: Melt viscosity at 100 s ⁻¹ of various Solef® grades vs. temperature.....	16
Fig. 9: DSC curves of Solef® PVDF 1010.....	17
Fig. 10: Rate of crystallinity measured by DSC and X-ray diffraction.....	18
Fig. 11: Incidence of cooling rate on crystallization temperature recorded by DSC (non-isothermal crystallization)	18
Fig. 12: Variation of crystallization half-time as a function of temperature (isothermal)	18
Fig. 13: HDT of various Solef® and Hylar® grades.....	19
Fig. 14: VICAT softening temperature (5 kg/11.0 lb) of various Solef® grades.....	19
Fig. 15: Specific heat of Solef® PVDF vs. temperature	20
Fig. 16: Thermal conductivity of Solef® PVDF 1010.....	20
Fig. 17: Thermal expansion curve of Solef® PVDF measured by TMA	21
Fig. 18: Density of Solef® PVDF vs. temperature	22
Fig. 19: pvT curves of Solef® PVDF 1008	23
Fig. 20: Thermogravimetric analysis under air of Solef® PVDF.....	24
Fig. 21: Extinction coefficient vs. wavelength for Solef® PVDF 1010.....	28
Fig. 23: IR-ATR spectrum of Solef® 1008 homopolymer film (transmission).....	28
Fig. 22: Absorption spectra of Solef® PVDF 1008 in UV and visible ranges - Influence of thickness	28
Fig. 24: IR-ATR spectrum of Solef® 11008 copolymer film (transmission).....	29
Fig. 25: Tensile curves for Solef® PVDF 1008 at various temperatures	30
Fig. 26: Tensile yield strength of Solef® PVDF vs. temperature	31
Fig. 27: Elongation at yield and at break of Solef® PVDF vs. temperature	31
Fig. 28: Tensile strength at yield or at break of PVDF vs. temperature.....	31
Fig. 29: Young's modulus of PVDF vs. temperature.....	32
Fig. 30: Flexural modulus of PVDF vs. temperature	33
Fig. 31: Ultimate flexural strength of various Solef® grades	33
Fig. 32: Compression modulus and ultimate compressive strength of Solef® PVDF vs. temperature	34
Fig. 33: Modeled isochrones at 23°C (73.4°F) of Solef® PVDF 1010 (extruded sheets)	35
Fig. 34: Experimental values for creep under tensile stress at 23°C (73.4°F) of Solef® PVDF 1010 (extruded sheets).....	35
Fig. 35: Creep under tensile stress at 140°C (284°F) of Solef® PVDF 1010 (extruded sheets).....	36
Fig. 36: Creep under tensile stress at 120°C (248°F) of Solef® PVDF 1010 and 60512.....	36
Fig. 37: Creep under tensile stress of Solef® 8808/0902 compound at 120°C (248°F).....	37
Fig. 38: Hoop stress of Solef® PVDF 1010 pipes vs. time until rupture	38
Fig. 39: Long term hoop stress of Solef® PVDF 1010 pipes extrapolated to 50 years (ISO/TR 9080)	39
Fig. 40: PVDF pipes in presence of water - Design stress extrapolated to 50 years (ISO 10931-2)	39
Fig. 41: Long term hoop stress of Solef® PVDF 1010 pipes using IPT test equipment (ISO/10931-2)	39
Fig. 42: Modulus E' and tg δ of Solef® homopolymers vs. temperature (DMTA)	40
Fig. 43: Modulus E' and tg δ of Solef® copolymers vs. temperature (DMTA)	41
Fig. 44: Fatigue under cyclical tensile stress for Solef® PVDF 1008 at 20°C (68°F).....	41
Fig. 45: Oligocyclic fatigue of Solef® PVDF 1010 at various temperatures	42
Fig. 46: Fatigue tests on notched specimens - Wöhler curve of Solef® PVDF at 25°C (77°F)	43
Fig. 47: Izod impact resistance of various Solef® grades vs. temperature.....	44
Fig. 48: Volume resistivity of Solef® PVDF vs. temperature	47
Fig. 49: Dielectric strength of Solef® PVDF vs. plate thickness	47
Fig. 50: Dielectric strength and breakdown voltage of Solef® PVDF 1008 films vs. thickness.....	47
Fig. 51: Dielectric constant of Solef® PVDF 1010 at low frequency vs. temperature	48
Fig. 52: Tangent of dielectric loss angle of Solef® PVDF 1010 at low frequency vs. temperature.....	48
Fig. 53: Dielectric constant of Solef® PVDF 11008/0003 at low frequency vs. temperature	48
Fig. 54: Tangent of dielectric loss angle of Solef® PVDF 11008/0003 at low frequency vs. temperature.....	49

LIST OF FIGURES

Fig. 55: Dielectric constant and $\tan \delta$ of Solef® PVDF 11008/0003 and 31508/0003 vs. frequency	49
Fig. 56: Water vapor permeability of Solef® PVDF vs. temperature	54
Fig. 57: Permeability to liquids of Solef® PVDF homo- and copolymers vs. temperature	54
Fig. 58: Permeability to gases of Solef® PVDF homopolymers vs. temperature.....	54
Fig. 59: Mechanical properties of cables jacketed with Solef® 31508/0003 copolymer, vs. aging at 158°C (316°F).....	56
Fig. 60: Mechanical properties of Solef® PVDF 1010 vs. doses of γ radiation	59
Fig. 61: Limiting oxygen index (LOI) of Solef® and Hylar® resins and various thermoplastics	60
Fig. 62: Example of sheet compression moulding – Sheet thickness of 1 cm	69

INTRODUCTION

The company

Solvay Solexis is the result of the acquisition of Ausimont by the Solvay Group in 2002. The merger of the Ausimont and Solvay activities in fluorinated materials into a single new company, Solvay Solexis, created a new leader on this market, totally dedicated to the development of fluoromaterials and their applications. Solvay Solexis is part of the Strategic Business Unit Specialty Polymers of the Solvay Group, and contributes to the group strategy by being a leader in specialty materials.

Solvay Solexis is an international company focused on socially sustainable and constantly growing businesses, based on the fluorine chemistry and benefits from a unique integrated value chain, from the Fluorspar to the ultimate fluorinated materials.

Solvay Solexis is operating worldwide through companies in five countries: Italy, France, Japan, Brazil and the USA. Solvay Solexis is headquartered in Bollate (Milan, Italy), which is also its main R&D facility. Local R&D support is also provided from Thorofare (NJ, USA) for the NAFTA area.

Solvay Solexis is organized in four Business Units.

Fluids – These sophisticated perfluoropolyethers, which are commercialized under the brands Fomblin[®], Fluorolink[®], Solvera[®] and Galden[®], are used as high performance lubricants and heat transfer agents offering unmatched chemical resistance and excellent thermal stability.

Fluoroelastomers – Tecnoflon[®] covers a wide range of elastomers offering excellent chemical and thermal resistance to atmospheric agents, especially to oxygen and ozone, which are notably used in automotive, aerospace, chemical, mining, oil and semi-conductors industries

PTFE and Coatings – Algoflon[®] PTFE and Polymist[®] PTFE exhibit outstanding physical, electrical and non-stick characteristics, and particularly excellent resistance in aggressive environments, in a wide range of temperatures. They are notably used for producing gaskets, seals, pipes, fittings, impregnated fabrics, additives for plastics compounds, elastomers and inks. Hylar[®] 5000 PVDF serves as the base resin for durable architectural coating. Hyflon[®] PFA

powders are used for very high temperature, harsh environment resistant coatings, in electronic, semi-conductors and processing fields. Halar[®] ECTFE in powder forms allows the production of particularly smooth and weather-resistant coatings, combined with extremely good chemical and flame resistance.

Melt Processable Fluoropolymers – Solvay Solexis offers a wide range of fluoropolymers easily processed by injection, extrusion, and all conventional processing techniques: Solef[®] and Hylar[®] PVDF (polyvinylidene fluoride), Halar[®] ECTFE (copolymer of ethylene and chlorotrifluoroethylene) and Hyflon[®] PFA (copolymer of tetrafluoroethylene and perfluoroalkylvinylethers).

Solef[®] and Hylar[®] PVDF

At a glance, the key properties of Solef[®] and Hylar[®] PVDF are the following:

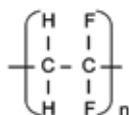
- Easy processing by extrusion, injection, compression and transfer molding, etc.
- Chemically inert to most acids, aliphatic and aromatic organic compounds, chlorinated solvents, alcohols, etc.
- Very high purity,
- Abrasion resistance comparable to that of polyamides, and relatively low coefficient of friction,
- Continuous use within a wide range of temperatures, from -40°C to +150°C (dependent on the grade and the stresses applied),
- Unaffected by UV (> 232 nm) and good resistance to γ radiation,
- Excellent intrinsic fire resistance: UL class 94 V-O and LOI from 44 to 65%, depending on the grade used,
- Very easily joined by welding and good capability for thermoforming,
- Physiologically harmless and approved for contact with food products.

Properties and processing techniques of both Solef[®] and Hylar[®] PVDF are detailed in this brochure.

CHEMISTRY

1. 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 D 3222 standard,
- The emulsion process to produce “E-PVDF” or type I PVDF according to the ASTM D 3222 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.

Table 1: Characteristics of PVDFs on the market according to ASTM D 3222 standard

	Type I Class 1	Class 2	Type II
Density, g/cm ³	1.75 to 1.79	1.75 to 1.79	1.76 to 1.79
Melting temperature (1), °C	156 to 162	162 to 170	164 to 180
Apparent melt viscosity (2), Pa.s:			
high viscosity	2800 to 3800	2800 to 3100	2500 to 4000
average viscosity	2300 to 2800	1300 to 2800	1300 to 2500
low viscosity		500 to 1300	500 to 1300

(1) According to the ASTM D 3418 standard; +/- 1 mg, from 20 to 200°C at 10°C/min Tf = peak of the endothermic curve
(2) According to the ASTM D 3835 standard: T° = 232°C, α = 60°, L/D = 15, γ = 100 s⁻¹ (capillary rheometer)

Solef® PVDF is made by suspension polymerization, and Hylar® PVDF is produced by emulsion polymerization.

Solef® and Hylar® 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).

2. Copolymers

In addition to the PVDF homopolymers, which are recognized worldwide for their excellent performance in a variety of applications, Solvay Solexis 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 Solexis manufacturing flexibility, based on two recipes, PVDF can be tailored to meet a wide range of property requirements. Solef® 11008 and Hylar® 20808 are ideal materials particularly for raceway and jacket applications. In situations where higher flexibility and lower shrinkage are required, such as jackets and fiber optic cable components, Solef® 31508 and Hylar® 21508 are recommended. All of these grades are offered with two patented fire retardant packages (see section “Product range, Material Selection”). They are very frequently used in applications which require great flexibility, such as communication cable sheathing and jacketing.

3. 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

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: ICP-MS

4. 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.

Table 3: PVDF and the other fluorinated polymers

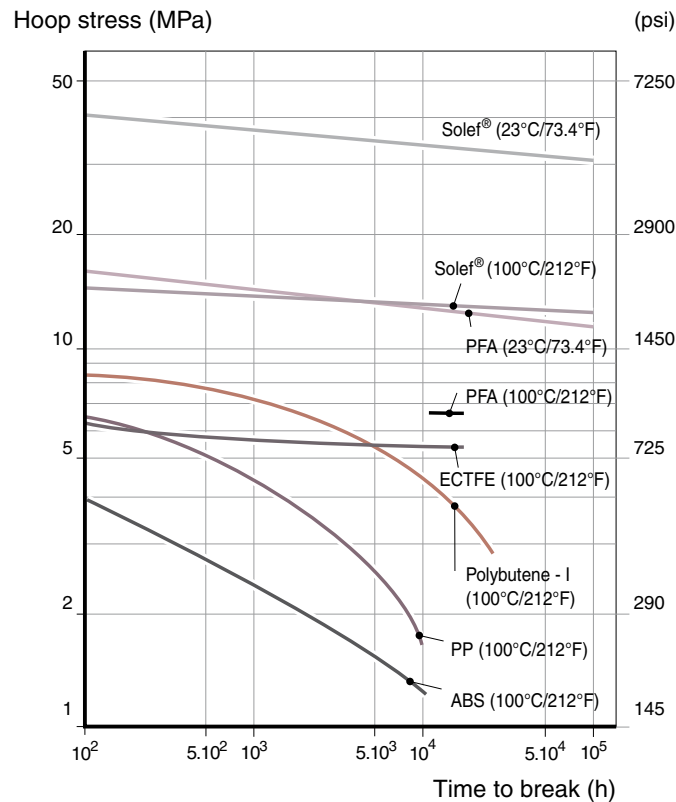
Average properties	Units	PVDF homopolymer	PTFE	FEP	PFA	ETFE	ECTFE
Density	g/cm ³	1.78	2.17	2.15	2.15	1.72	1.68
Melting point	°C	160 - 172	330	270	305	-	242
	°F	320 - 342	626	518	581		468
Tensile properties at 23°C (73°F)							
Yield strength	MPa	45 - 55	10	12	16	25	30
	psi	6500 - 8000	1450	1700	2300	3600	4300
Stress at break	MPa	40	30	22	30	40	54
	psi	5800	4300	3200	4300	5800	7800
Elongation at break	%	20 - 100	350	300	300	250	250
Modulus of elasticity	MPa	1300 - 2200	750	550	500	1000	1655
	psi	190000 - 320000	109000	80000	72500	145000	240000
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 x 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 Temperature = 23°C (73.4°F)

Stress (MPa)	Stress (psi)	Material	100 Hours Total Strain (%)	1000 Hours Total Strain (%)
4	580	Solef®1010	0.3	0.4
8	1160		0.7	0.9
12	1740		1.1	1.4
4	580	Halar® ECTFE	0.3	0.3
8	1160		0.7	0.8
12	1740		1.2	1.4
4	580	FEP	0.9	1.0
8	1160		3.3	3.8
12	1740		> 40	Fail - Full Yield
4	580	Hyflon® PFA	1.2	1.3
8	1160		4.7	5.3
12	1740		39	52
4	580	PTFE	1	Fail - Full Yield
8	1160		10	Fail - Full Yield
12	1740		Fail - Full Yield	Fail - Full Yield

ASTM D 2990. Compression moulded 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)



TYPICAL APPLICATIONS

High purity application: Semiconductor, Pharmaceutical, Food and Biotech industry

For over 25 years Solef® PVDF has been the material of choice for Ultra-Pure Water (UPW) systems because the qualities of the fluoropolymer ensure high purity and long-term performance. Solef® PVDF offers exceptional chemical and thermal resistance, standing up to aggressive chemicals without degradation. It also provides exceptional surface smoothness to prevent bacterial and bio-film growth.

Specific examples include ultra-pure water production, transport and storage systems, notably pipes, fittings, pumps, valves, tanks and tanks linings.

Chemical Processing Industry

Industries such as chemical processing, pulp and paper, textile and nuclear rely on Solef® PVDF to withstand heat and pressure, aggressive chemicals, mechanical stress, and abrasive particles in varied applications: chemical production, transport and storage systems, filtration and separation equipment (filters, membranes, housings), and heat exchangers.

Oil and gas industry

Solef® PVDF has been used in the harsh environments of down-hole and sub-sea oil production for many

years due to its proven thermal, chemical resistance and barrier properties.

Solef® PVDF is used in multilayer flexible pipes, such as risers and flow-lines, which bring the crude oil from the under-sea wells up to the fixed platforms or floating installations.

Wire and cable

Solef® and Hylar® PVDF are prime materials for use in jacketing plenum cables and fiber optic cable applications. They exhibit outstanding fire resistance and low smoke generation, and excellent thermal stability that sustain performance within a wide temperature range.

Solef® and Hylar® PVDF 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. These applications include telecommunication, security systems, automotive, aerospace, mass transportation, and oil and gas exploration.

Water treatment

Thanks to excellent chemical resistance, high purity as well as superior thermal and mechanical properties



Cleanroom production of high purity equipment
(Courtesy of Gemü Apparatebau GmbH)



Valves, T-pieces, connections for semiconductor and chemical process industries
(Courtesy of AGRU Kunststofftechnik GmbH)



Oil and Gas. Industry Wellstream 10-inch insulated flowlines
(Courtesy of Wellstream)



W&C Industry. Solef® and Hylar® PVDF meet industry standards for various cable constructions. (Source: Solvay)



Solef® PVDF fittings for sanitary applications
(Courtesy of Henco Industries N.V.)



Lithium-ion batteries.
(Courtesy of Samsung Electronics)

Solef® PVDF is ideal for water treatment applications, including acid waste plenum piping, and plumbing (sanitary application).

For acid waste plenum piping, outstanding creep resistance and chemical inertness of the system are a must.

In plumbing, the use Solef® PVDF brings serious advantages to metal fittings: no galvanic corrosion, ease and cost of installation, no potential contamination of water by heavy metals, no bio-film adhesion.

Membranes

Solef® PVDF is a choice material for porous membranes for an impressive range of end use, including water purification, medical purification, gas separation, food and beverages filtration, battery separators and fuel cell membranes.

Lithium-ion batteries

The intrinsic properties of Solef® PVDF including electrochemical stability in a wide voltage window, thermo-mechanical properties, chemical resistance,

and solubility in selected solvents make it well fit for use as an electrode binder.

Specific Solef® copolymers have also been developed in order to provide the base for polymers batteries types. Swelling in typical electrolyte used today is enhanced, improving therefore the ionic conductivity compared with standard Solef® homopolymer.

Films

Solef® PVDF can be extruded into gel-free films whose application sectors include capstocks for the automotive and building industry, piezoelectric films, and greenhouse. Capstock is defined as a single or multilayer film, which serves to protect a plastic substrate such as PVC, ABS or polyamides. It provides protection against UV, environmental degradation and soiling, and can be formulated to last from 10 to 30+ years.

Piezoelectric PVDF films can particularly be used in medical and non-destructive evaluation transducers, loudspeaker, sonar detection, vehicle detection, and literally hundreds of other types of sensors.

PRODUCT RANGE

The Solef® and Hylar® ranges are continuously expanding. Contact us for more details.

1. Material Selection

a. Homopolymers

PVDF grades	Characteristics and main uses
Solef® 1000 series	Virgin homopolymers
1006	Applications requiring high fluidity (multi-filaments...)
1008	General injection moulding Extrusion of thin walls, filaments and films.
1010	General injection and extrusion grade. Extrusion of pipes, films, sheets, and thin plates.
1012	Applications where high viscosity is required. Extrusion of thick walls, notably large-diameter pipes.
1015	Resin with very high viscosity - Membranes.
Solef® 6000 series	Virgin homopolymers
6008	General injection moulding
6010	Thick semi-finished products
6012	High viscosity - Thick semi-finished products
6020	Very high viscosity – Membranes – Lithium Batteries
Hylar® series	
460*	Broad MWD grade for extrusion. Branched molecular structure.
*The branched molecular structure makes Hylar® 460 readily cross-linkable with ionizing radiation after compounding with co-agents such as TAIC.	

b. Copolymers

PVDF grades	Characteristics and main uses
Solef® 11000 series	Flexible copolymers
11008	Injection for uses requiring greater flexibility
11008/0003*	Copolymer for raceway and jacketing of cables with fire resistance and smoke emission levels satisfying the Underwriters' Laboratories (UL) 910 Test - Rating at 150°C (302°F)
11010	General use, cable jacketing, extrusion of plates, sheets and films
11010/0003*	Copolymer for raceway and jacketing of cables with fire resistance and smoke emission levels satisfying the UL 910 test - Rating at 150°C (302°F)
Solef® 20000 series	High-flexibility copolymers
21216	Lithium Polymer Batteries
21508/0003*	Jackets and optic cables component, with higher flexibility and fire resistance and smoke emission levels satisfying the UL 910 test-Rating at 125°C (257°F)
21508	Extrusion of films
Solef® 30000 series	High-flexibility copolymers with broader range of service temperature
31008/0003*	Jackets and fiber optic cables components, with higher flexibility, lower shrinkage, low
31508/0003*	brittleness temperature, fire resistance and smoke emission levels satisfying the UL 910 test
32008/0003*	- Rating at 150°C (302°F)
Solef® 60000 series	Flexible copolymer resins with specific characteristics in terms of chemical resistance, mechanical strength and impermeability
60512	Barrier layer of multi-layer flexible pipes used in oil and gas industry.
Hylar® series	Flexible copolymers with specific characteristics
20808/0003*	Copolymer for raceway and jacketing of cables with fire resistance and smoke emission levels satisfying the UL 910 Test - Rating at 150°C (302°F)
21508**	Jackets and fiber optic cables component, with higher flexibility and lower shrinkage
SN	Copolymer with low melting temperature (105°C / 221°F). Solution coatings, inks.
* Special formulations with a LOI > 90% are available on request. They are identified as follows: xxxxx/0009	
** New copolymer grade also offered with two patented fire retardant packages (xxxxx/0003 and xxxxx/0009). Contact Solvay Solexis for more information.	

Note:

For Solef® PVDF, in addition to the grade designation (4 digits for homopolymers, 5 digits for copolymers), the delivered products include a 4-digit reference number, which is an internal code defining its formula. For simplicity's sake, virgin Solef® and Hylar® resins are defined in this brochure solely by their grade.

Nevertheless, the products containing low levels of additives for special applications, such as the copolymers for wire and cable industry, and the compounds, are cited with their full reference. For example, Solef® 11008/0003 and Hylar® 20808/0003 = resins containing low levels of additives for plenum cable jacketing.

c. Compounds for specific applications

Grades	Characteristics and main uses
Solef® 3000 series	Filled grades for special applications
3108/0903	Antistatic: formula filled with carbon black Injection moulding of antistatic parts
3110/0907	Antistatic: formula filled with carbon black Extrusion, compression and transfer moulding of semi-finished parts
3208/0150	Self lubricating: formula lubricated with PTFE. Applications requiring a low coefficient of friction (valve seats, for example)
3410/0905	Grade with improved resistance to radical chlorine.
Solef® 8000 series	Reinforced grade
8808/0902	Carbon fiber-reinforced
Solef® 1000 series	Colored compounds
1010/0900	Black compound for extrusion.
1010/0901	Black compound for extrusion or injection (sanitary applications).
1008/0702	Blue compound for injection.
1008/0955	Grey compound for injection
N.B. Other colored compounds are available on request.	

2. Packaging and storage

Solef® resins (pellets) are available in 25 kg (55.1 lbs) bags or in containers of 1000 kg (2204.6 lbs). Solef® powders are available in 50 kg (110.2 lbs) drums or in 350 kg (770.9 lbs) containers.

Hylar® pellets and powders are available in 25 kg (55.1 lbs) boxes.

Though PVDF resins have an indefinite shelf life, it is recommended to store them in a clean area, protected from direct sunlight, and possible contamination. Please refer to the Material Safety Data Sheets for more information on handling and safety.

PHYSICAL PROPERTIES

1. Structural properties

Molecular weight

Table 5 below presents several characteristics of the molecular structure of various grades of Solef® 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.

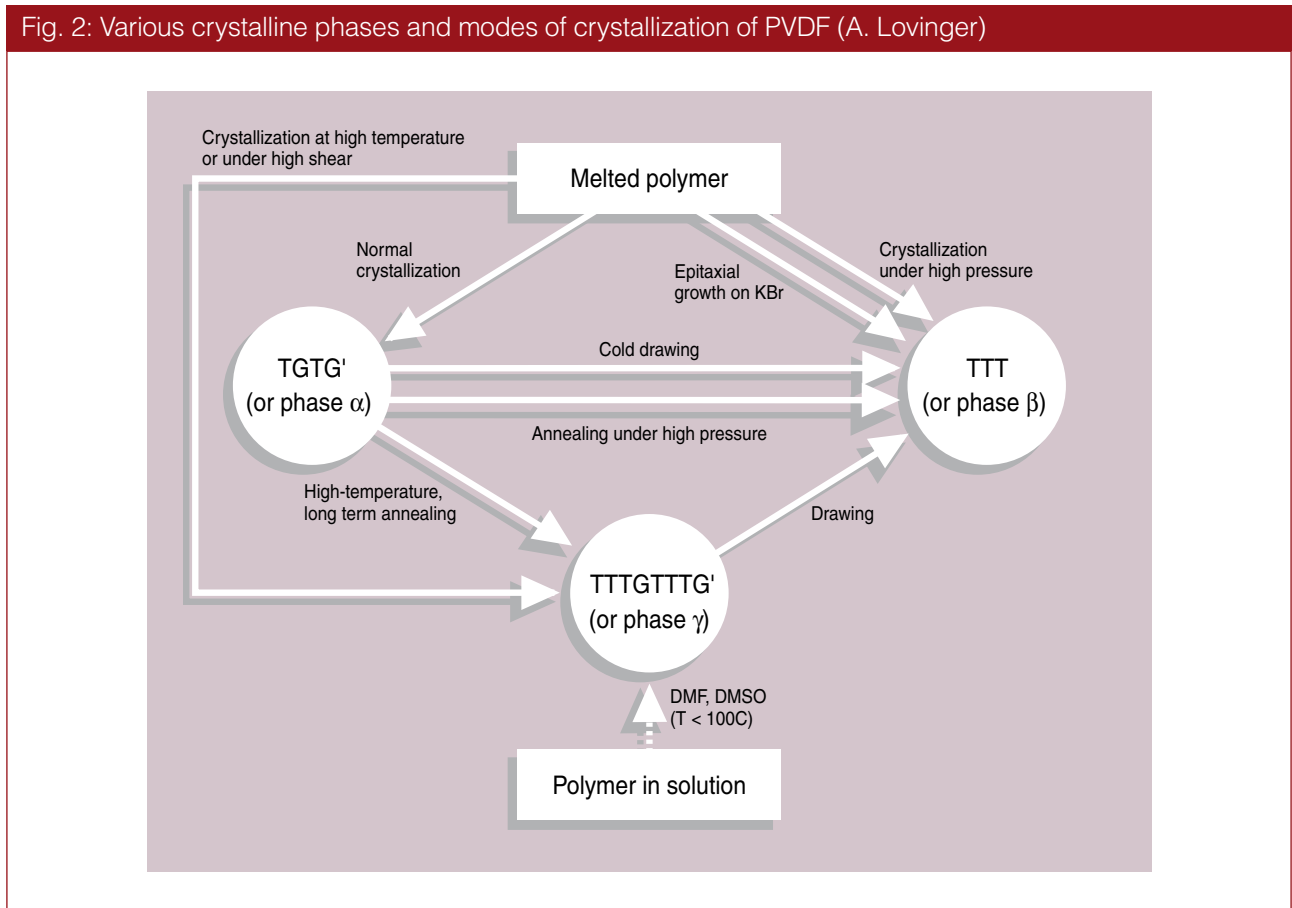
Depending on processing conditions, several crystalline forms can be observed, the most important

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® resins measured by Gel Permeation Chromatography

PVDF Grades	Number average molecular weight $M_n \times 10^{-3}$	Weight average molecular weight $M_w \times 10^{-3}$	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



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 cooling 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 Solexis for more details about the annealing procedure.

Rheological properties

Melt flow index (MFI)

(ASTM D 1238, DIN 53 735)

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

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

PVDF 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® resins			
1006	40	-	-
1008, 6008, 11008, 21508	8	24	-
31008/0003, 31508/0003	5	15	-
1010, 6010, 11010, 21510	2	6	18
1012, 6012	0,5	1,5	5
60512	-	1	3
Solef® compounds			
3108/0903	1,5	4,5	13,5
3208/0150	8	24	-
3410/0905	2	6	18
8808/0902	3	9	24
Hylar® resins			
460	-	0,6	2,6
SN	45	-	-
20808	-	15	-
21508	-	24	-

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

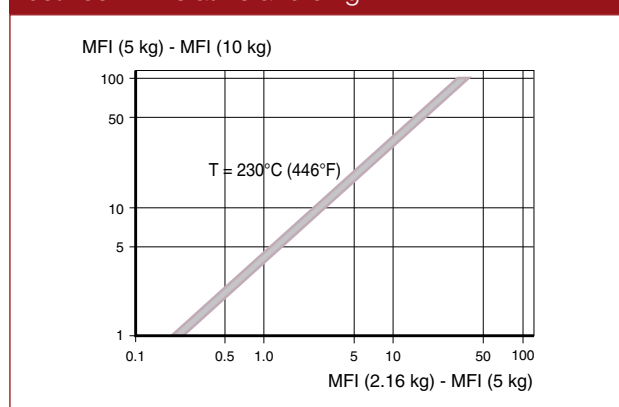


Figure 3 represents, for Solef® homo- and copolymer resins, the existing correlations between the MFIs under 5 kg and under 2.16 kg, as well as the MFIs under 10 kg and under 5 kg (at 230°C/446°F).

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

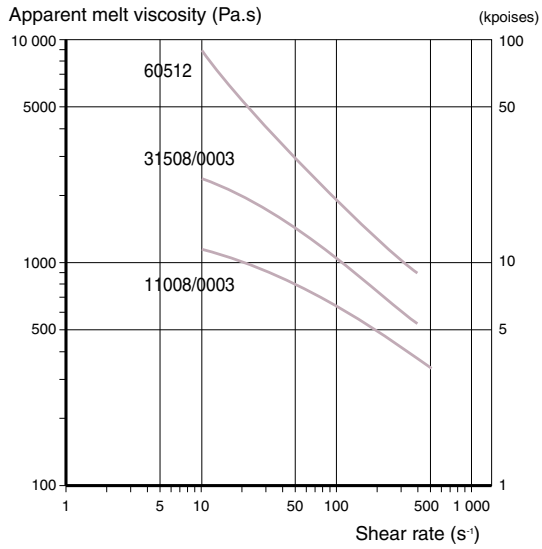


Fig. 5: Melt viscosity at 200°C (392°F) of the 1000 series Solef® PVDFs

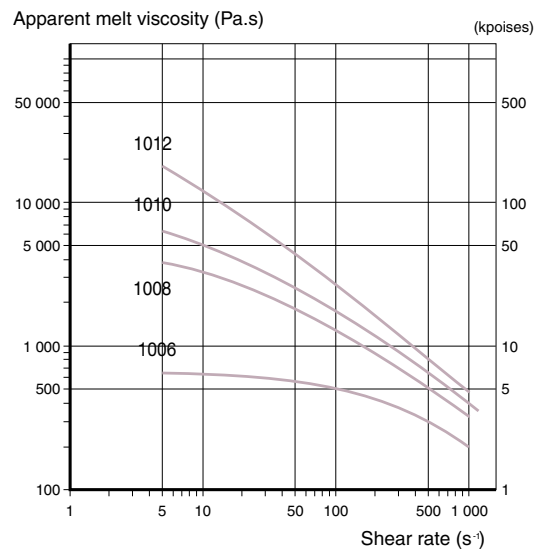


Fig. 6: Melt viscosity of Solef® PVDF 1010 at various temperatures

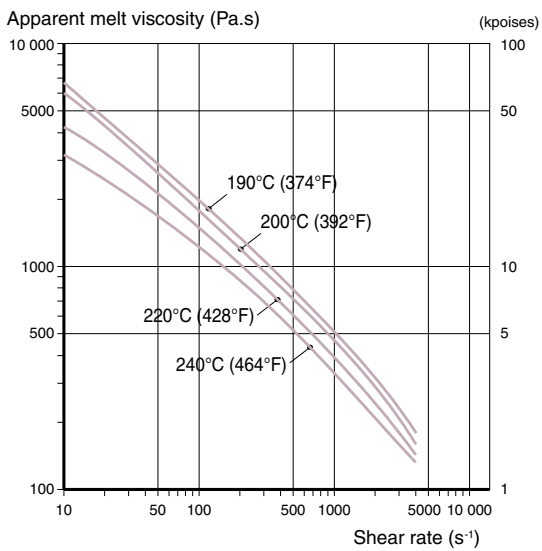


Fig. 7: Melt viscosity of Solef® PVDF 11008/0003 at various temperatures

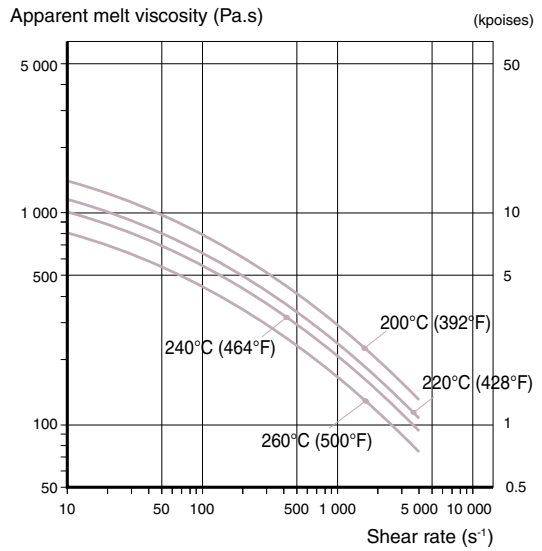
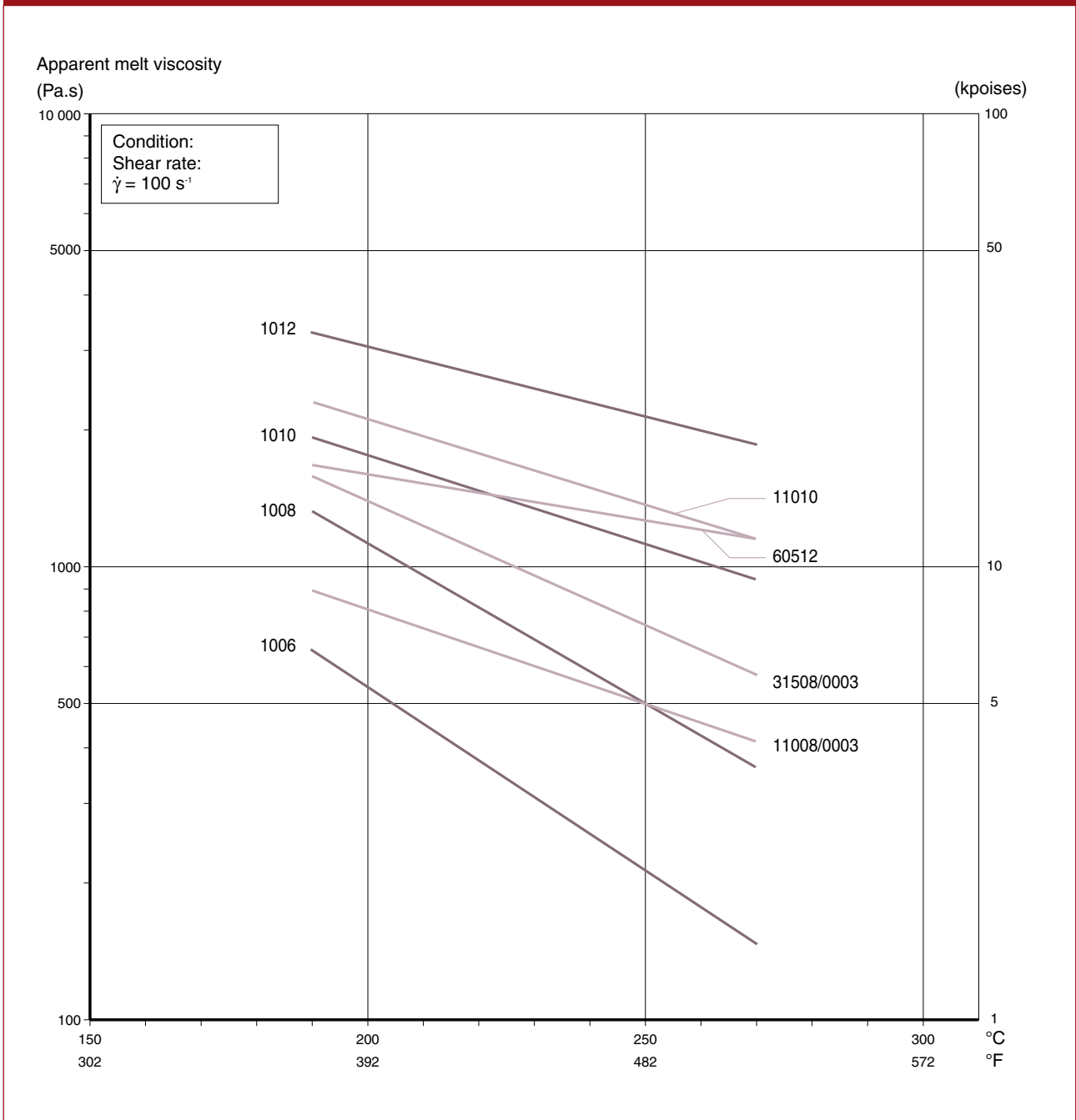


Fig. 8: Melt viscosity at 100 s⁻¹ of various Solef[®] grades vs. temperature



2. Thermophysical properties

DSC curves

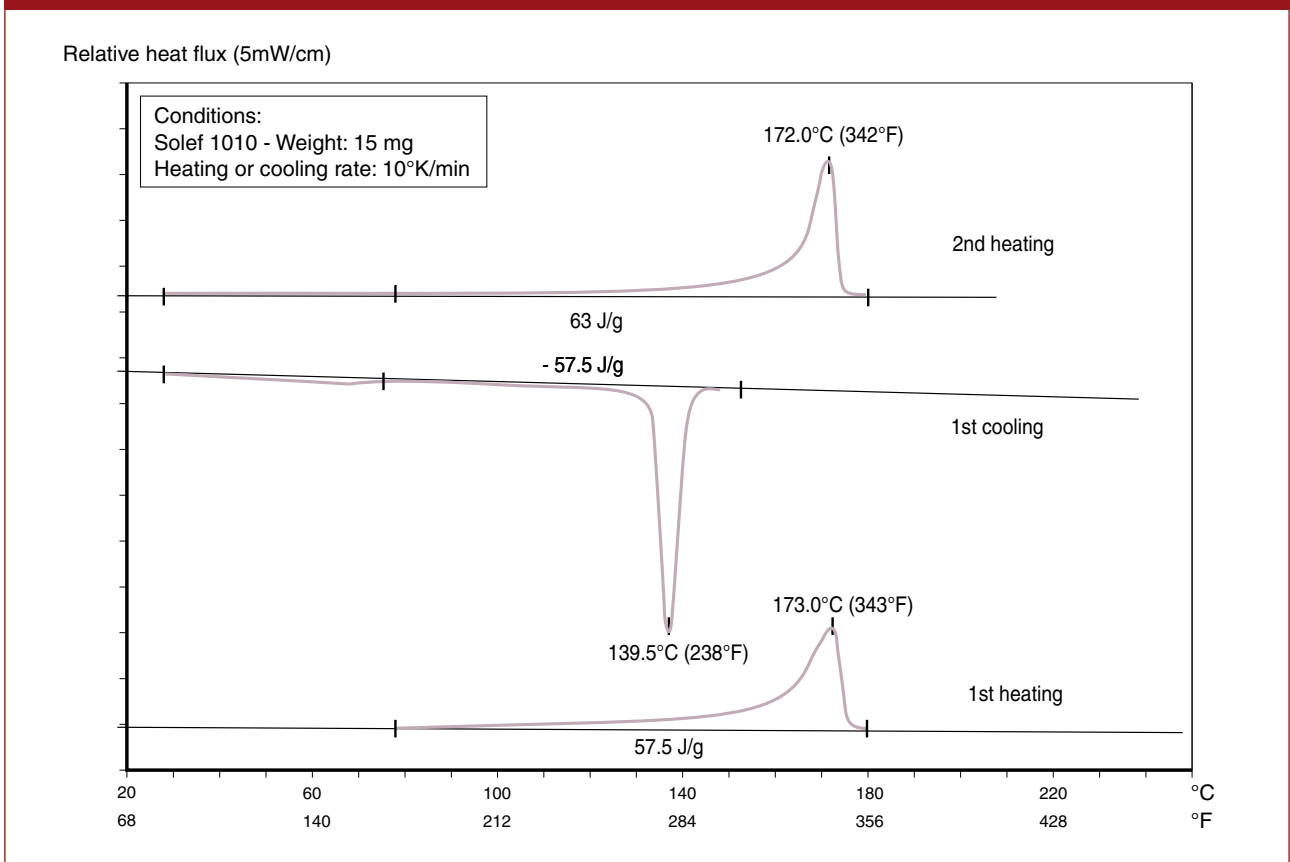
The crystalline melting temperatures and corresponding heats of fusion ΔH_f of Solef[®] and Hylar[®] resins, recorded by DSC under defined operating conditions (ASTM D 3418), are presented in Table 7.

Figure 9 illustrates the relative heat flux curves as a function of the temperatures obtained in DSC of Solef[®] 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

PVDF grade	Melting temperature T_f , °C (°F)	Heat of fusion ΔH_f , J/g (Btu/lb)	Calculated rate of crystallinity, %
Solef® homopolymers			
1000 and 6000 series	171–172 (340-342)	59 - 64 (25 - 28)	56 - 61
Hylar® homopolymer			
460	160 (320)	46 (20)	44
Solef® copolymers			
11008 and 11010	160 (320)	37 - 39 (16 - 17)	-
21510	135 (275)	23 (9.9)	-
31508	168 (334)	26 (11.2)	-
32008	168 (334)	17 (7.3)	-
60512	171 (340)	51 (22)	-
Hylar® copolymers			
20808/0001	150 (302)	-	-
21508/0001	135 (275)	-	-
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			

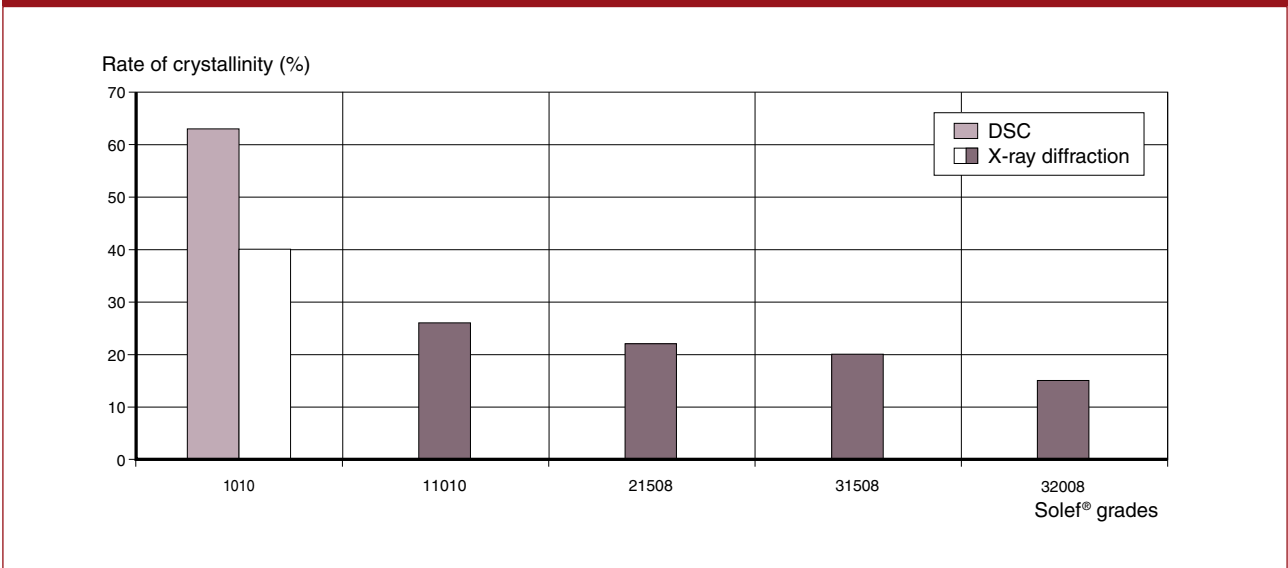
Fig. 9: DSC curves of Solef® PVDF 1010



By way of comparison, the rate of crystallinity of Solef® 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)

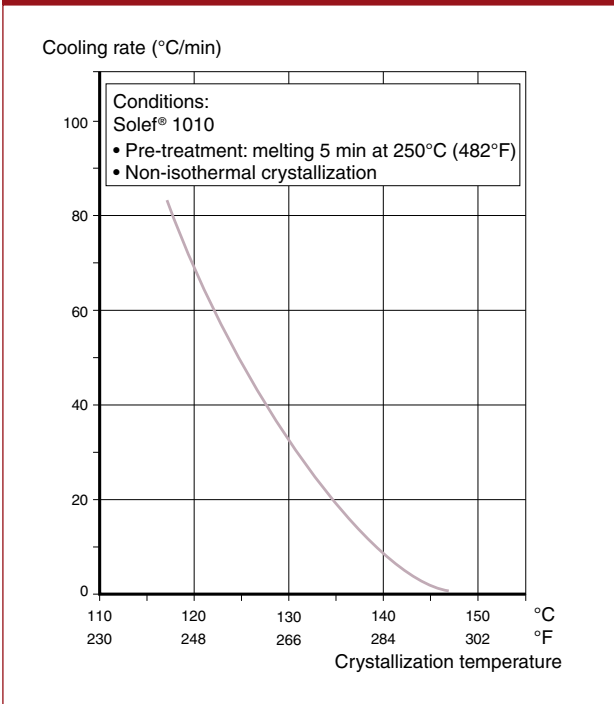
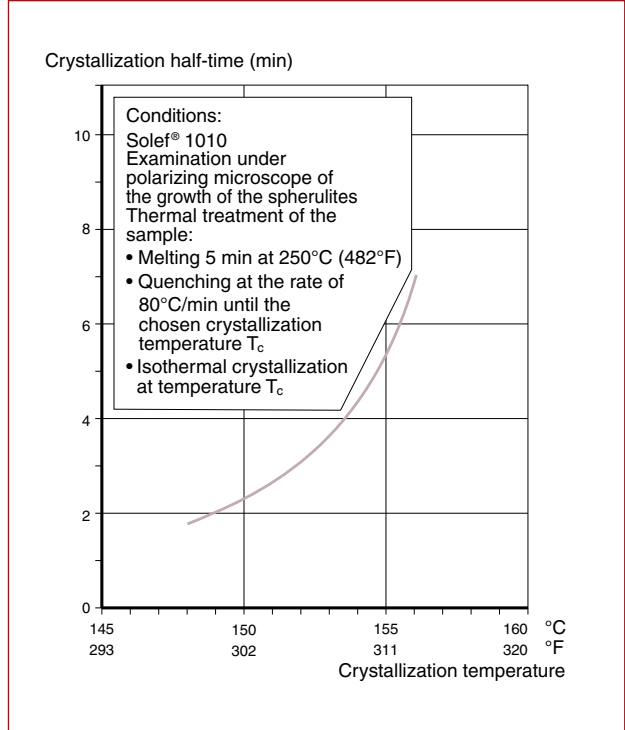


Fig. 12: Variation of crystallization half-time as a function of temperature (isothermal)



Softening temperatures

Heat deflection temperature (HDT)
(ASTM D 648)

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 (66.7psi).

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

Fig. 13: HDT of various Solef® and Hylar® grades

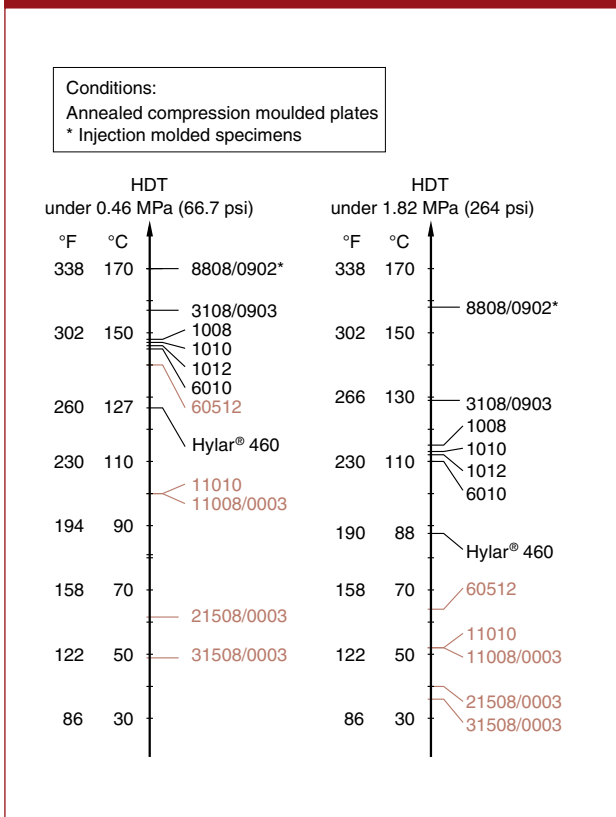
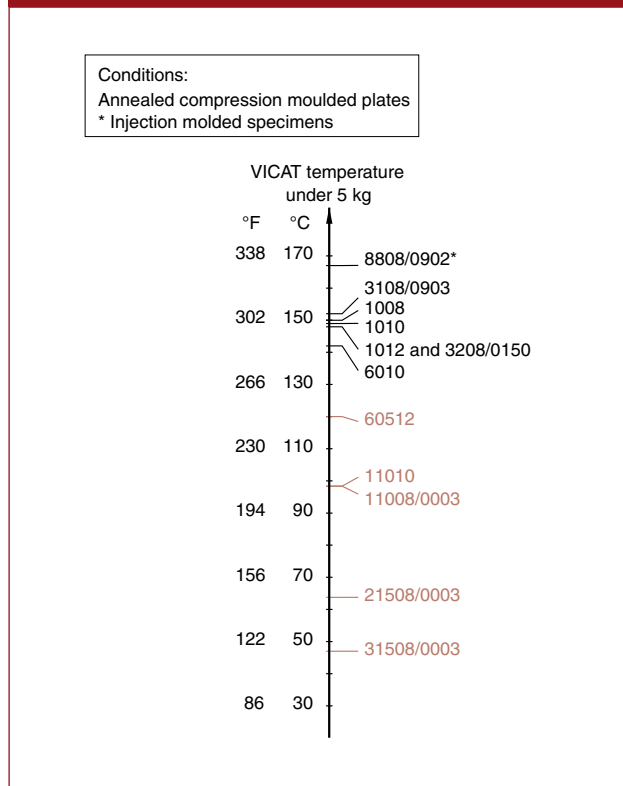


Fig. 14: VICAT softening temperature (5 kg/11.0 lb) of various Solef® grades



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® grades.

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® PVDF 1010, 11008/0003 and 31508/0003.

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.

Thermal conductivity

The thermal conductivity λ of Solef® PVDF 1010 was measured as a function of the temperature, using the heating wire method (ASTM D 2326-70). 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® and Hylar® resins and compounds.

Table 8:
Thermal conductivity of Solef® and Hylar® PVDF

Grades	Thermal conductivity λ	
	W/m.K	Btu-in/h-ft².°F
PVDF homopolymers		
Solef® 1000 and 6000 series	0.20	1.39
Hylar® 460	0.19	1.32
PVDF copolymers		
Solef® 11010	0.19	1.32
Solef® 21508/0003	0.18	1.25
Solef® 31508/0003	0.18	1.25
Solef® 32008/0003	0.18	1.25
Solef® 60512	0.20	1.39
Hylar® 20808/0003	0.19	1.32
Hylar® 21508/0001	0.18	1.25
PVDF compounds		
Solef® 3108/0903	0.30	2.08
Solef® 3110/0907	0.30	2.08
Solef® 3208/0150	0.20	1.39
Solef® 8808/0902	0.33	2.29

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

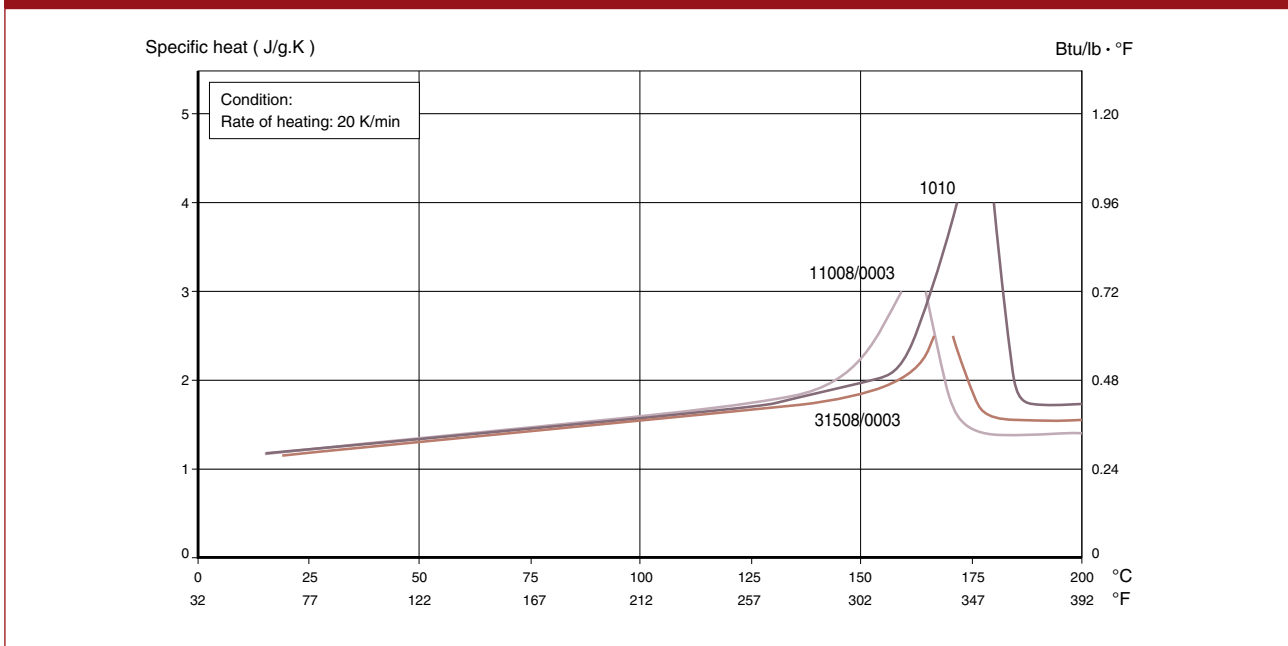
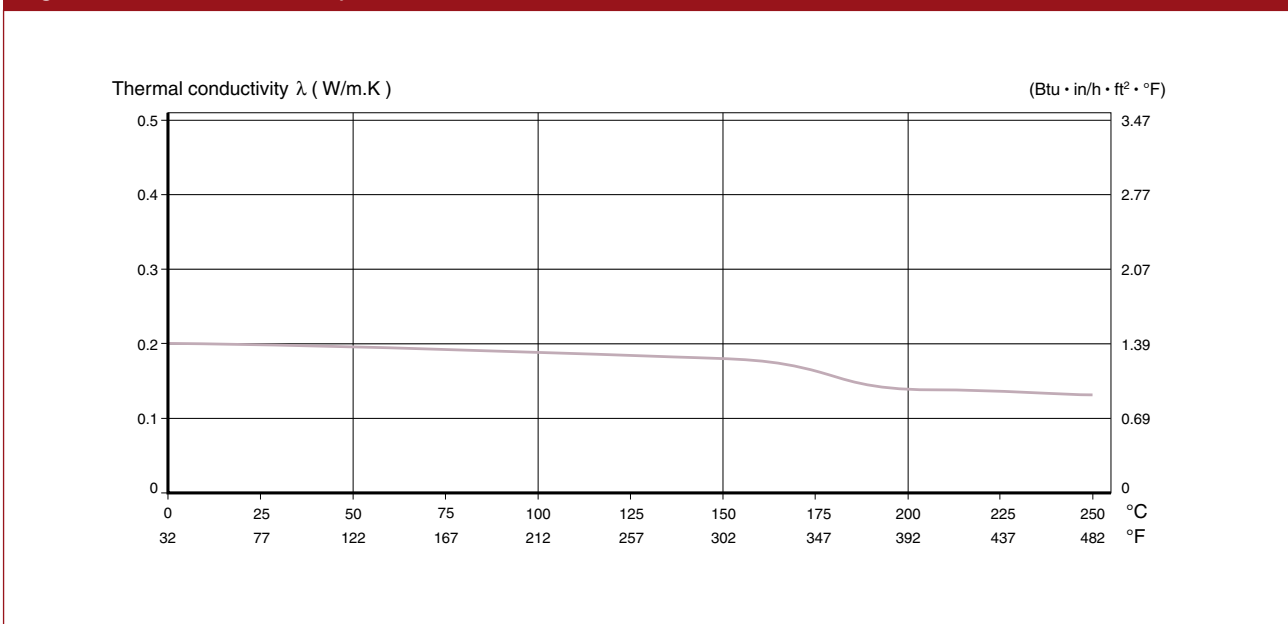


Fig. 16: Thermal conductivity of Solef® PVDF 1010



Coefficient of linear thermal expansion
(ASTM D 696)

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°C/(68°F): from 0 to 40°C (32 to 104°F)

α (120°C/248°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® and Hylar® grades.

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

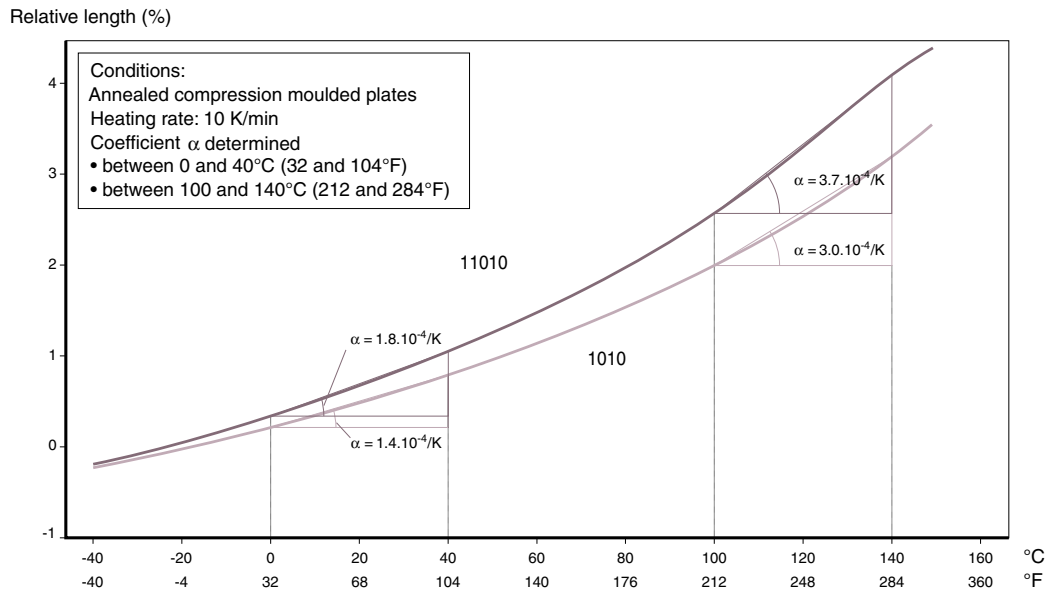


Table 9: Coefficient of linear thermal expansion for Solef® and Hylar® PVDF

Grade	Coefficient of linear thermal expansion, $10^{-4} / K$ ($10^{-4} / ^\circ F$)	
	At 20°C (68°F) (0 to 40°C / 32 to 104°F)	At 120°C (248°F) (100 to 140°C / 212 to 284°F)
Solef® 1000 series	1.35 – 1.45 (0.75 – 0.81)	3.00 - 3.30 (1.67 – 1.83)
Hylar® 460	1.20 – 1.30 (0.67 – 0.72)	-
Solef® 11010	1.80 (1.0)	3.70 (2.06)
Solef® 31508/0003	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 D 696 standard

Density

(ISO R 1183, ASTM D 792)

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[®] 31508/0003 copolymer.

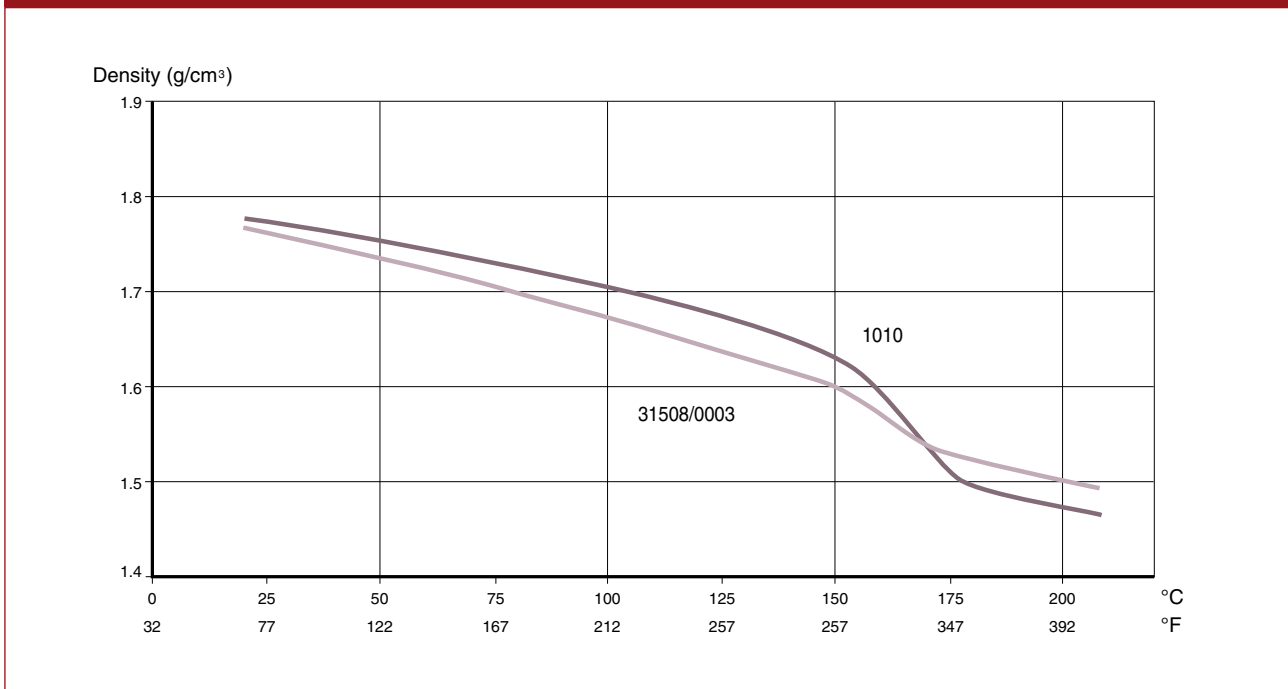
Table 10 presents the densities at 23°C (73.4°F) of filled or reinforced PVDF.

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[®] compounds

Solef [®] grade	Density, g/cm ³
3108/0903	1.83
3208/0150	1.80
3410/0905	1.79
8808/0902	1.78

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



Specific volume - pVT curves

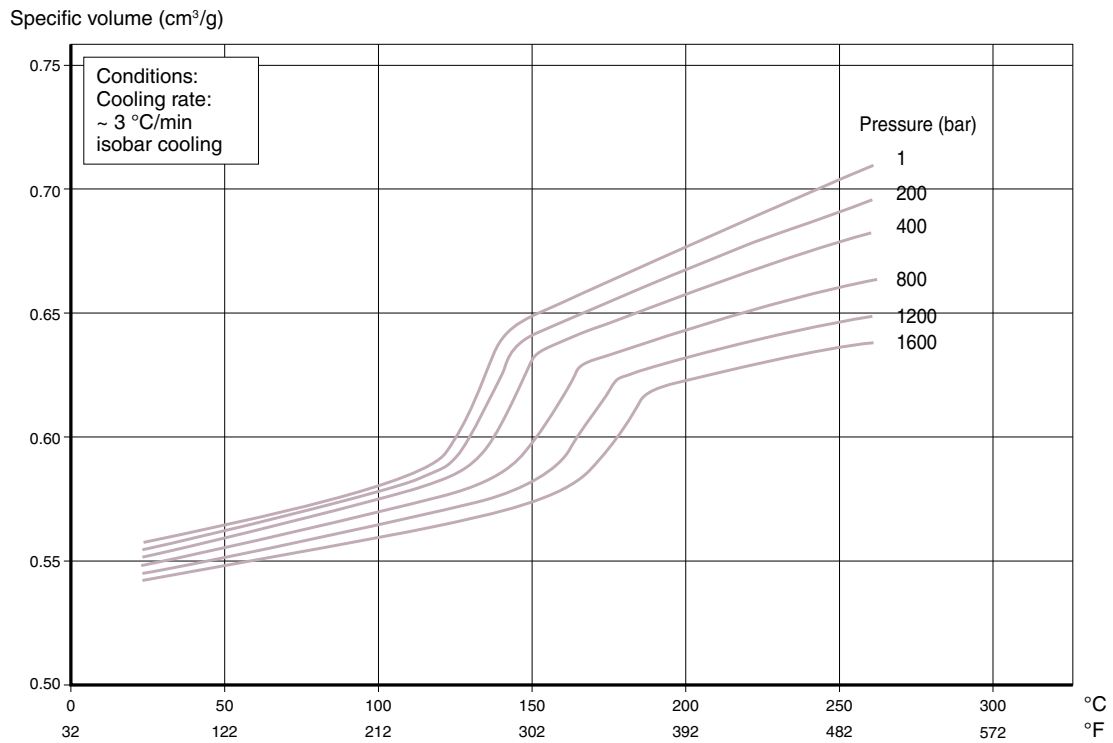
The specific volume v (cm³/g) of Solef[®] PVDF 1008 was measured under different pressures as a function of temperature. The variation curves are presented in Figure 19.

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 1600 bars.

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

Fig. 19: pvT curves of Solef® PVDF 1008



3. 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® PVDF 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.

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 Solexis before adding any fillers or pigments to PVDF.

4. 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.

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

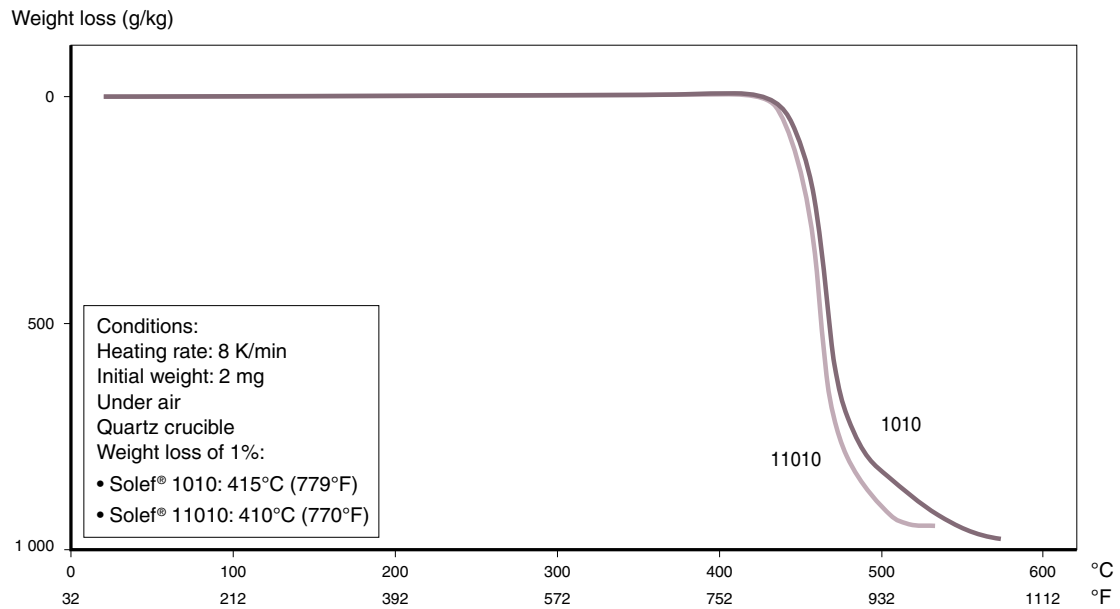


Table 11 gives the values of the angle of contact θ for water and the surface tension of various polymers compared with those for PVDF.

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.

Hardness

Shore hardness

(ISO 868, ASTM D 2240)

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

Ball hardness

Ball hardness was measured on compression molded plates according to the DIN 53456 standard for Solef® 1010 and 11008/0003 grades (see Table 13).

Rockwell hardness

(ASTM D 785)

Table 14 presents the Rockwell M and R hardness of Solef® PVDF 1010 and 11008/0003, measured on compression molded plates.

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 semi-conductor 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 x 50 μm scan and 0.018 μm for the 5 μm x 5 μm scan were calculated (average on 8 measurements).

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

Table 12: Shore D hardness of Solef[®] and Hylar[®] PVDF

PVDF grade	Shore D hardness
Solef[®] resins	
1000 series	78
6010	77
11010	72
31008/0003	63
31508/0003	53
32008/0003	47
61512	70
Solef[®] compounds	
3208/0150	78
3108/0903	82
3410/0905	79
8808/0902	82
Hylar[®] resins	
460	78

Table 14: Rockwell hardness of Solef[®] PVDF

Solef [®] grade	Rockwell hardness	
	M direction (*)	T direction (*)
1010		
as moulded	68	109
annealed	69	110
11008/0003		
as moulded	11	94
annealed	18	96

(*): M: machine direction; T: transversal direction

Table 13: Ball hardness of Solef[®] PVDF

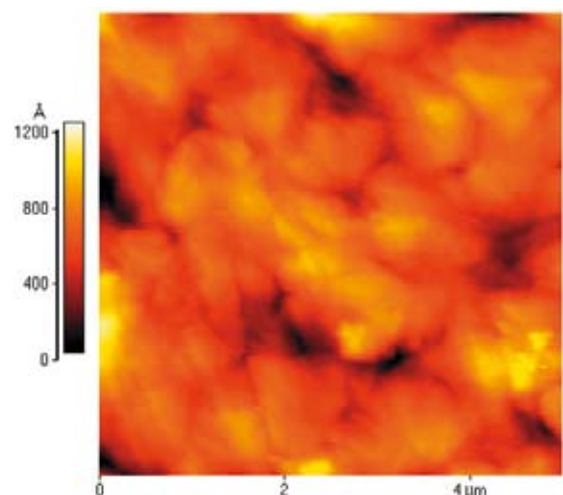
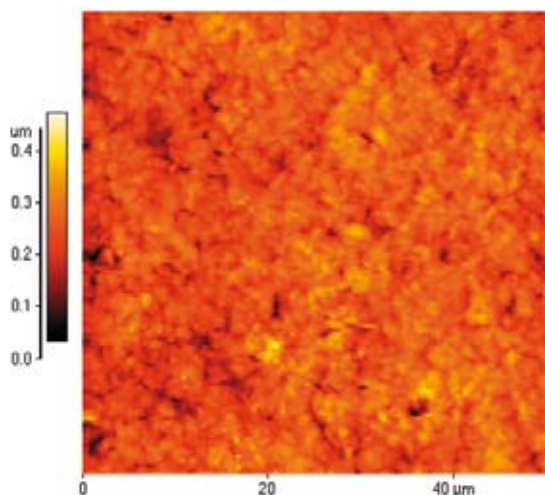
Solef [®] grade	Hardness, N/mm ² (F = 132 N, after 30s)
1010	
as moulded	58
annealed	59
11008/0003	
as moulded	33
annealed	37

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

Type of object	Roughness R_a , μm	
	M direction (*)	T direction (*)
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 pictures of Solef[®] PVDF pipes
 D=63 mm pipes. Scanned surfaces: 50 μm x 50 μm and 5 μm x 5 μm .**



Coefficient of friction

(ASTM D 1984)

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

According to the ASTM D 1984 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® and Hylar® 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 18:
Abrasion resistance of PVDF (TABER test)

Material	Abrasion, % vol
Solef® PVDF	0.18
NBR rubber	0.19
Rigid PVC	0.24
PP	0.51

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 9.81N (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 1000 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 17:
Coefficient of friction of Solef® 3208/0150 grade

Surfaces in contact	μ_0	μ
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		

Table 19:
Abrasion resistance of PVDF (AKRON test)

Materials	Abrasive disk	Weight loss mg/1000 rev.
Solef® and Hylar® PVDF homopolymers	CS-10	5-10
	CS-17	7-10
Solef® 21508/0003 and 31508/0003	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	500-1000

5. 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 values* present the soluble quantities at 23°C (73.4°F) until the formation of a gel.

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*	—

* Maximum quantity of resin that can be introduced into the solution without formation of gel

6. Optical properties – Appearance

Solef[®] and Hylar[®] 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.

Refraction index

The refraction index of Solef[®] and Hylar[®] PVDF 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 Beer-Lambert law) between 200 and 900 nm, in the case of compression moulded Solef[®] PVDF 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 D 1746, ASTM D 1003 and ASTM D 2457)

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® PVDF 1010

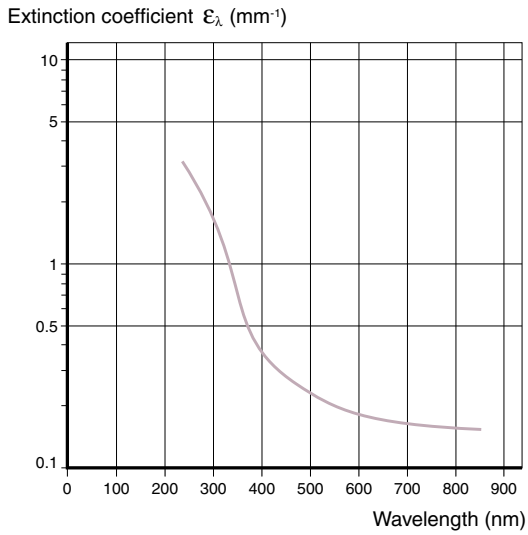


Fig. 22: Absorption spectra of Solef® PVDF 1008 in UV and visible ranges - Influence of thickness

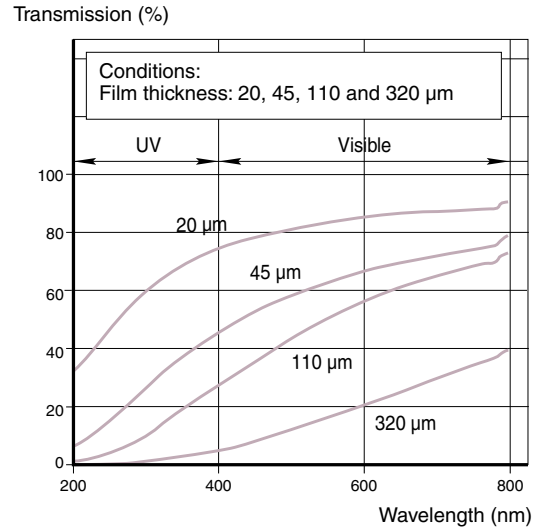


Fig. 23: IR-ATR spectrum of Solef® 1008 homopolymer film (transmission)

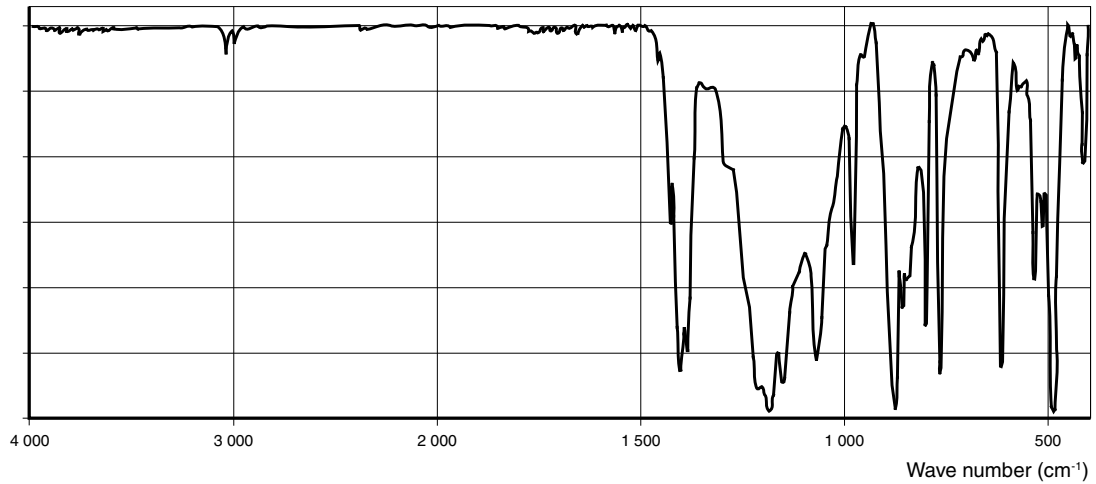


Fig. 24: IR-ATR spectrum of Solef® 11008 copolymer film (transmission)

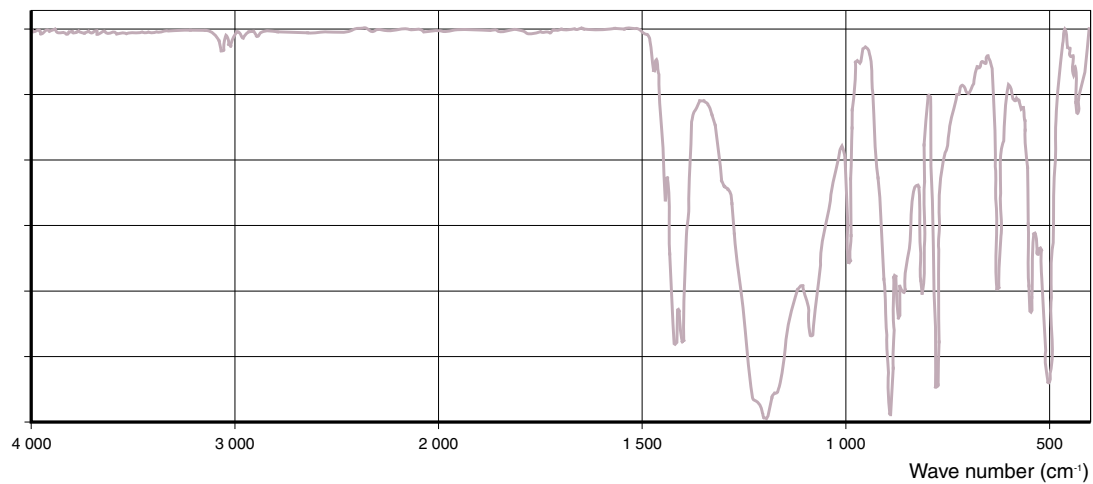


Table 21: Optical properties of Solef® PVDF films vs. thickness

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		

MECHANICAL PROPERTIES

1. Short-term stresses

Tensile properties

(ASTM D 638, 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 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® PVDF 1008 specimens.

Comments

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® PVDF 1010 as a function of temperature.

Comments

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

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

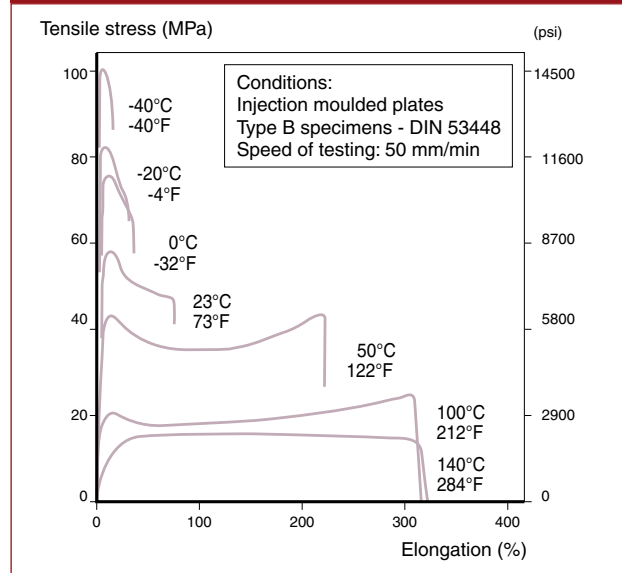


Figure 28 gives the tensile yield strength for Solef® 1010, 11010, 60512 and Hylar® 460 grades, and the strength at break (no yield point) of Solef® 8808/0902 compound in a temperature range of 20 to 150°C (68 to 302°F).

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

Tables 22a and 22b present the tensile properties of extruded films made of Solef® 1010 and 11010 resins.

Flexural properties

(ASTM D 790, 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® and Hylar® grades are presented in Figures 30 and 31. (page 33)

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

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

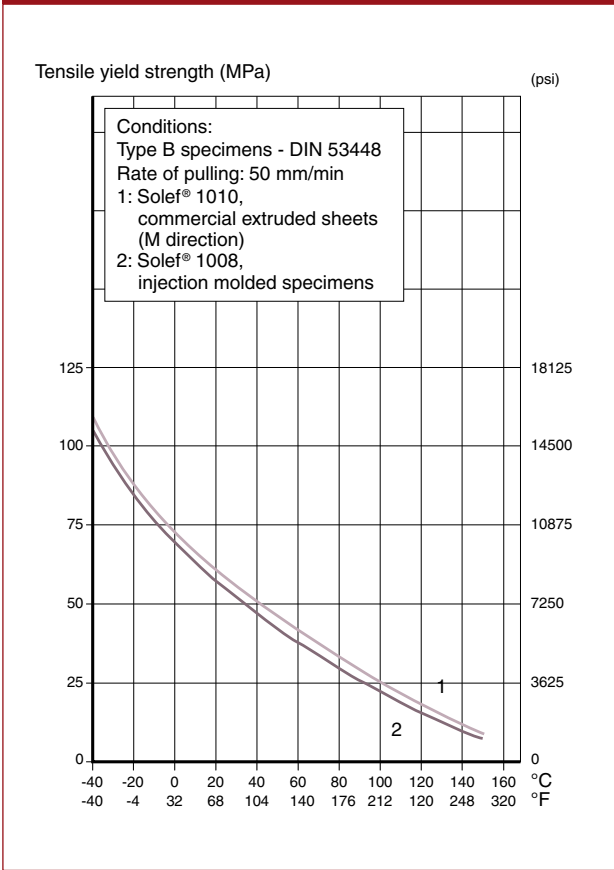


Fig. 27: Elongation at yield and at break of Solef® PVDF vs. temperature

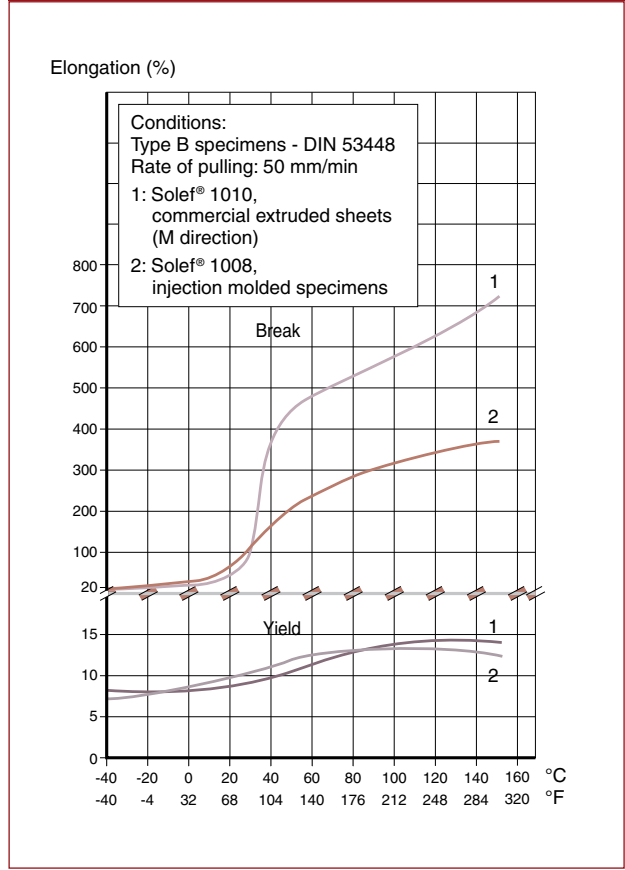


Fig. 28: Tensile strength at yield or at break of PVDF vs. temperature

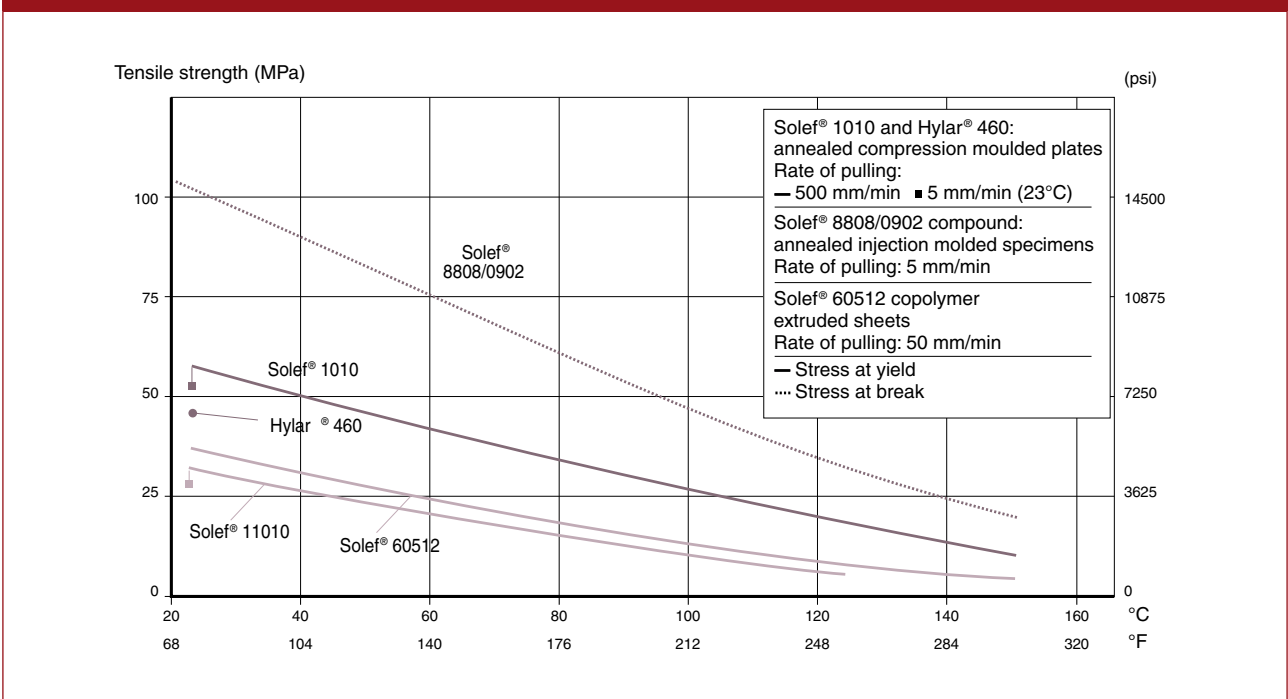


Fig. 29: Young's modulus of PVDF vs. temperature

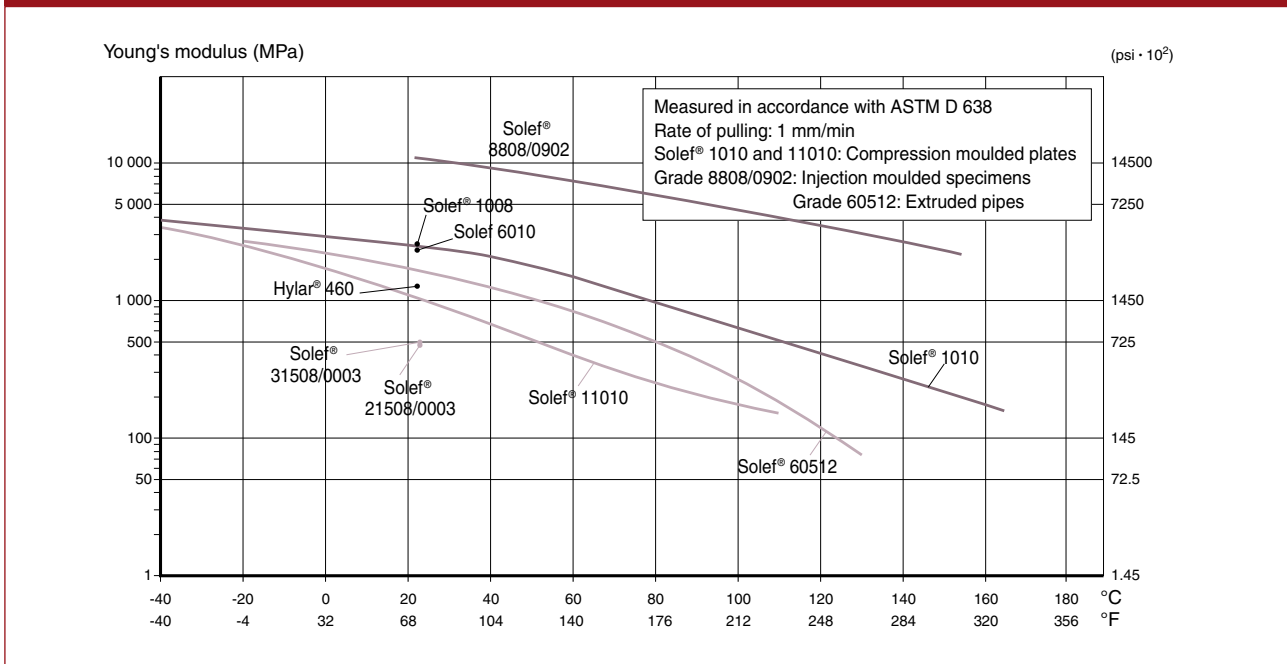


Table 22a: Tensile properties of Solef® PVDF films (SI Units)

Solef® grade	Thickness of the film μm	Stress				Elongation at break, %	
		At yield, MPa		At break, MPa			
		M	T	M	T	M	T
1010	50	50.1	52	70.6	44.2	285	230
	100	52.9	56.4	70.2	51.1	380	265
	200	52.3	58.1	43.4	40.4	465	590
11010	50	32.8	29.7	66.9	46.7	435	535
	100	31.6	32.2	63.2	49.4	610	560
	200	32.2	34.4	56.9	44.0	675	580

Conditions:
 Films produced by extrusion with flat die and chill roll
 Tensile measurement according to the ASTM D 882 standard at 23°C
 Rate of pulling: 500 mm/min
 M: machine direction; T: transversal direction

Table 22b: Tensile properties of Solef® PVDF films (US Customary Units)

Solef® grade	Thickness of the film μm	Stress				Elongation at break, %	
		At yield, psi		At break, psi			
		M	T	M	T	M	T
1010	50	7265	7540	10237	6409	285	230
	100	7671	8178	10179	7410	350	265
	200	7584	8425	6279	5858	465	590
11010	50	4756	4307	9701	6772	435	535
	100	4582	4669	9164	7163	610	560
	200	4669	4988	8251	6380	675	580

Conditions:
 Films produced by extrusion with flat die and chill roll
 Tensile measurement according to the ASTM D 882 standard at 73.4°F
 Rate of pulling: 500 mm/min
 M: machine direction; T: transversal direction

Fig. 30: Flexural modulus of PVDF vs. temperature

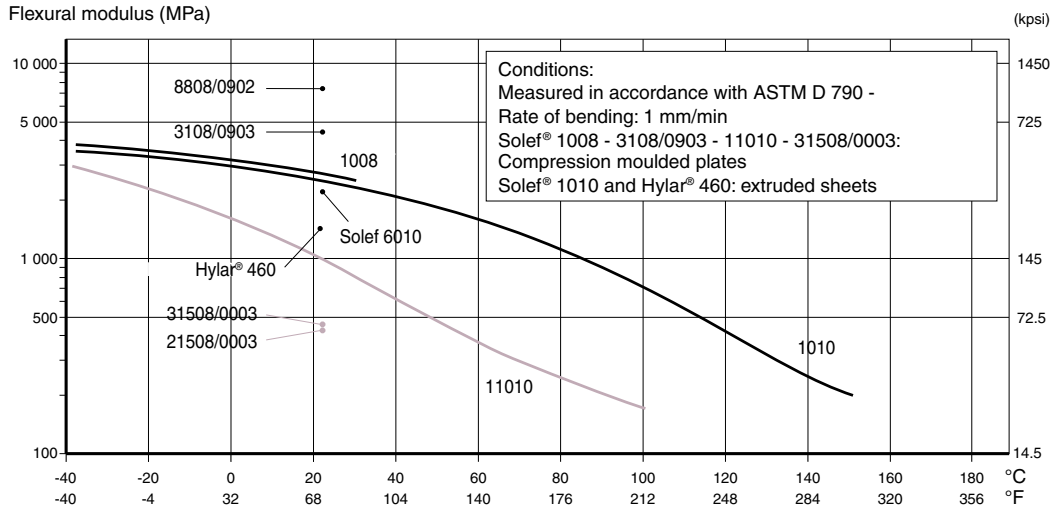
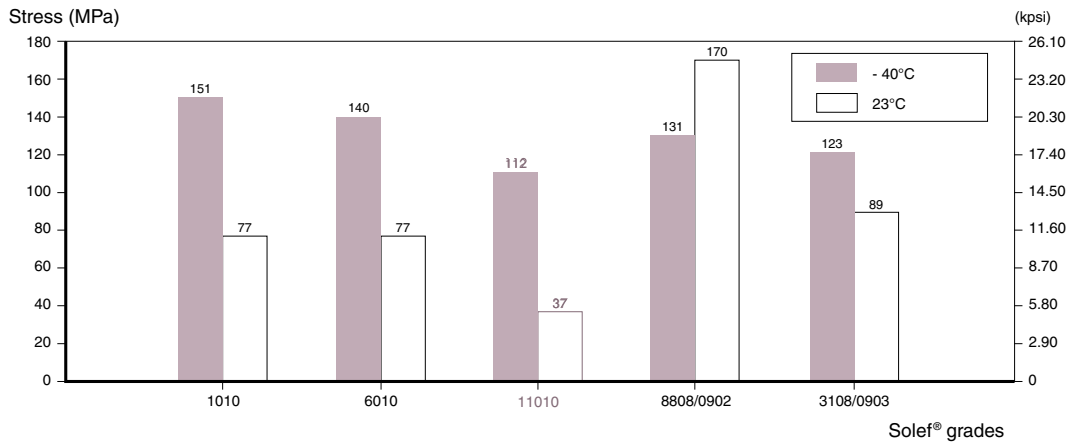


Fig. 31: Ultimate flexural strength of various Solef® grades



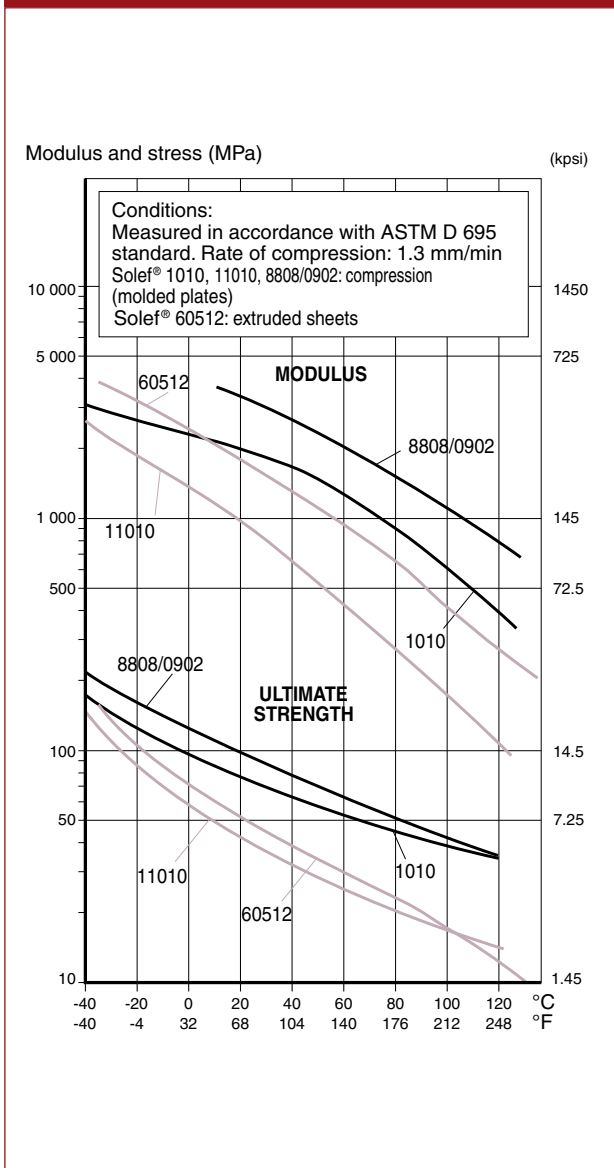
Compressive properties
(ASTM D 695)

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® PVDF 1010 at 20°C (68°F) are 75 MPa (10.9 kpsi) and 2150 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



2. Long term static stress - Creep

Creep under tensile stress (ASTM D 2990)

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):

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

where 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,

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

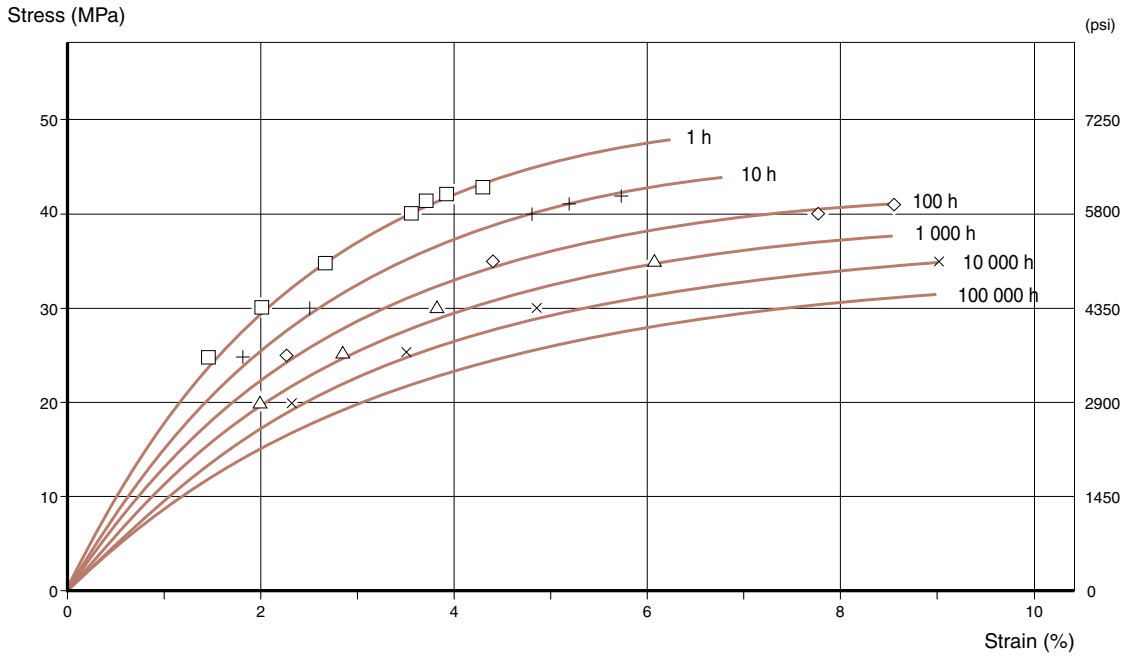


Fig. 34: Experimental values for creep under tensile stress at 23°C (73.4°F) of Solef® PVDF 1010 (extruded sheets)

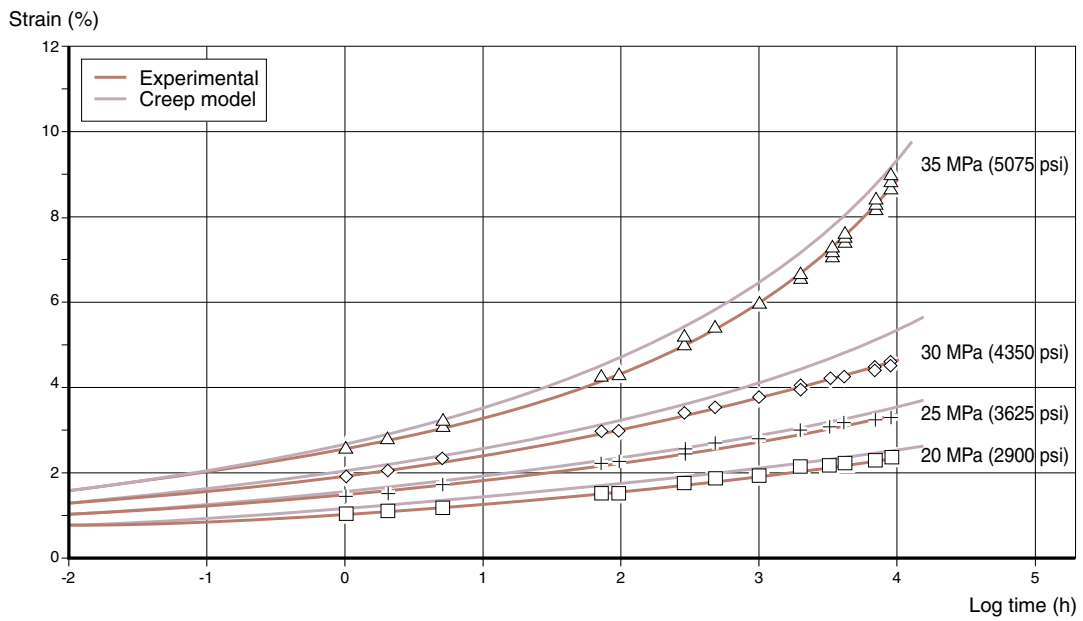


Fig. 35: Creep under tensile stress at 140°C (284°F) of Solef® PVDF 1010 (extruded sheets)

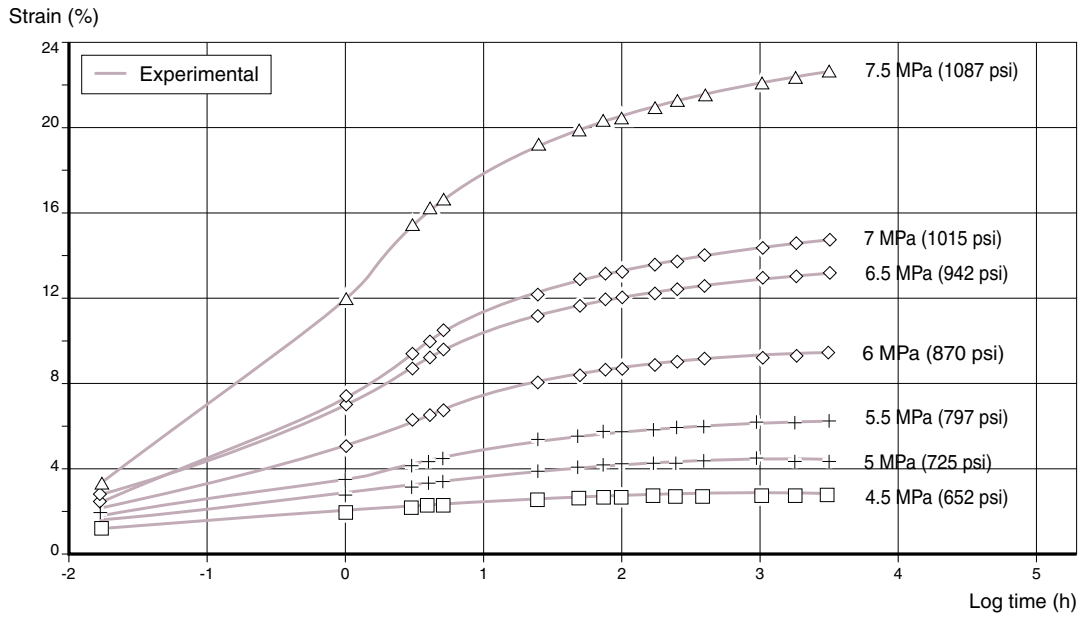


Fig. 36: Creep under tensile stress at 120°C (248°F) of Solef® PVDF 1010 and 60512

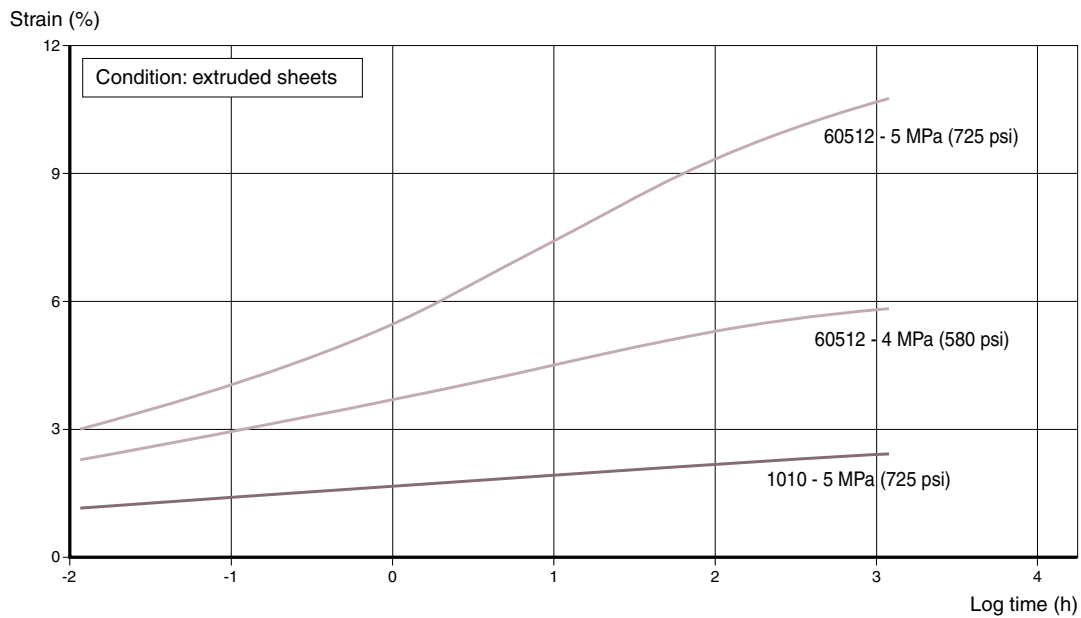
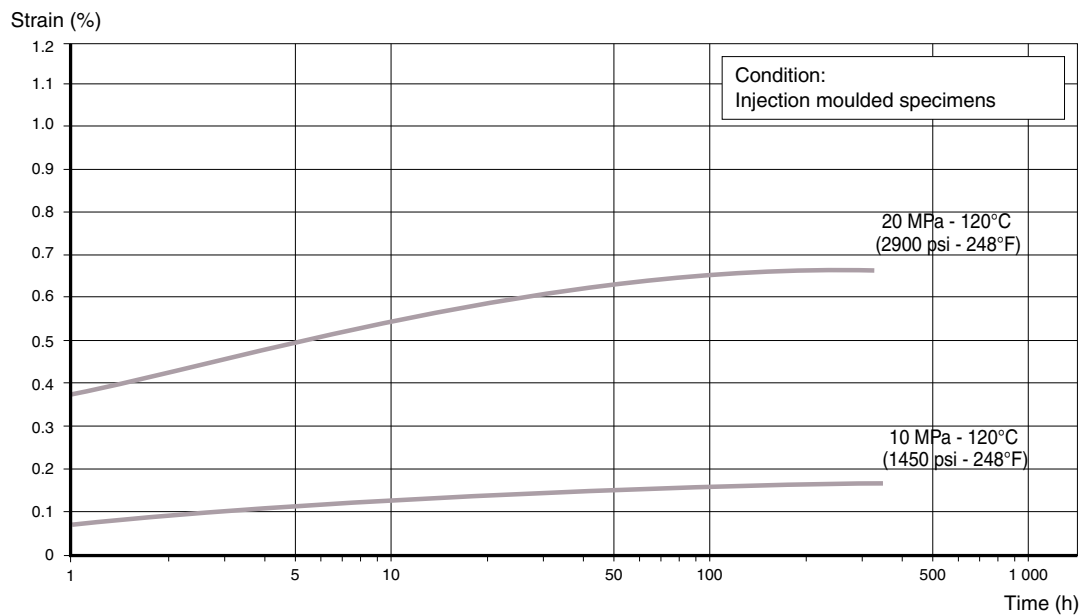


Fig. 37: Creep under tensile stress of Solef® 8808/0902 compound at 120°C (248°F)



- 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 3/4ths 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.

- 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

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

Solef® grade	Bursting temperature °C (°F)	Bursting pressure bar (psi)	Hoop stress MPa (psi)
1010*	23 (73.4)	94 – 139 (1364 – 2017)	55 – 61 (8000 – 8800)
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 \varnothing 8 mm and 12 mm. D/e = 9 to 13
 ** pipes \varnothing 12 mm. D/e = 10

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 (LTHS) 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® PVDF 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 (3625 psi) and safety coefficient (Cmin) of 1.6.

- 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® PVDF 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 3000 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.

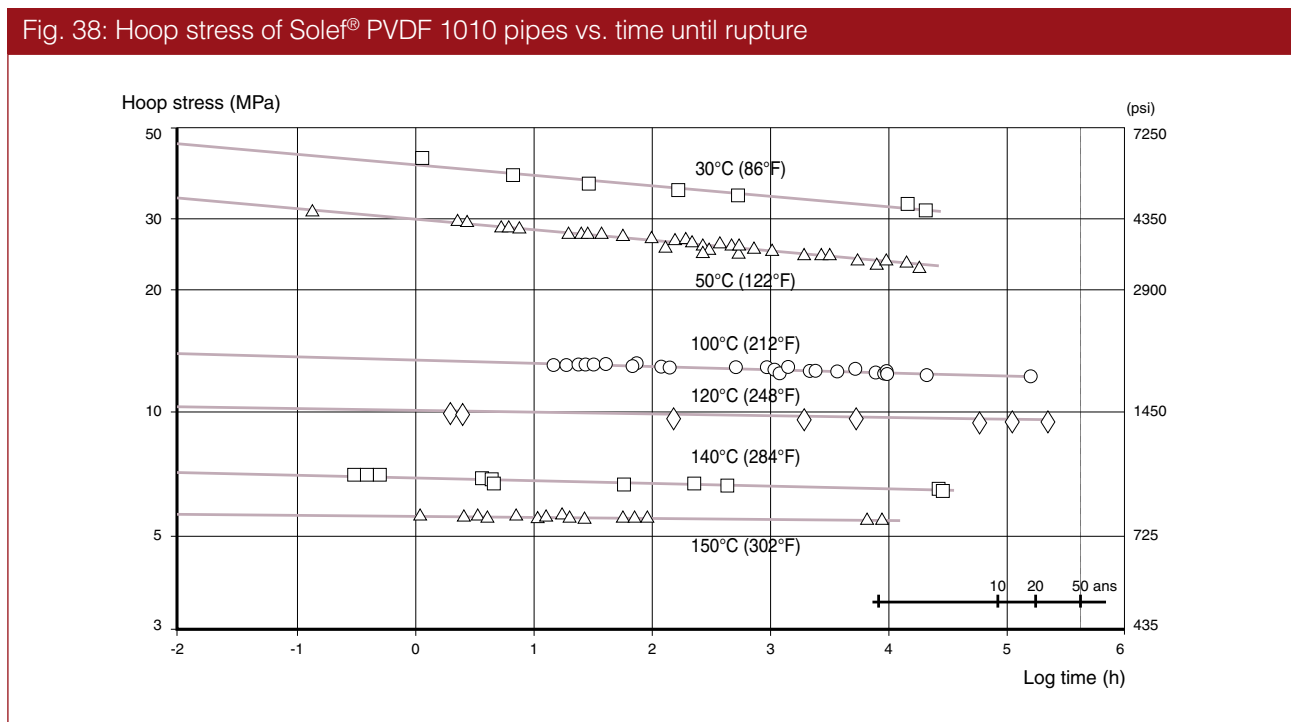


Fig. 39: Long term hoop stress of Solef® PVDF 1010 pipes extrapolated to 50 years (ISO/TR 9080)

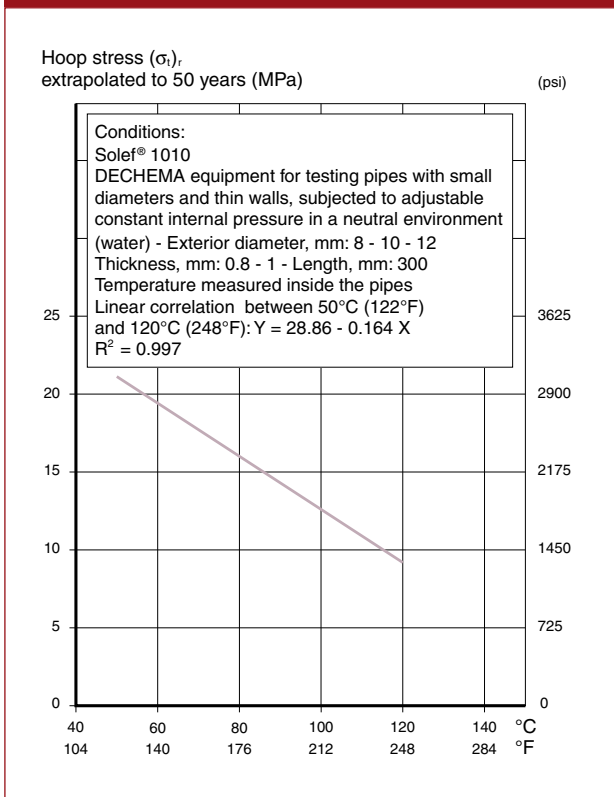
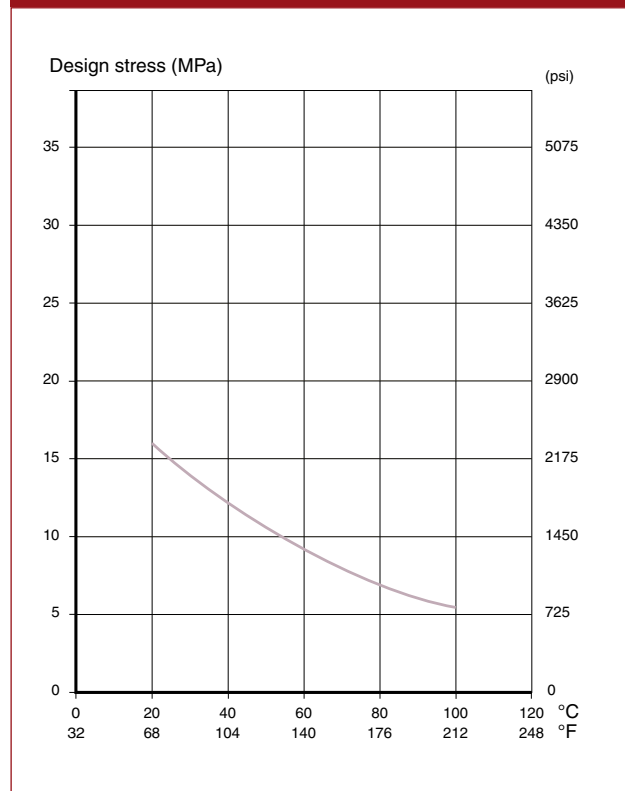


Fig. 40: PVDF pipes in presence of water - Design stress extrapolated to 50 years (ISO 10931-2)



3. Dynamic loading

Alternating low amplitude, short term stresses - DMTA (Dynamic modulus)

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

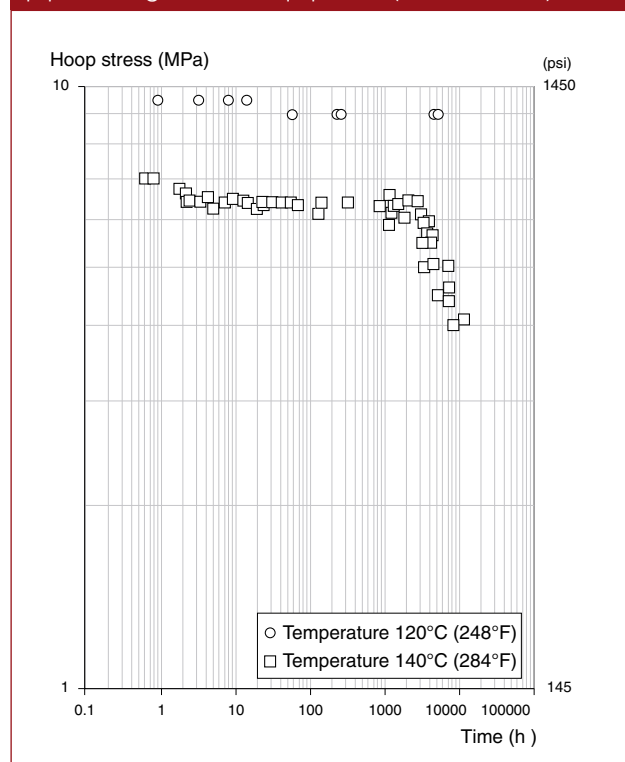
Under a forced harmonic stress system, one measures the amplitude and the phase displacement δ of the resulting deformation. When it is performed over a wide range of temperatures, this method of evaluation makes it possible to identify the thermo-mechanical spectrum of the material at a given frequency,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

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



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 alternating flexion with a frequency of 1 Hz.

Figures 42 and 43 show the curves of E' and $tg \delta$ respectively of the Solef® 1010 and 6010 homopolymers and Solef® 11010, 31508/0003 and 60512 copolymers.

In particular, for the Solef® 1010 resin, one observes primarily:

- A $tg \delta$ curve with a maximum at -32°C (-25.6°F), main glass transition, also called T_{g_L}
- A modulus E' curve displaying a clearly visible inflection point (T_{g_L}) at -32°C (-25.6°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.

Alternating long term stresses - Fatigue tests (ASTM D 671, 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® PVDF 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.

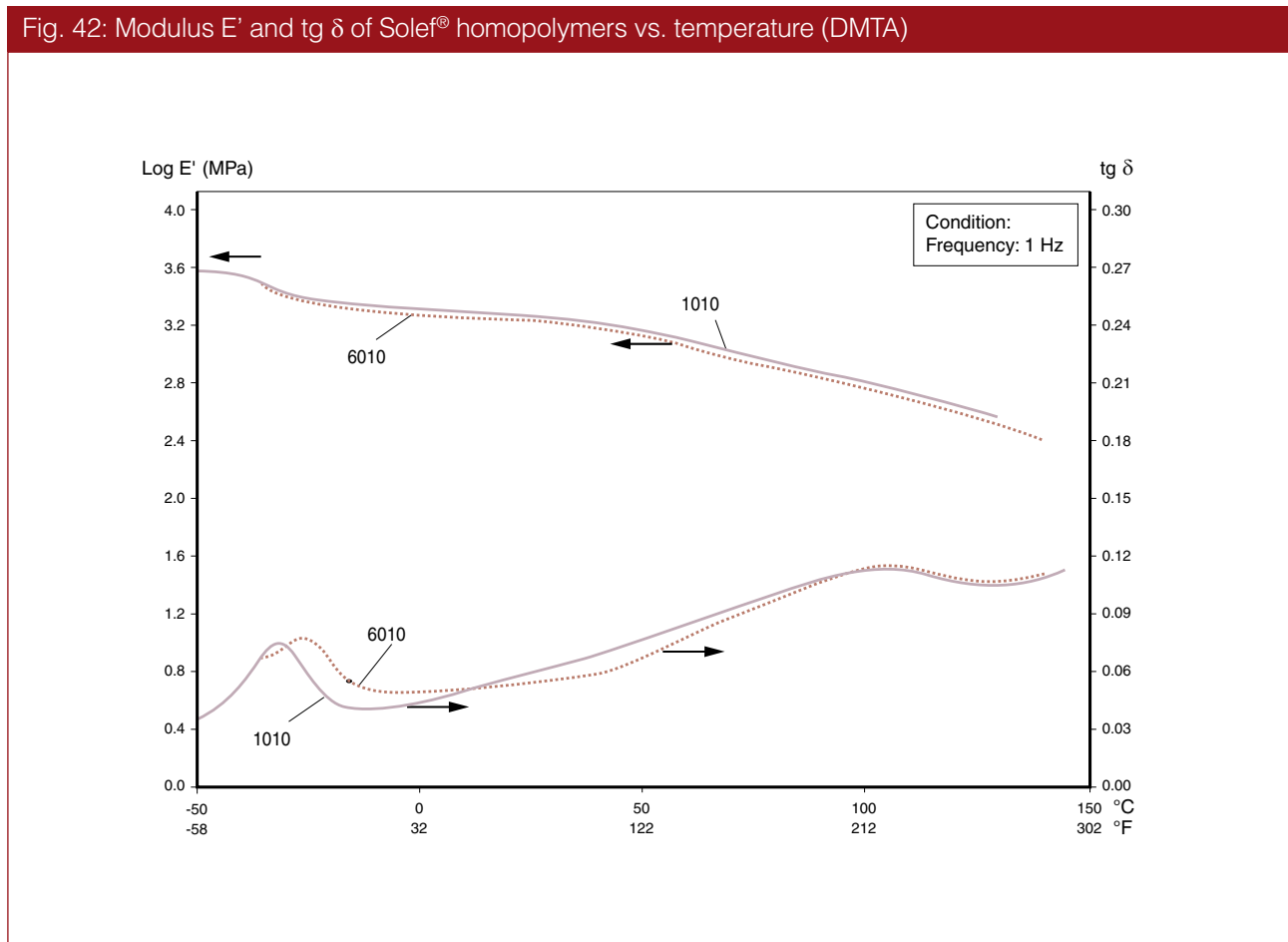


Fig. 43: Modulus E' and $tg \delta$ of Solef[®] copolymers vs. temperature (DMTA)

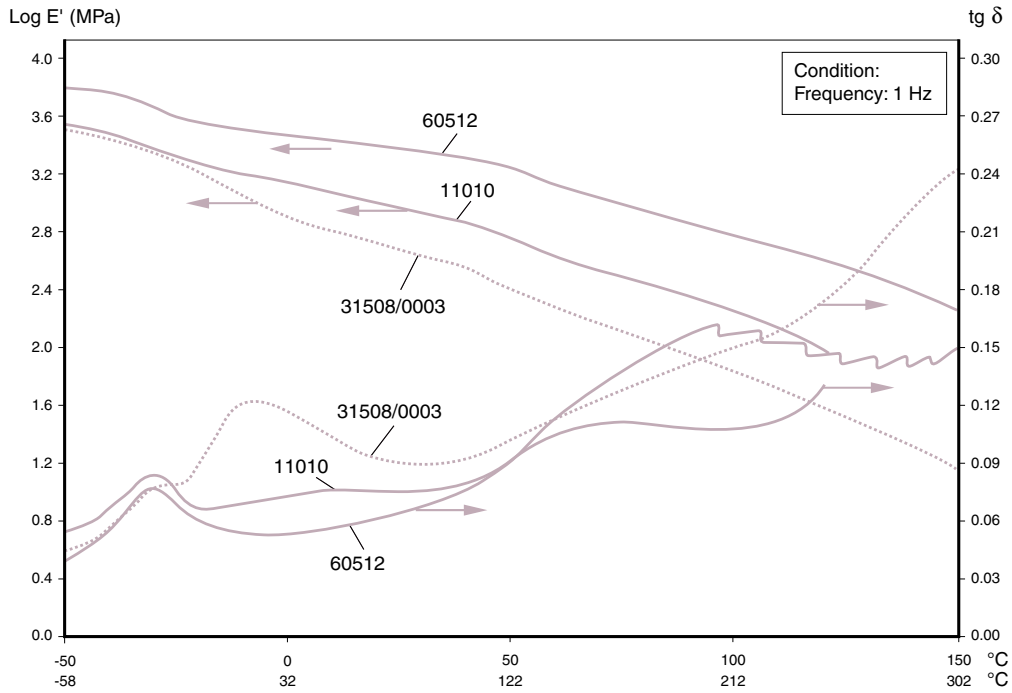


Fig. 44: Fatigue under cyclical tensile stress for Solef[®] PVDF 1008 at 20°C (68°F)

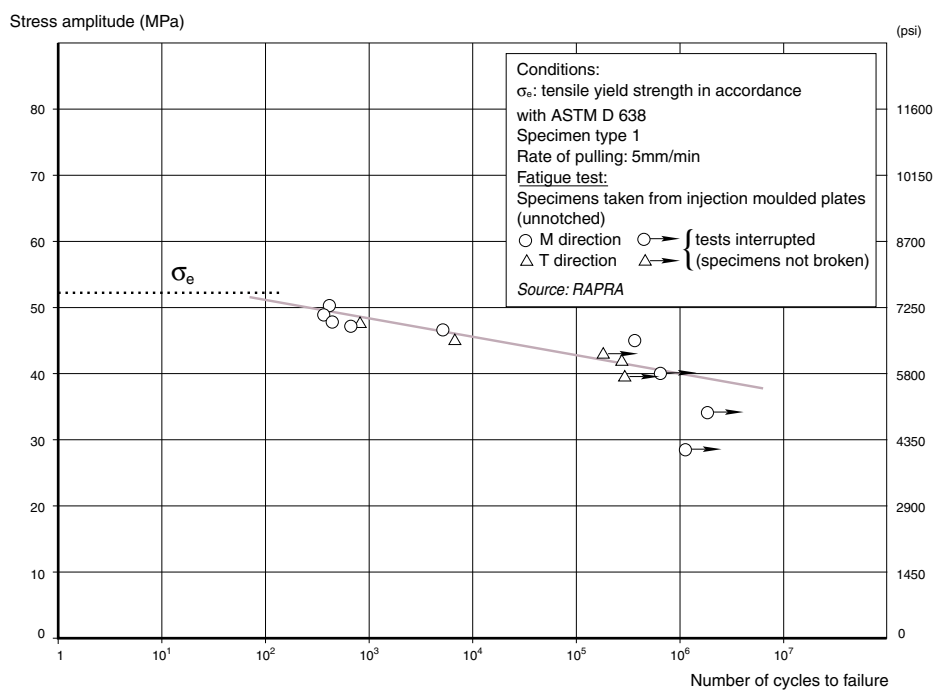


Figure 45: Wöhler curves for the Solef® 1010 grade at 20, 60 and 100°C (68, 140 and 212°F). The fatigue tests were limited to the oligocyclic range (< 104 cycles). The fatigue is evaluated under alternating uniaxial tensile stress, between a maximum adjustable value σ and a low residual value (2.5 MPa / 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.

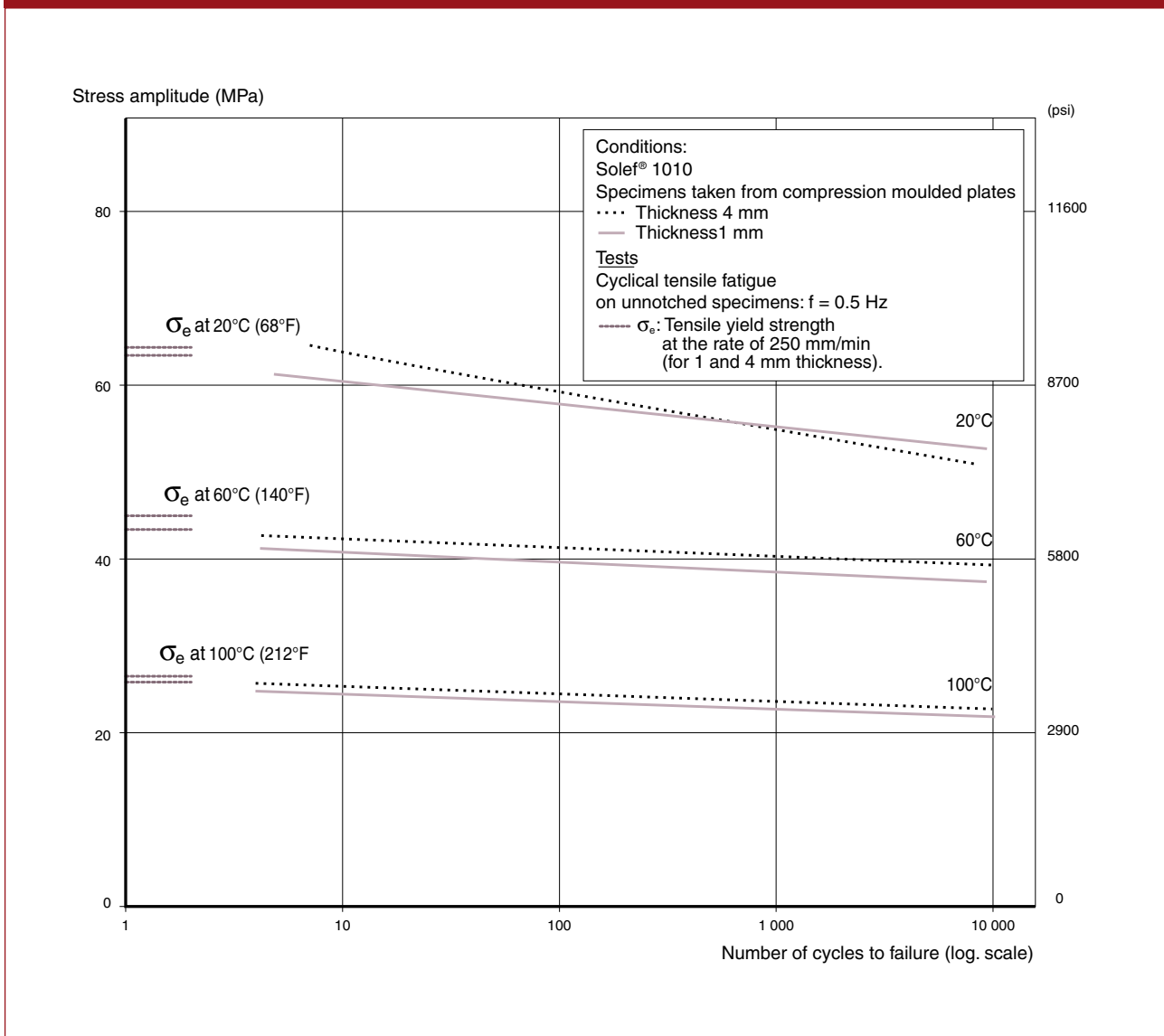
Like in the preceding case, the fatigue failures of a ductile nature are only obtained under stresses close to σ_e (> 0.8 σ_e). In the absence of notches, Solef® PVDF is so characterized by a very high endurance limit, far above that of a large number of thermoplastics.

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

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



δ (crack opening displacement = COD) by plastic deformation is expressed by the relationship:

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

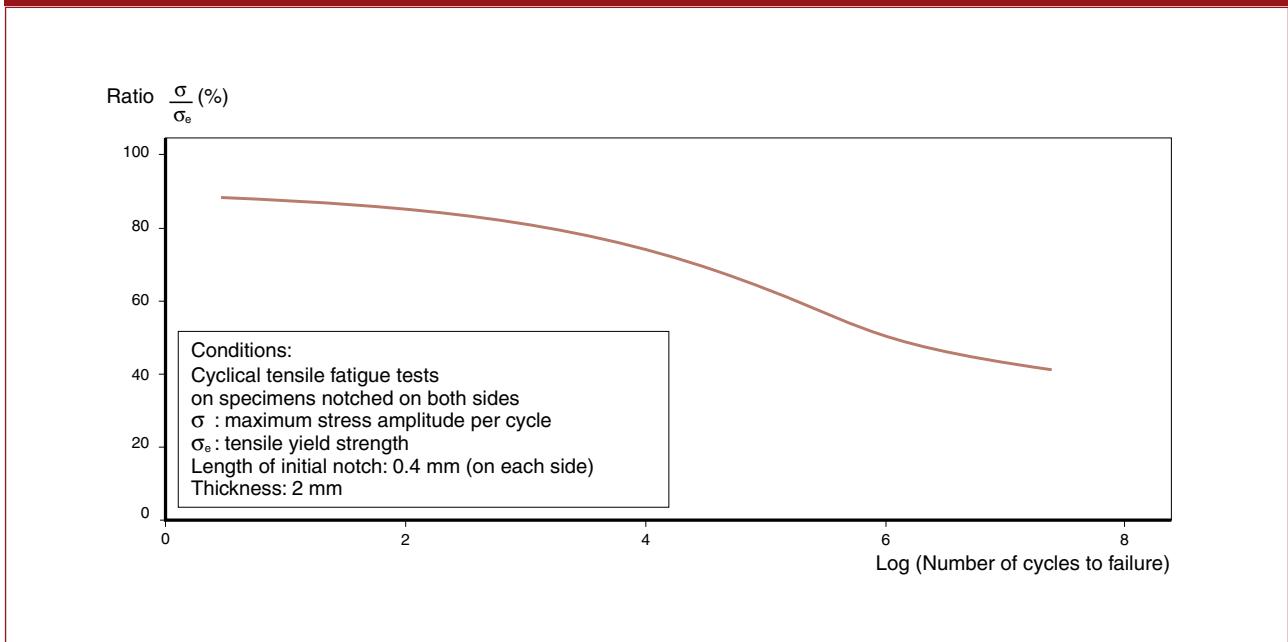
where σ : nominal stress applied to the specimen
 σ_y : real stress along the crack
 c : half-length of the crack
 E : modulus of elasticity
 K_I : stress intensity factor at the tip of the crack
 The K_{IC} factor corresponds to the maximum value of K_I , beyond which failure occurs by sudden propagation 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® PVDF 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% as a function of the number of cycles to failure, at a temperature of 25°C (77°F).

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



4. 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 D 256) 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® grades (notched Izod).

Charpy flexural impact strength (ASTM D 256)

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.

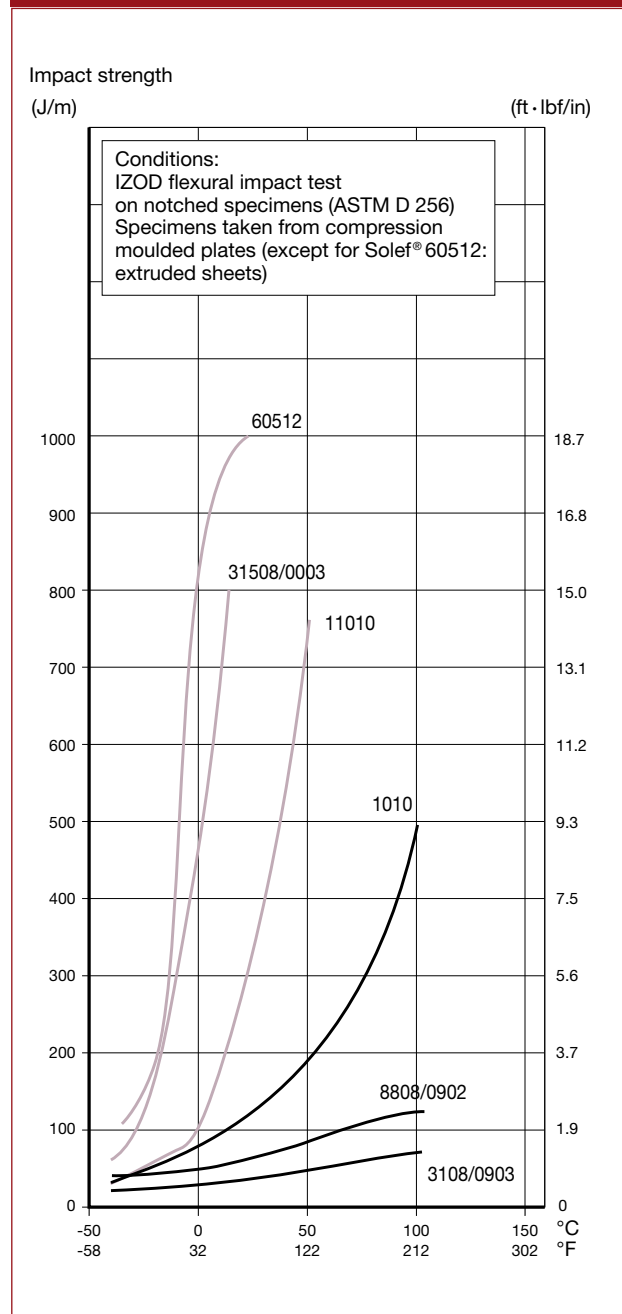
Flexural impact strength of Solef® PVDF 1010 and 1012 was evaluated using the Charpy method (see Table 24).

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 moulded plate)	18.1	8.6
Solef® 1012 (compression moulded plate)	24.5	11.6

(*) M: Machine direction; T: transversal direction.

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



Brittleness temperature

This test method covers the determination of the temperature at which plastics exhibit brittle failure under impact conditions specified in the ASTM D 746 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® 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 D 3763, DIN 53443-2)

The behavior under multiaxial impact stresses of plastic materials is evaluated by the perforation

Table 25: Brittleness temperature of Solef® PVDF according to ASTM D 746. Compression moulded plate

Solef® grade	Brittleness Temperature °C (° F)
Homopolymers	
1010	0 to +10 (32 to 50)
6010	-5 to +5 (23 to 41)
1012	0 to +10 (32 to 50)
1015	-12 (10.4)
Copolymers	
11010	-18 (-0.4)
11008/0003	-17 (1.4)
21508/0003	-22 (-8)
31008/0003	-30 (-22)
31508/0003	-37 (-35)
32008/0003	-53 (-63)
60512	-31 (-24)

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

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)	4.0 (75)
	-40 (-40)	0,4 (7.5)
Solef® 11010	23 (73.4)	9.5* (178)
	-40 (-40)	0,5 (9.4)
Solef® 31508/0003	23 (73.4)	7.0* (131)
	-40 (-40)	1,2 (22.5)
PET (indicative values)	23 (73.4)	0,15 (2.8)
POM (indicative values)	23 (73.4)	0,6 (11.2)
PP (homopolymer/indicative values)	23 (73.4)	0,15 (2.8)
Test conditions <ul style="list-style-type: none"> • 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® PVDF 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 D 1709 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.

5. 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). Tables 28a and 28b give the mechanical properties recorded before and after reprocessing (up to 30 times).

These Tables show that, after 30 reprocessing steps:

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

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

Type of film	Thickness µm	Dart Drop test g for 50% breakage (ASTM D 1709)	Elmendorf tearing force per unit of thickness, mN/µm (ISO 6383/2)	
			M direction	T direction
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

Table 28a: Reprocessing effects on mechanical properties of Solef® 1010 grade (SI Units)

	Number of complete reprocessings	0	5	10	15	20	25	30
		MFI at 230°C (ASTM D 1238)	g / 10 min (5kg)	6,34	6,42	6,64	6,83	6,96
Mechanical properties (on compression moulded plates) Tension (*) - ASTM D 638								
• Yield strength	MPa	52.6		54.1		54.3		53.9
• Elongation at yield	%	7		9		10		9
• Stress at break	MPa	32.3		36.9		43.9		44.3
• Elongation at break	%	29		24		30		25
• Modulus (secant)	MPa	2430		2430		2350		2590

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

Table 28b: Reprocessing effects on mechanical properties of Solef® 1010 grade (US Customary Units)

	Number of complete reprocessings	0	5	10	15	20	25	30
		MFI at 230°C (ASTM D 1238)	g / 10 min (5kg)	6,34	6,42	6,64	6,83	6,96
Mechanical properties (on compression moulded plates) Tension (*) - ASTM D 638								
• Yield strength	psi	7642		7845		7874		7816
• Elongation at yield	%	7		9		10		9
• Stress at break	psi	4684		5351		6366		6424
• Elongation at break	%	29		24		30		25
• Modulus (secant)	kpsi	352		352		341		376

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

ELECTRICAL PROPERTIES

1. General characteristics

Solef® and Hylar® 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.

2. Volume and surface resistivities

(ASTM D 257, 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 ($\Omega \cdot \text{cm}$) vs. temperature for Solef® 1008 grade.

The surface resistivity under 500 V of this grade at 23°C (73.4°F) is $\geq 1 \cdot 10^{14} \Omega / \text{sq}$. The PVDF resin is a good electrical insulator.

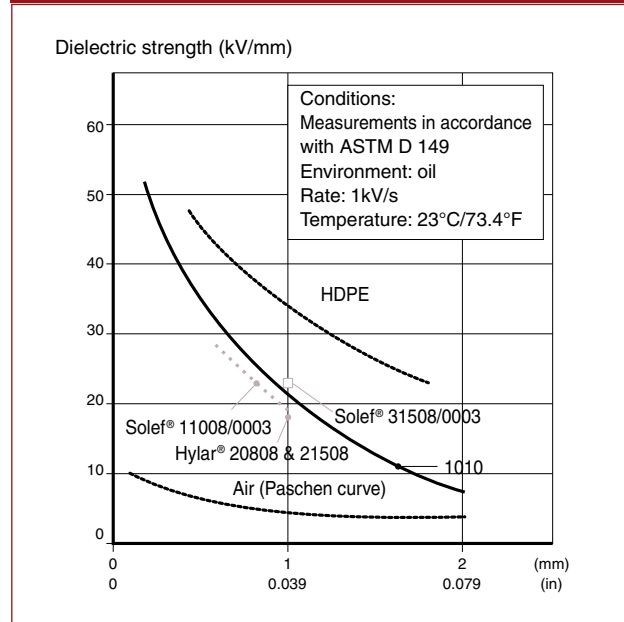
Solef® 3108/0903 and 3110/0907 grades, filled with carbon black, were developed for antistatic applications. In these cases, the surface resistivity is lower than 1000Ω (500 V, 23°C / 73.4°F).

3. Dielectric strength

(ASTM D 149, DIN 53481)

Dielectric strength is a measure of a materials ability to resist high voltage without dielectric breakdown. It is measured by placing a specimen between

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



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 moulded plates as a function of thickness. The values are within the range of those recorded for polyolefins.

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

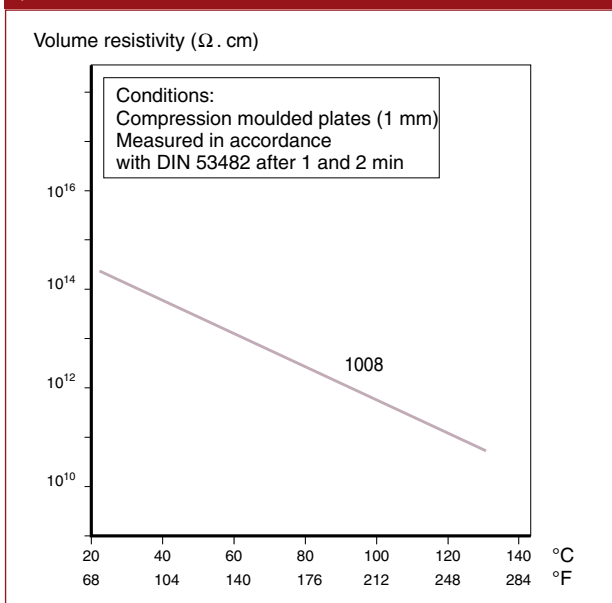


Fig. 50: Dielectric strength and breakdown voltage of Solef® PVDF 1008 films vs. thickness

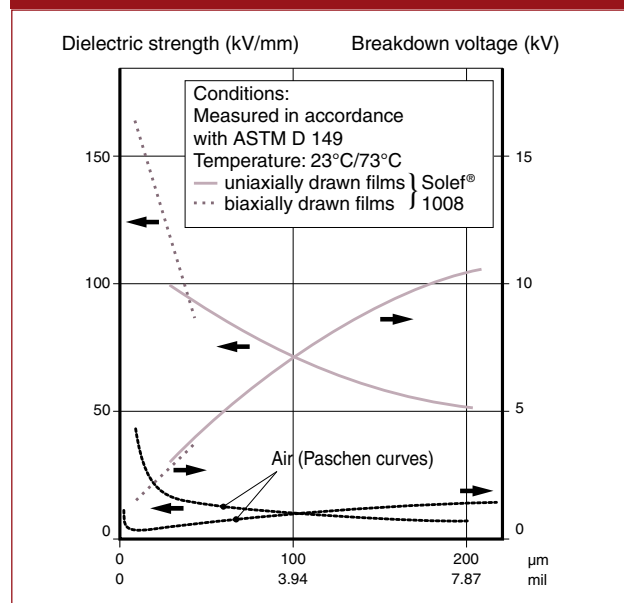


Figure 50: variation of dielectric strength and breakdown voltage of films as a function of thickness.

4. Dielectric constant and tangent of loss angle

(IEC 250, ASTM D 150, 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® PVDF 1010 as a function of temperature measured at different frequencies (Compression moulded 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. 52: Tangent of dielectric loss angle of Solef® PVDF 1010 at low frequency vs. temperature

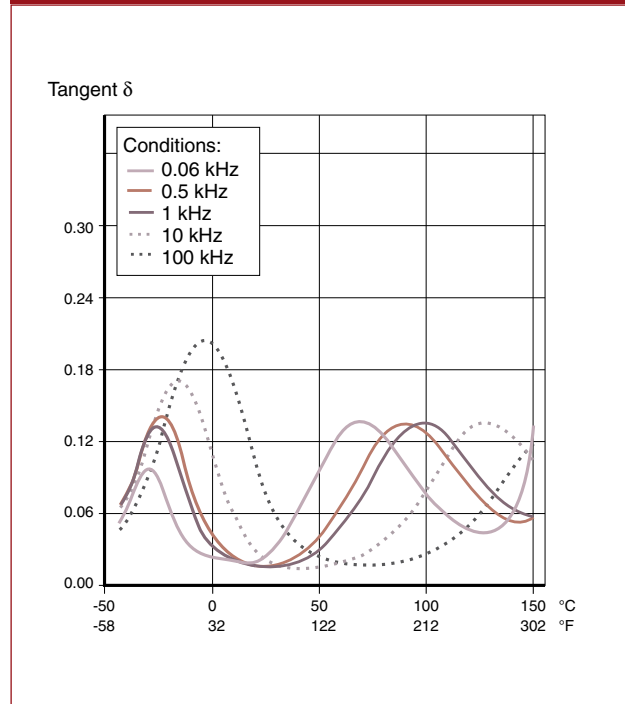


Fig. 51: Dielectric constant of Solef® PVDF 1010 at low frequency vs. temperature

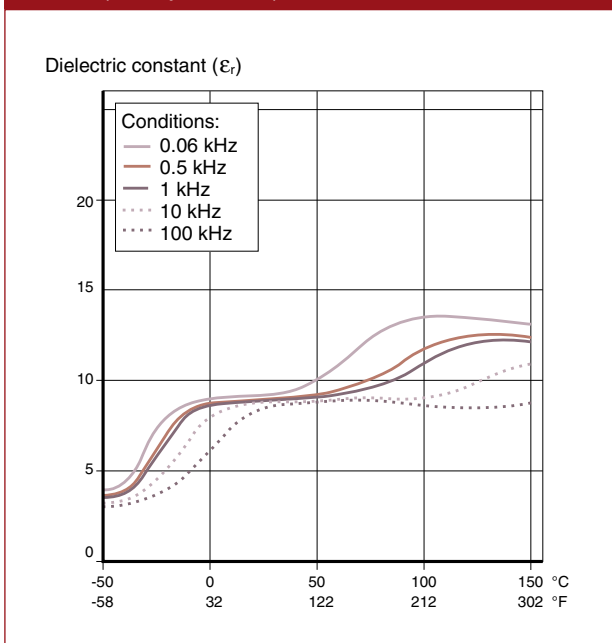


Fig. 53: Dielectric constant of Solef® PVDF 11008/0003 at low frequency vs. temperature

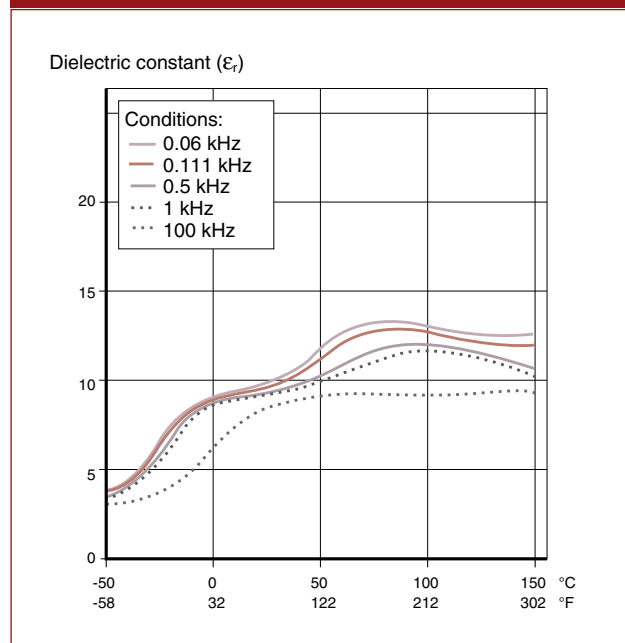


Fig. 54: Tangent of dielectric loss angle of Solef® PVDF 11008/0003 at low frequency vs. temperature

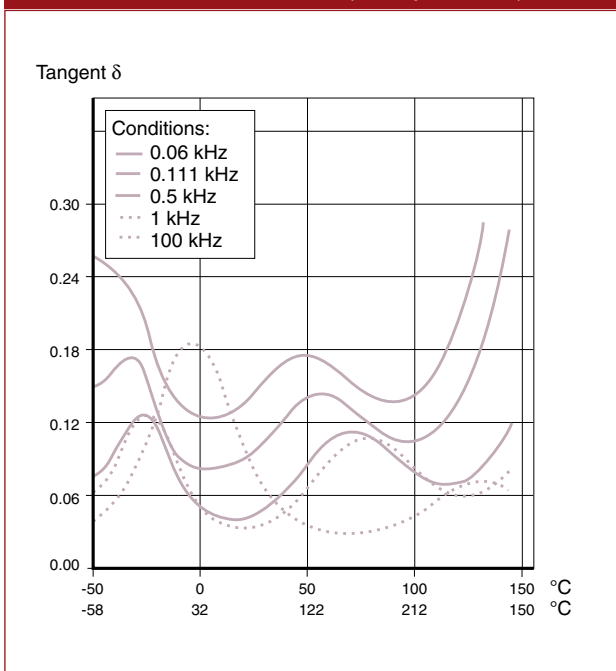
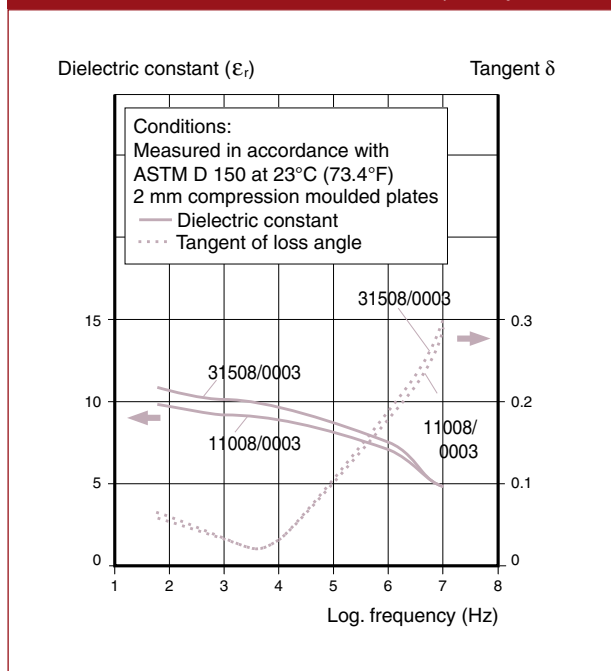


Fig. 55: Dielectric constant and tg δ of Solef® PVDF 11008/0003 and 31508/0003 vs. frequency



5. Comparative Tracking Index

(IEC 112, ASTM D 3638, 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® and Hylar® resins have a CTI value greater than 600 volts.

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

PVDF gradeS	CTI, volts
Solef® resins	
1010	600+
6010	600+
11010	600+
21508/0003	600+
31508/0003	600+
Hylar® resins	
460	600+
Solef® Compounds	
3410/0905	525
8808/0902	< 100

6. 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. This Table also gives those of solvane copolymer developed by Solvay Solexis for piezoelectric applications.

Table 30: Piezo- and pyroelectricity of Solef® PVDF films and sheets of various thicknesses (23°C/73.4°F)							
	Biaxially drawn films				Uniaxially drawn sheets		solvane film
	9 µm 0.35 mil	25 µm 0.98 mil	40 µm 1.6 mil	130 µm 5.1 mil	0.5 mm 0.020 in	1 mm 0.040 in	25 µm 0.98 mil
d_{33} , pC/N	-17.5	-16.5	-19.5	-33	-30	-30	-18.5
d_{31} , pC/N	6.5	8.5	9.5	23	18	18	8.5
d_{32} , pC/N	6.5	8.5	9.5	3	3	3	8.5
g_{33} at 1 kHz, V.m/N	-0.17	-0.16	-0.19	-0.3	-0.3	-0.3	-0.22
p_{33} , µC/m ² .K	-27	-26	-32	—	—	—	-28
Diel. const ant ϵ_r at 1 kHz	11.5	11.5	11.5	12	12	12	9.4
tg δ at 1 kHz	$15 \cdot 10^{-3}$	$15 \cdot 10^{-3}$	$15 \cdot 10^{-3}$	$15 \cdot 10^{-3}$	$18 \cdot 10^{-3}$	$18 \cdot 10^{-3}$	$16 \cdot 10^{-3}$
DC breakdown voltage (V/µm)	750	585	540	—	—	—	395

ENVIRONMENTAL RESISTANCE

1. Chemical resistance

Overview of chemical resistance of PVDF

In general, Solef® and Hylar® PVDF have excellent

resistance to a wide range of chemicals. Although the two polymers are produced via a different process, the chemical resistance of PVDF homopolymers can be regarded as very similar.

Table 31: Overview of the chemical resistance of Solef® and Hylar® 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
Organic acids, esters and ketones				
Acetic acid	CH ₃ COOH	100%	50	122
		50%	75	167
Acetone	CH ₃ COCH ₃	100%	not resistant	
		5%	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	$\text{N(CH}_3\text{)CO(CH}_2\text{)}_3\text{}$	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

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® and Hylar® 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 ≥ 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.

Comparison with other plastics

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

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

Environment	Temp.	PVDF			PP			PVC			FRP		
	°C	30	60	90	30	60	90	30	60	90	30	60	90
	°F	68	140	194	68	140	194	68	140	194	68	140	194
H ₂ SO ₄ , 90%		+	+	0	0	0	-	+	0	-	-	-	-
HCl, conc.		+	+	+	+	0	-	+	+	0	+	0	-
HNO ₃ , 50%		+	+	+	-	-	-	+	0	-	-	-	-
HF, 40%		+	+	+	+	+	-	+	0	-	-	-	-
NaOH, 50%		-	-	-	+	+	+	+	+	-	+	+	-
NaOCl, 15%		0	0	0	0	-	-	+	+	-	+	0	-
Cl ₂ , dry gas		+	+	+	-	-	-	0	0	-	0	0	0
Cl ₂ , moist gas		0	0	0	-	-	-	0	0	-	0	0	0
Ketones, esters		0	-	-	+	-	-	-	-	-	-	-	-
Aromatic hydrocarbons		+	+	0	0	-	-	-	-	-	-	-	-
Chlorinated solvents		+	0	0	-	-	-	-	-	-	-	-	-

+: no significant change of properties
 0: 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® 60000 series 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® 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

2. Permeability

Water absorption

(ISO 62, ASTM D 570, 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 and 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 Solexis.

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.

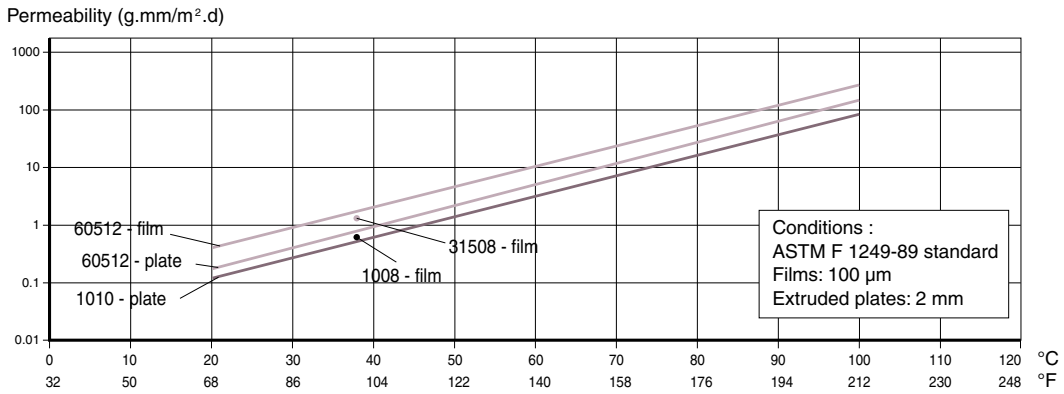
- Water Permeability

Table 34:
Water permeability of Solef® PVDF 1010

Type of sample	Temperature, °C (°F)	Permeability, g.mm/m ² .d
Film of 100 μm	23 (73.4)	0.2
	38 (100.4)	0.9
Sheet of 0.5 mm	23 (73.4)	0.2
	38(100.4)	0.6
	50 (122)	1.5
	100 (212)	30
Plate of 2 mm	23 (73.4)	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



- Permeability to liquids and gases

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

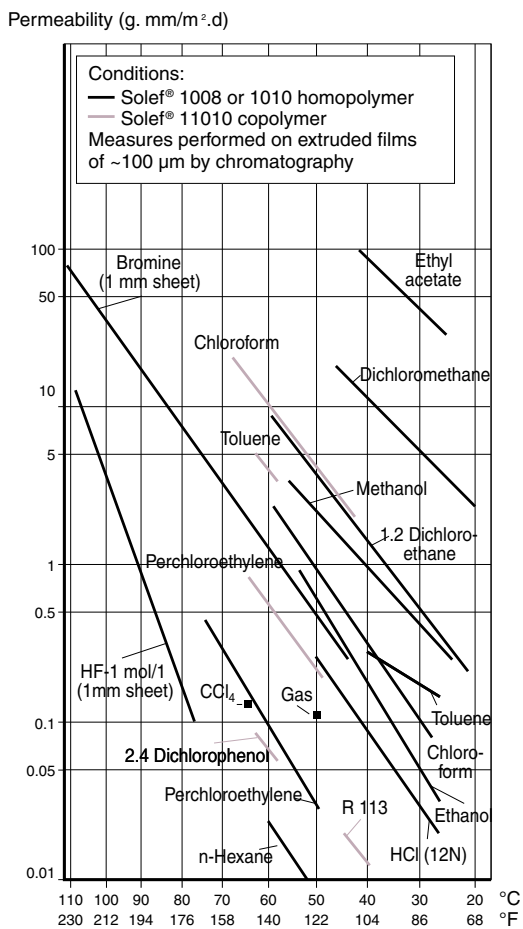
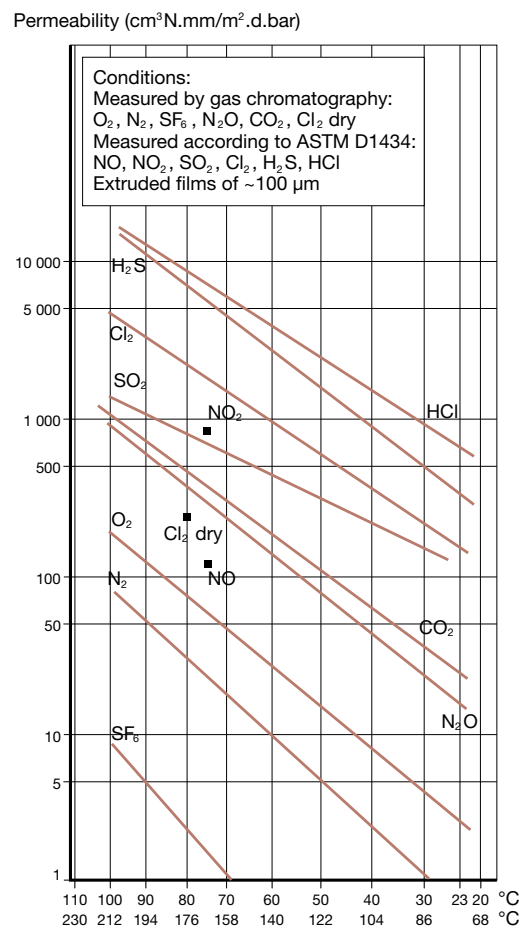


Fig. 58: Permeability to gases of Solef® PVDF homopolymers vs. temperature



3. 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® PVDF 1008 injection moulded specimens after 2 years aging at

20°C (68°F), 120°C (248°F) and 150°C (302°F). See Tables 35a and 35b.

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

In the case of Solef® 11010 copolymer, aging tests up to 1000 hours at 150°C (302°F) on compression moulded 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 35a: Thermal aging tests at various temperatures on Solef® PVDF 1008 (SI Units)

Aging period days	Tensile yield strength (MPa)			Secant modulus at 1% deformation (MPa)			Elongation at break (%)		
	20°C	120°C	150°C	20°C	120°C	150°C	20°C	120°C	150°C
1	50	53	51	1900	1700	1600	9.5	10.5	11.8
11	49	54	51	2000	1900	1800	8.5	10.0	13.0
160	53	54	51	2300	2100	1800	7.0	9.0	11.5
358	54	55	53	2300	2300	2200	7.0	10.0	>11.0
730	52	54	—	2300	1800	—	6.6	10.4	—

Source: RAPRA - Injection moulded specimens

Table 35b: Thermal aging tests at various temperatures on Solef® PVDF 1008 (US Customary Units)

Aging period days	Tensile yield strength (psi)			Secant modulus at 1% deformation (kpsi)			Elongation at break (%)		
	68°F	248°F	302°F	68°F	248°F	302°F	68°F	248°F	302°F
1	7250	7685	7395	275	246	232	9,5	10,5	11,8
11	7105	7830	7395	290	275	261	8,5	10,0	13,0
160	7685	7830	7395	333	304	261	7,0	9,0	11,5
358	7830	7975	7685	333	333	319	7,0	10,0	11,0
730	7540	7830	-	333	261	-	6,6	10,4	-

Source: RAPRA - Injection moulded specimens

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

Aging period (h)		0	8	100	1000
Tensile properties					
Yield stress	MPa	28	28	29	28
	psi	4060	4060	4205	4060
Strength at break	MPa	41	34	34	40
	psi	5945	4930	4930	5800
Elongation at break	%	>500	>480	>480	>500
Modulus	MPa	1020	1070	1020	870
	kpsi	148	155	148	126
Thermal properties					
HDT under 0.46 MPa (66.7 psi)	°C	113	122	132	149
	°F	235	252	270	300

Compression moulded plates, thickness 2 mm - Rate of pulling: 10 mm/min (modulus: 1mm/min)

4. 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

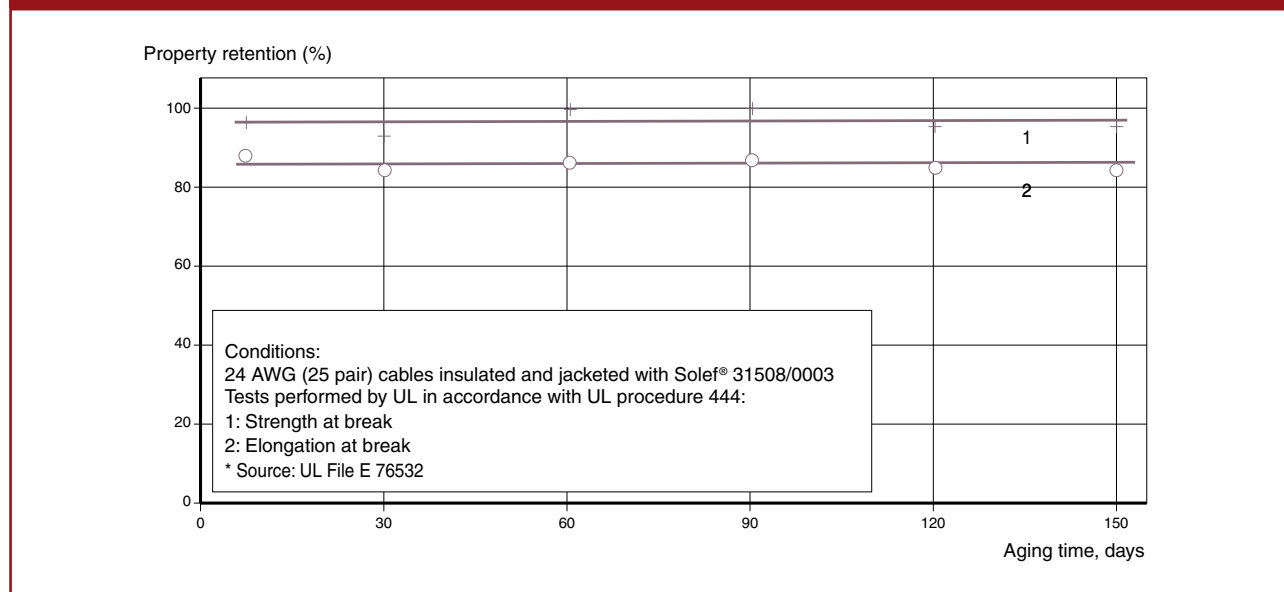
communications cables, Solef® 11010/0003 and 31508/0003 grades received the “UL rating 150°C (302°F)”, while the 21508/0003 grade received the “UL rating 125°C (257°F)”.

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).

5. Weathering resistance

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

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



a) Artificial aging using Weather-O-Meter equipment

Solef® PVDF 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 7200 hours exposure (which is enough to affect most plastics), no measurable modification was identified with regard to the mechanical properties (tensile and impact strength).

b) Artificial aging using Xenon-arc Weather-O-Meter and water exposure in accordance with the UL 746C procedure

Solef® PVDF 6008 considered stable for outdoor use (1000 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 in flammability test (see Table 37).

c) Accelerated tests, using Q-U-V equipment

Solef® PVDF 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 2600 MPa (377 kpsi) unchanged.

Solef® PVDF 31508 and 32008: 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).

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

Initial properties			Percent retention after conditioning					
UL 94 Flame test Class	Tensile impact test kJ/m ² (ft·lbf/in ²)	Tensile strength MPa (psi)	1000 h UV			7 days water @ 70°C (158°F)		
			UL 94 Flame test Class	Tensile impact test	Tensile strength	UL 94 Flame test Class	Tensile impact test	Tensile strength
V-0	81 (38.5)	45 (6525)	V-0	99	100	V-0	100	95

Test conditions:
 Solef® PVDF 6008 plates - 1 mm thick
 Tensile impact test measured in accordance with ASTM D 1822
 Tensile strength measured in accordance with ASTM D 638

d) Accelerated natural aging test

EMMAQUA method (ASTM D 838 standard) on 80 µm thick films made of Solef® PVDF 1008: no alteration after 1 year weathering (see Tables 38a and 38b).

Table 38a: Accelerated natural aging of Solef® PVDF 1008 films (SI Units)
EMMAQUA tests – DSET Lab. Inc.

	Aging period (months)			
	0	4	8	12
Yellowing index (ASTM 1925)	1.7	2.9	2.9	3.0
Melting temperature (DSC) (°C)	174	174	172	173
Tensile test at 50 mm/min:				
• Tensile yield stress (MPa)	40	40	43	42
• Strength at break (MPa)	63	44	47	45
• Elongation at break (%)	520	440	320	460
• Modulus* (MPa)	1280	1490	—	1310
Tensile impact strength (DIN 53448) (ft·lbf/in ²) (kJ/m ²)	450	430	600	380

80 µm thick films produced by flat die extrusion on chill roll
 Mechanical properties measured in the machine direction
 * Rate = 1 mm/min

Table 38b: Accelerated natural aging of Solef® PVDF 1008 films (US Customary Units)
EMMAQUA tests – DSET Lab. Inc.

	Aging period (months)			
	0	4	8	12
Yellowing index (ASTM 1925)	1,7	2,9	2,9	3
Melting temperature (DSC) (°F)	345	345	342	343
Tensile test at 50 mm/min:				
• Tensile Yield stress (psi)	5800	5800	6235	6090
• Strength at break (psi)	9135	6380	6815	6525
• Elongation at break (%)	520	440	320	460
• Modulus* (kpsi)	86	216	—	190
Tensile impact strength (DIN 53448) (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

e) Natural aging in Arizona

Aging of 80 µm films made of Solef® PVDF 1008 and 11010: no property alteration was found after several

years, as shown by tests performed after 9 years aging (see Tables 39a and 39b).

Table 39a: Natural aging tests performed in Arizona on Solef® PVDF films (SI Units) DSET Lab. Inc. – New River											
Properties of Solef® PVDF 1008 (I) and 11010 (II) grades	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	
Tensile test at 50 mm/min											
• Tensile yield stress (MPa)	40	22	41	23	39	25	42	24	44	25	
• Strength at break (MPa)	63	54	48	44	35	49	60	56	59	54	
• Elongation at break (%)	520	470	440	370	320	380	450	410	425	420	
• Modulus* (MPa)	1280	590	1350	670	1150	660	1350	700	1370	670	
Tensile impact (DIN 53448) (kJ/m²)	450	3400	450	2800	250	2300	400	2700	–	–	
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	
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											

Table 39b: Natural aging tests performed in Arizona on Solef® PVDF films (US Customary Units) DSET Lab. Inc. – New River											
Properties of Solef® PVDF 1008 (I) and 11010 (II)	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) (°F)	345	318	345	316	345	318	343	316	347	320	
Tensile test at 50 mm/min											
• Tensile yield stress (psi)	5800	3190	5945	3335	5655	3625	6090	3480	6380	3625	
• Strength at break (psi)	9135	7830	6960	6380	5075	7105	8700	8120	8555	7830	
• Elongation at break (%)	520	470	440	370	320	380	450	410	425	420	
• Modulus* (kpsi)	186	86	196	97	167	96	196	102	199	97	
Tensile impact (DIN 53448) (ft-lbf/in²)	214	1618	214	1332	119	1094	190	1285	-	-	
Resistance to Elmendorf tearing (ASTM 1922) (lbf)	0,43	0,56	0,32	0,34	0,34	0,34	0,63	0,72	0,59	0,70	
80 µm thick films manufactured by flat die extrusion on chill roll Mechanical properties measured in the machine direction *Rate of pulling = 1 mm/min											

6. 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 Co^{60} source were performed on injection moulded specimens of Solef® PVDF 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.

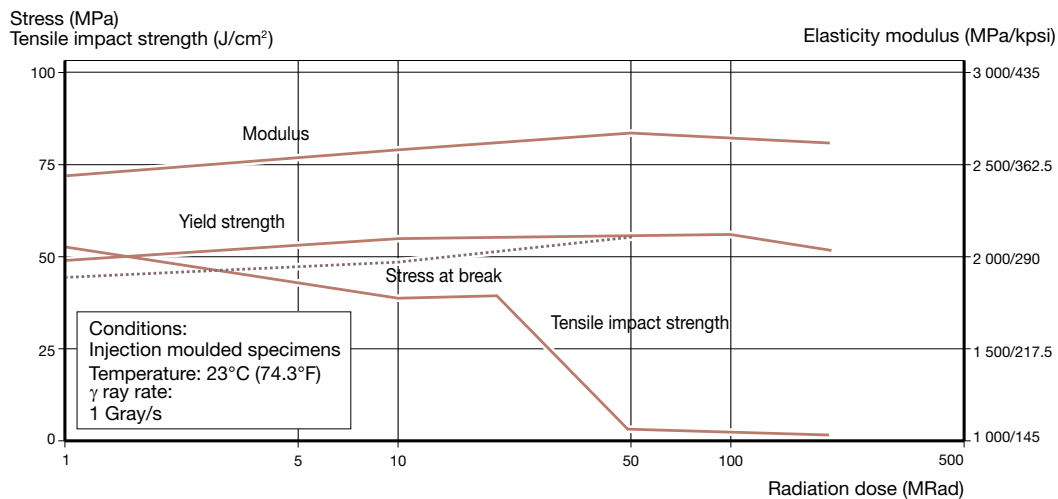
In sterilization under a γ radiation dose of 2.5 and 5 MRad, Solef® PVDF preserves virtually all its properties, despite a discoloration which gradually appears with the radiation dose increase.

7. Resistance to fire

Solef® and Hylar® 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 (6.32×10^3 Btu/lb), in accordance with the calorimetric bomb test DIN 51 900 Part 3.

In addition, the lower flammability limit for the Solef® 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/m^3 ($5.0 \times 10^{-3} \text{ lb/ft}^3$) for an average particle diameter (d_p) $\sim 60 \mu\text{m}$ (class St1 following VDI 3673: slightly explosive).

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



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.

Limiting Oxygen Index – LOI

The oxygen index is defined by ASTM D 2863 as the minimum concentration of oxygen, in a mixture of oxygen and nitrogen that will support flaming combustion of a test material.

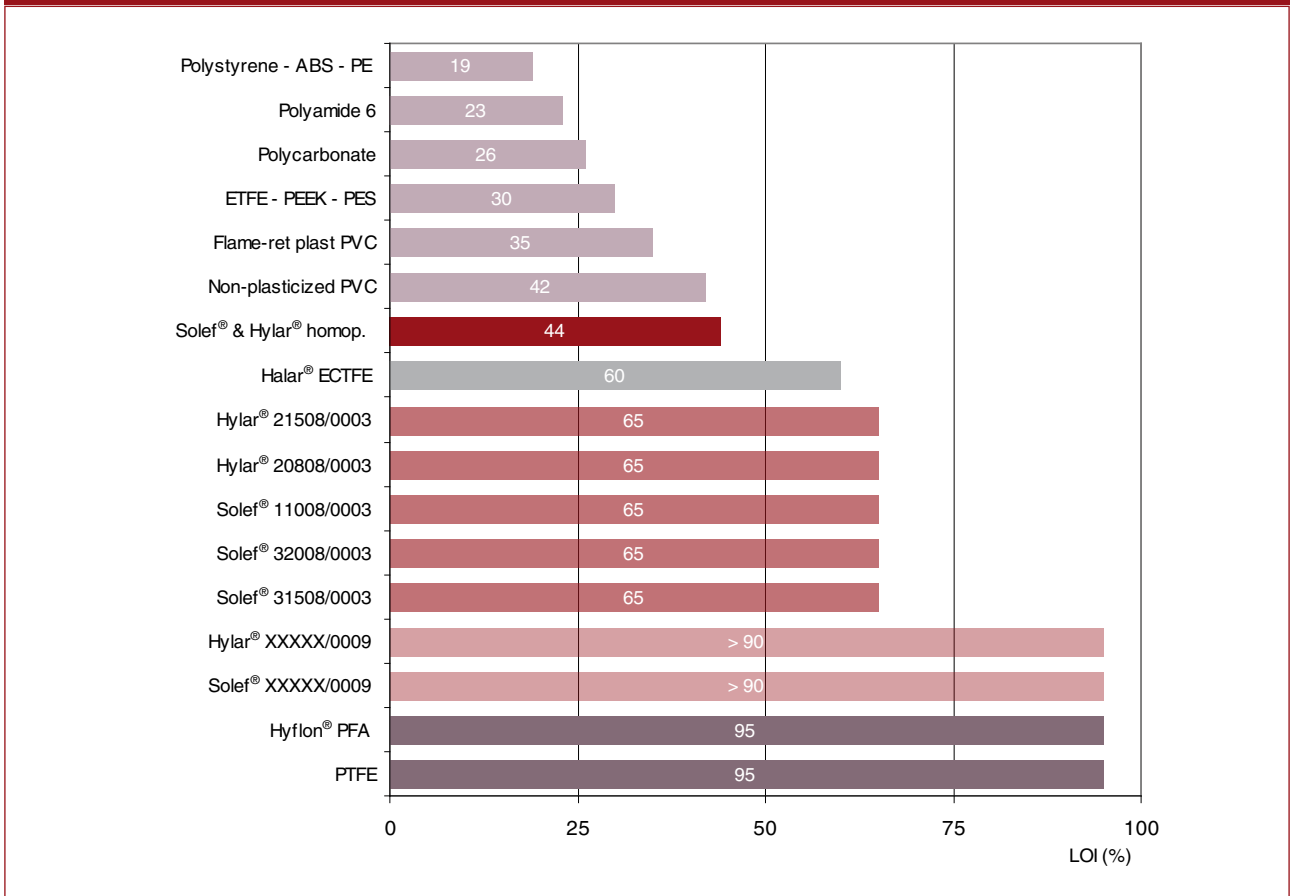
Since ordinary air contains roughly 21% oxygen, a material whose oxygen index is appreciably higher than 21 is considered flame resistant because it will only burn in an oxygen-enriched atmosphere.

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

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

Grade	
Solef® 1006/0001	Hylar® 460
Solef® 1008/0001	Hylar® 21508/0001
Solef® 1009/0001	Hylar® 20808/0003
Solef® 1010/0001	
Solef® 1012/0001	
Solef® 6008/0001	
Solef® 6008/0000	
Solef® 6010/0000	
Solef® 11008/0003	
Solef® 31508/0003	

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



Flame spread in UL 723

“ Steiner tunnel test ” (ASTM E 84, UL 723)

The test ASTM E 84 (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® PVDF 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® PVDF 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® 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 x 76 x 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	31508/0003	21508/0003	31508/0003
Temperature rating, °C/°F	—	150/302	125/257	150/302	150/302
Max. flame spread, ft	≤ 5	3	2.5	2	2
Average optical density	≤ 0.15	0.01	0.02	0.02	0.06
Maximal optical density	≤ 0.5	0.06	0.1	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® and Hylar® 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® and Hylar® 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"

1. Toxicity of decomposition products

The main Solef® and Hylar® 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 overexposure 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 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.

2. 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 EC Directive 2002/72 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® and Hylar® PVDF homopolymers (vinylidene fluoride) and copolymers (vinylidene fluoride, hexafluoropropylene, chlorotrifluoroethylene) meet the requirements of the above mentioned Directive.

Solef® and Hylar® homopolymers comply with the specifications of the United States Food and Drug

Administration (FDA) 21CFR 177.2510; Solef® and Hylar® VDF/HFP and VDF/CTFE copolymers comply with the specifications of 21CFR 177.2600.

The compliance with these regulations depends on the Solef® and Hylar® polymer family and on the grade used; consequently, users should contact the Solvay Solexis 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 Solexis 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	
Solef® grades tested by KTW	Solef® grades tested by DVGW W270
Solef® 1008/0001	Solef® 1008/0001
Solef® 1010/0001	Solef® 1010/0001
Solef® 6008/0001	Solef® 4010/0901 (black master batch)

United Kingdom

Table 44 lists the Solef® 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® 1008/0955
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® 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® grades in compliance with NSF Standard 51	
Solef® 1008/0001	Solef® 11008/1001
Solef® 1010/0001	Solef® 21216/1001
Solef® 1015/1001	Solef® 21508/1001
Solef® 6008/0001	Solef® 31508
Solef® 6010/1001	
Solef® 6020/1001	

NSF Standard 61 – Drinking Water System Components – Health Effects

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

Table 46: Solef® grades in compliance with NSF Standard 61	
Solef® 1008/0001	Solef® 11008/1001
Solef® 1010/0001	Solef® 21216/1001
Solef® 6008/0001	Solef® 21508/1001
Solef® 6010/0001	Solef® 31508/0000
Solef® 6010/0000	

Medical applications

Solef® PVDF 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 Solexis 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 Solexis representative.

PROCESSING BASICS AND SAFETY

Solef® and Hylar® 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.

1. 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).

2. 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 Table below.

Feeding zone	15 – 20 D
Compression zone	0.5 – 3 D
Metering zone	5 – 7 D
Total Length	25D (e. g. 15D+3D+7D or 18.5+0.5D+6D – 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 later 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 Hylar® and 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 Solexis 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 back-pressure 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 (276C), 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.

3. 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 to 200°C (356-392°F)
zone 2	200 to 220°C (392-428°F)
zone 3	210 to 230°C (410-446°F)
zone 4	210 to 230°C (410-446°F)
breaker	220 to 240°C (428-464°F)
head	220 to 240°C (428-464°F)
die	220 to 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® or Hylar® 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® 30,000 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).

4. Recommendations for tube extrusion

Solef® PVDF pipes are widely used in semi-conductors and CPI. For more information about optimal extrusion conditions, contact your Solvay Solexis representative.

5. General recommendations for other types of extrusion

Films, sheets, plates

Solef® and Hylar® 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 (230-248°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.

Table 47: Typical temperature profiles for film extrusion

Processing conditions			Homopolymers		Copolymers	
PVDF GRADES			Solef® 1008 and 6008	Solef® 1010 and 6010	Solef® 21508	Solef® 31508
Extruder Temperature Profile	ZONE1	°C (°F)	190 (374)	190 (374)	160 (320)	190 (374)
	ZONE2	°C (°F)	210 (410)	230 (446)	180 (356)	210 (410)
	ZONE3	°C (°F)	220 (428)	230 (446)	200 (392)	220 (428)
	ZONE4	°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)

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 (392-482°F).

6. Recommendations for injection moulding

Equipment

Plasticizing unit

A conventional polyolefin screw extruder type can be employed.

Nozzle

An open nozzle should be used.

Mould

Hot channels can lead to stagnation at high temperature, which could induce degradation problems. For this reason Solvay Solexis 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 mould has to be designed in order to account for that shrinkage. It is recommended to heat the mould 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 mould 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:

feed 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 - 1500 bar (8700-21000 psi)

Hold-on pressure: 600 - 1500 bar (8700-21000 psi)

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

General recommendations

Temperature

Verify the temperature of the mould 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 mould 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 mould 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 mould, in order to check that the resin has not turned yellow.

7. Recommendations for compression and transfer moulding

In every field where Solef® and Hylar® PVDF are used (chemical industry, electronic industry...) thick parts may be needed to build complete installations. Such thick items can be machined from thick semi-finished rod or block. These can be either extruded or compression moulded 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 mould (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 semi-finished item.

Process description

Basically, compression moulding 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 mould or outside the mould

First step: heating and melting the granules

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

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

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

The melting time in the mould 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 mould in order to reduce the melting time.

Melting outside the mould (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 mould. 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 mould as previously described.

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

Second step: molten cake compression

Melting inside the mould

In this case, the mould 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 2cm layers in a ventilated oven
2 - Mould preheating:	At 210°C (410°F) 60 min
3 - Granules melted:	30min/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) 60min/cm thickness under maximum pressure.

Melting outside the mould

In this case, the mould 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 mould clearance is not small enough, some molten resin may flow out of the mould 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 mould or outside the mould).

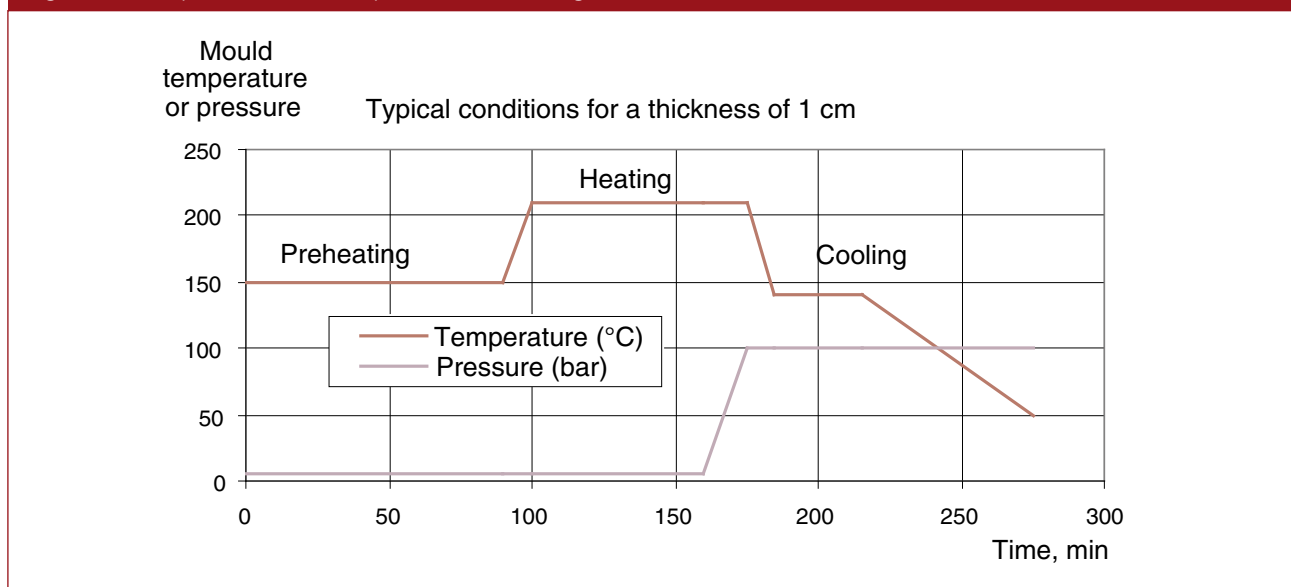
Pressure: Pressure must be maintained at the maximum value throughout the cooling period (at least 100 bar/1451 psi, ideally 150 bar/2176 psi), down to about 50°C (122°F). The top force must be deep enough to take up the shrinkage during cooling and to prevent void formation.

Temperature: Decrease the mould 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

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



pressure must be maintained for several hours. With such a long cooling time, annealing should not be necessary.

Equipment required

Mould

The mould should have adequate size and sufficiently fine clearance to prevent excessive flowing out of the mould 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 mould should also be equipped to control the temperature of each face of the mould.

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

Press

The press should be able to reach at least 50 bar (725 psi), ideally up to 150 bar (2176 psi).

Oven

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

8. Machining

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

9. Welding

Items produced from all non-reinforced grades of Solef® and Hylar® 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 to 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® and Hylar® PVDF. Please contact Solvay Solexis for detailed information.

Solvay Solexis S.p.A.
Viale Lombardia, 20
20021 Bollate (MI), Italy
Tel. +39 02 3835 1
Fax +39 02 3835 2129

Solvay Solexis Inc.
10 Leonard Lane
Thorofare NJ 08086, USA
Tel. +1 856 853 8119
Fax +1 856 853 6405

www.solvaysolexis.com

To our actual knowledge, the information contained herein is accurate as of the date of this document. However neither Solvay Solexis S.p.A., nor any of its affiliates makes any warranty, express or implied, or accepts any liability in connection with this information or its use. This information is for use by technically skilled persons at their own discretion and risk and does not relate to the use of this product in combination with any other substance or any other process. This is not a license under any patent or other proprietary right. The user alone must finally determine suitability of any information or material for any contemplated use in compliance with applicable law, the manner of use and whether any patents are infringed. This information gives typical properties only and is not to be used for specification purposes. Solvay Solexis S.p.A., reserves the right to make additions, deletions or modifications to the information at any time without prior notification.

Trademarks and/or other Solvay Solexis S.p.A. products referenced herein are either trademarks or registered trademarks of Solvay Solexis S.p.A. or its affiliates, unless otherwise indicated.

Copyright 2006, Solvay Solexis S.p.A. All Rights Reserved.

