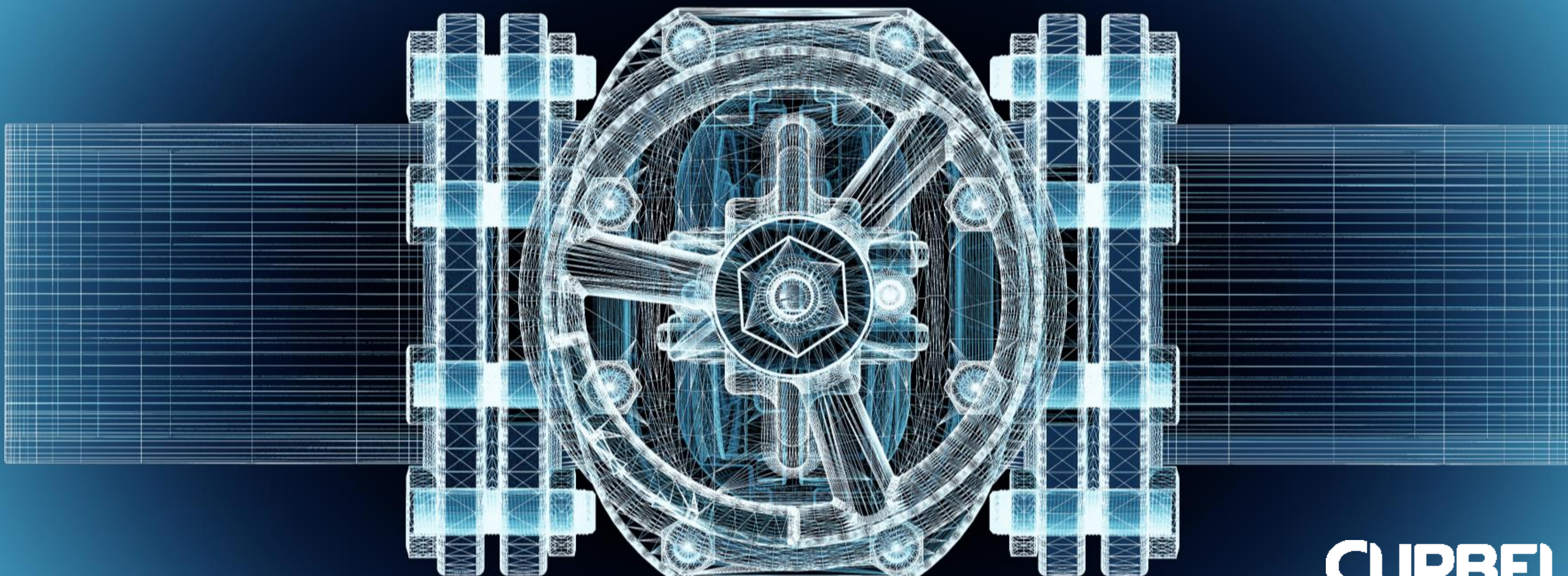
Design Considerations When Choosing Plastic Materials for Use in High Performance Valves and Regulators

Webinar Presented by Curbell Plastics



Agenda

- CTQs for the Plastics used in Valves and Regulators
- Assuring Consistent Quality of Plastic Materials
- Overview of the Plastic Materials used in Valves and Regulators

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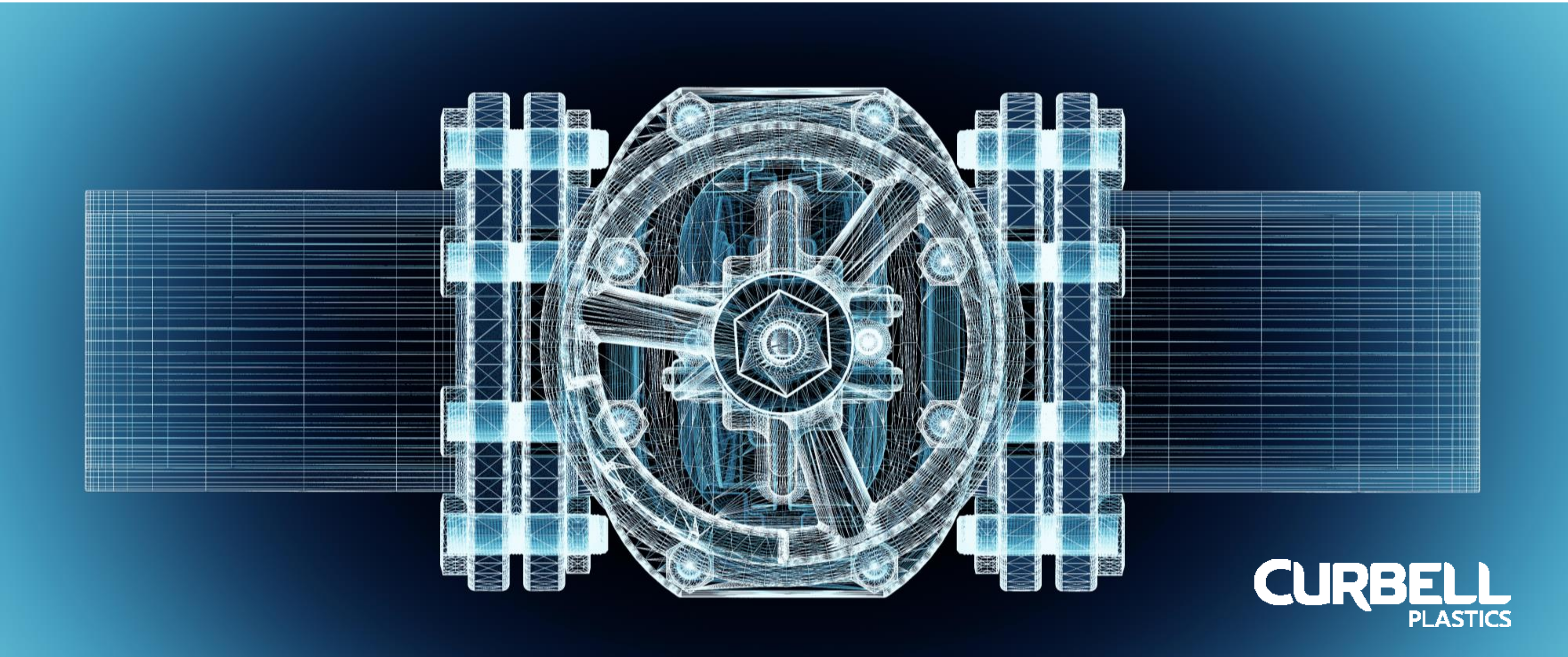
CTQs for the Plastics used in Valves and Regulators



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Moderate Compressive Modulus to Conform to Mating Surfaces

- PTFE: 70 kpsi
- Nylon: 420 kpsi
- Glass Filled PEEK: 700 kpsi
- Stainless Steel: 30,000 kpsi
  - Not easy to conform to mating surface
  - Cold welding, galling, wear, contamination

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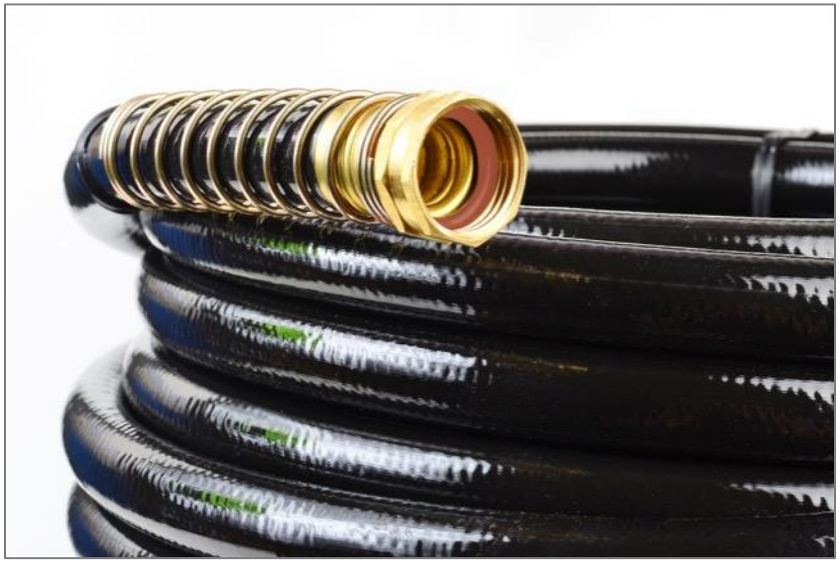
Moderate compressive modulus to conform to mating surfaces (throughout the operating temperature range)



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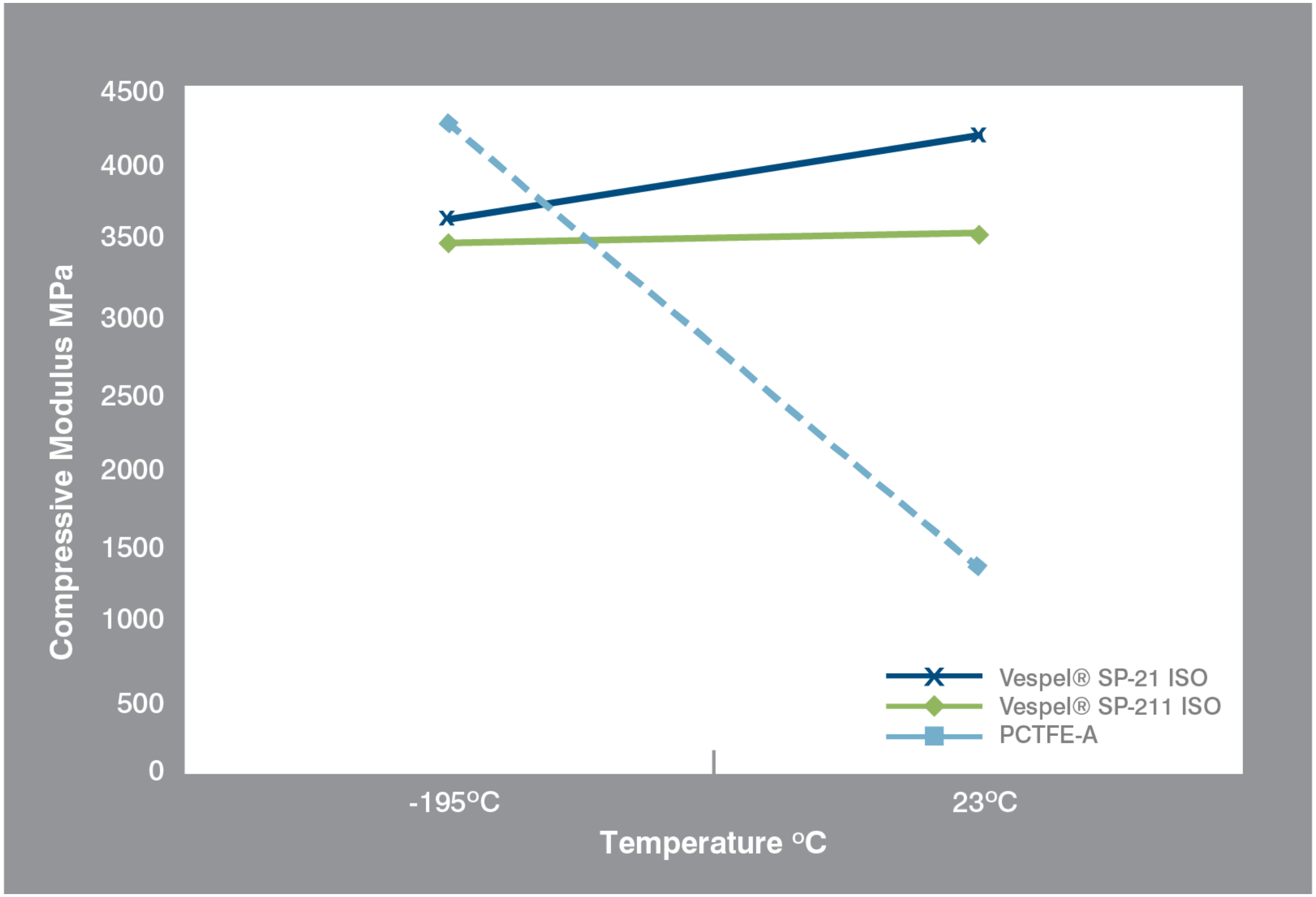
Compressive Modulus

Compressive Modulus (ASTM D695)



Source: Geoff Lewis, DuPont 2015 – LNG Seals

Compatibility with Process Fluids

- Can’t degrade the polymer
- Can’t contaminate the process fluid

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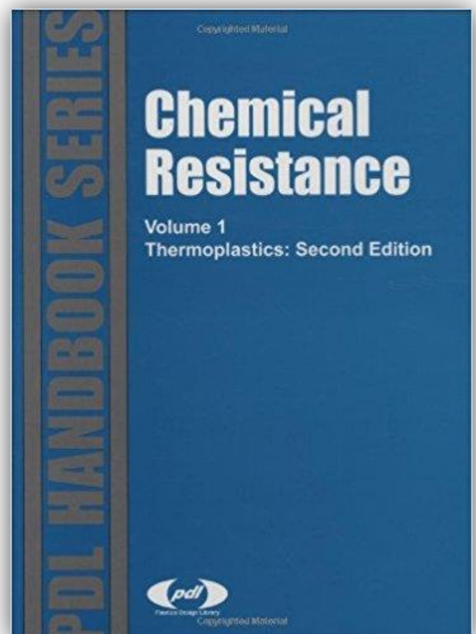
Chemical Resistance and ESC (Environmental Stress Cracking)

Chemical Resistance Data



Weighted Value	Weight Change*	Diameter; length* Change	Thickness* Change	Volume Change*	Mechanical** Property Retained	Visual / Observed *** Change
10	0-0.25	0-0.1	0-0.25	0-2.5	>=97	no change
9	>).25-0.5	>0.1-0.2	>0.25-0.5	>2.5-5.0	94-<97	
8	>0.5-0.75	>0.2-0.3	>0.5-0.75	>5.0-10.0	90-<94	
7	>0.75-1.0	>0.3-0.4	>0.75-1.0	>10.0-20.0	85-<90	slightly discolored slightly bleached
6	>1.0-1.5	>0.4-0.5	>1.0-1.5	>20.0-30.0	80-<85	discolored yellows slightly flexible
5	>1.5-2.0	>0.5-0.75	>1.5-2.0	>30.0-40.0	75-<80	possible stress crack agent flexible possible oxidizing agent slightly crazed
4	>2.0-3.0	>0.75-1.0	>2.0-3.0	>40.0-50.0	70-<75	dostorted, warped softened slight swelling blistered known stress crack agent
3	>3.0-4.0	>1.0-1.5	>3.0-4.0	>50.0-70.0	60-<70	cracking, crazing brittle plasticizer oxidizer softened swelling surface hardened
2	>4.0-6.0	>1.5-2.0	>4.0-6.0	>60.9-90.0	50-<60	severe distortion oxidizer and plasti-cizer deteriorated
1	>6.0	>2.0	>6.0	>90.0	>0-<50	decomposed
					0	solvent dissolved disintegrated

Source: PDL, 1994

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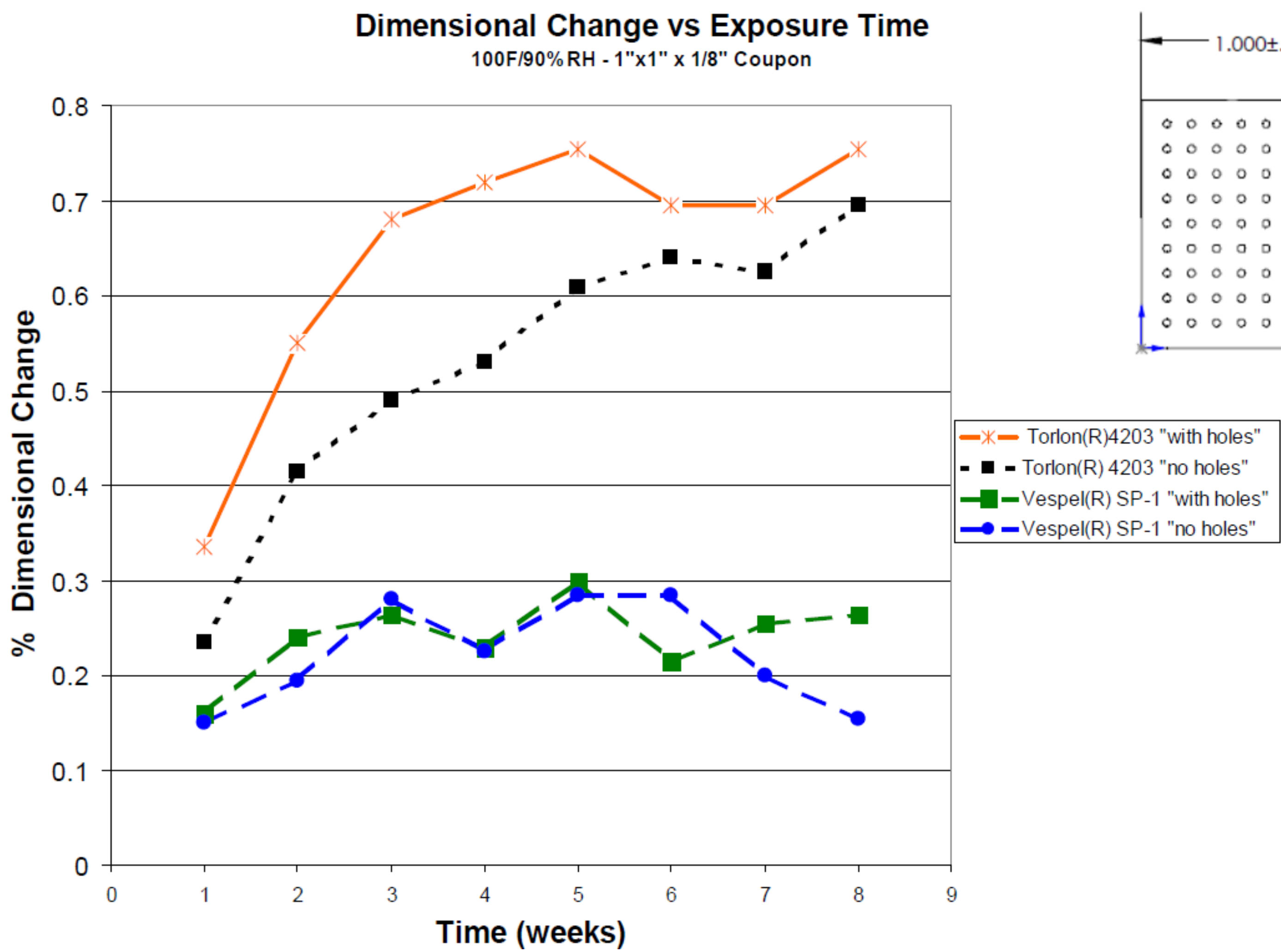
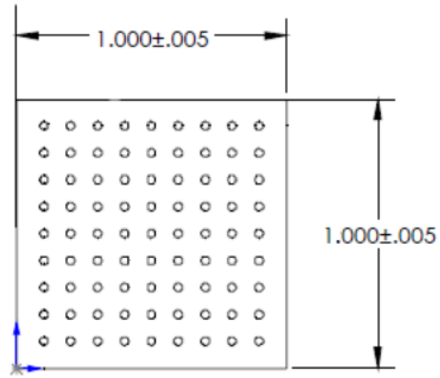
Dimensional Stability
Swelling / Softening Due to Water Absorption

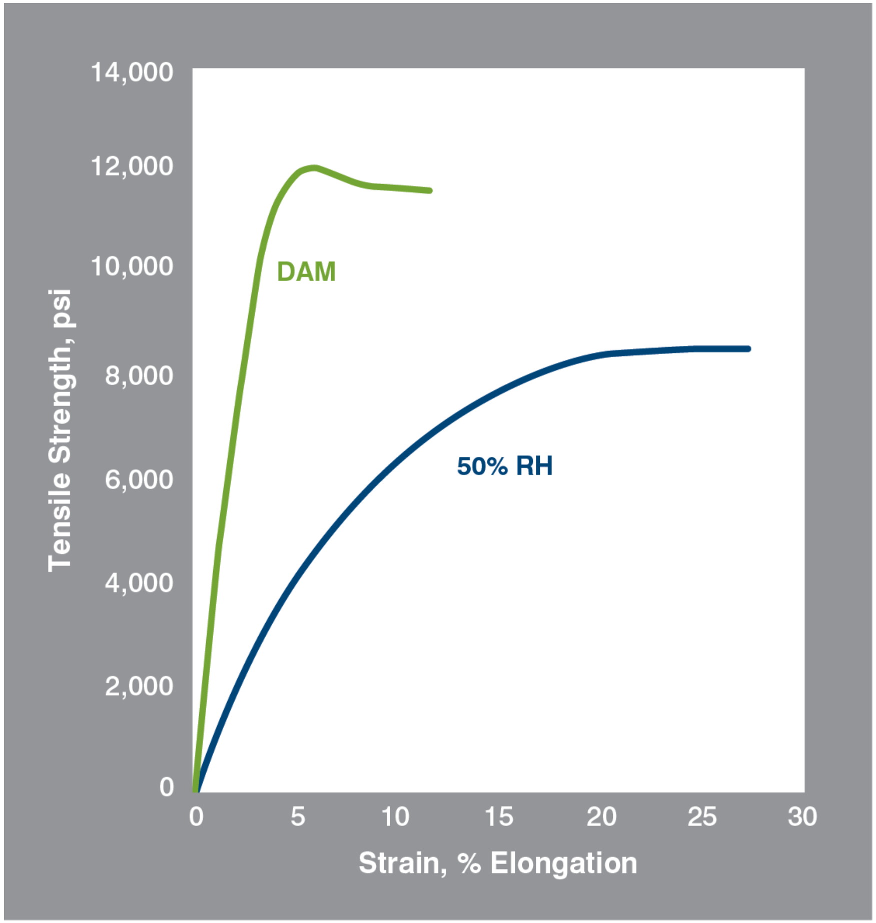




Source: Paul Kane, DuPont, 2004 – Semiconductor Test Sockets

Dimensional Stability
Swelling / Softening Due to Water Absorption

Stress-Strain Curves for Nylon 6/6 Dry-as-Molded and at 50% Relative Humidity



Source: DuPont™ Zytel® Minlon Design Guide – Module II

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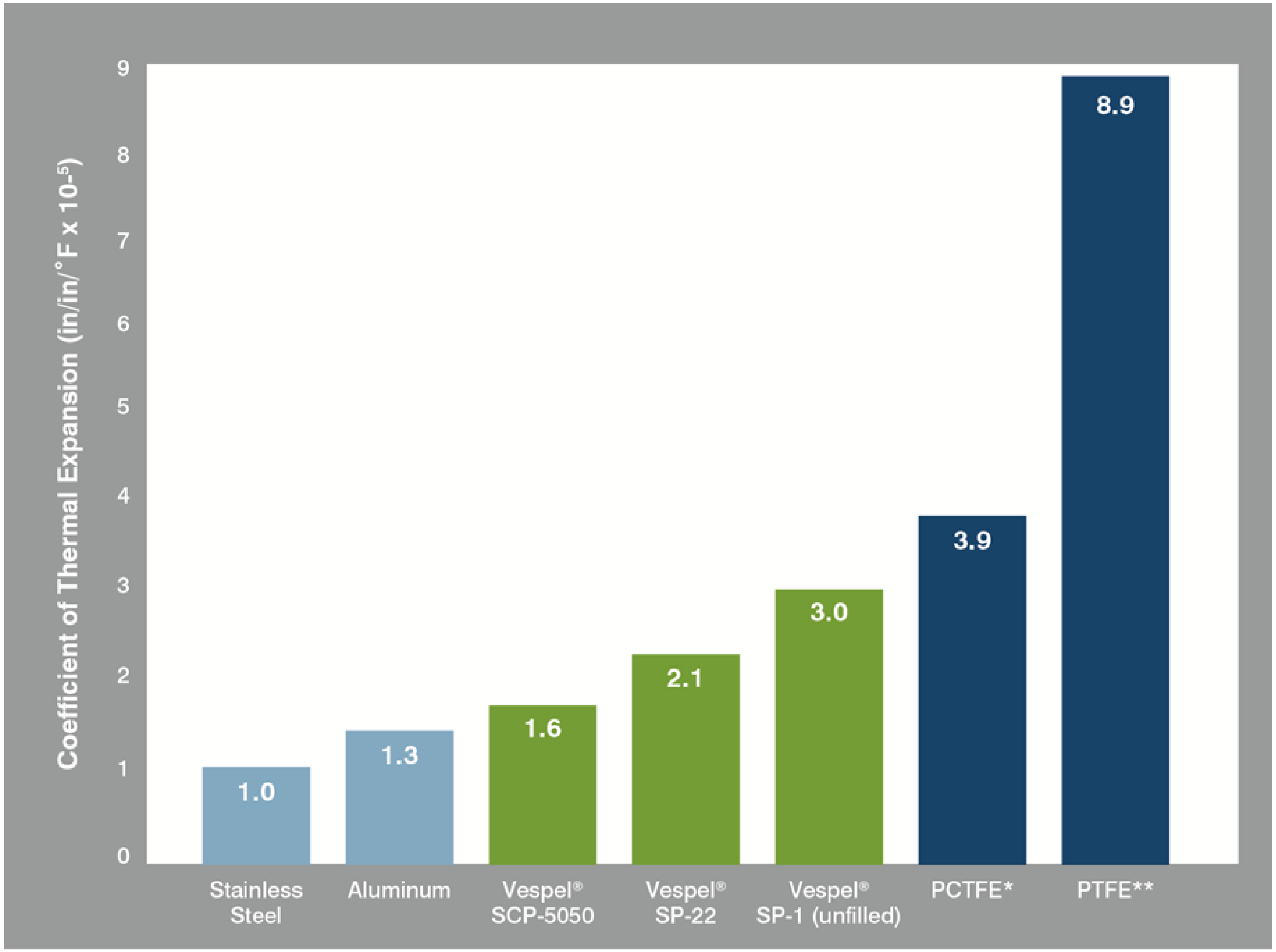
Thermal Expansion

CTE Mismatch

Thermal Expansion
(as close as possible to the mating metal surfaces)

Coefficient of Thermal Expansion (CTE) of Various Materials



Source: DuPont™, Properties of DuPont™ Vespel®

* Polychlorotrifluoroethylene
** Polytetrafluoroethylene

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Thermal Expansion of PTFE

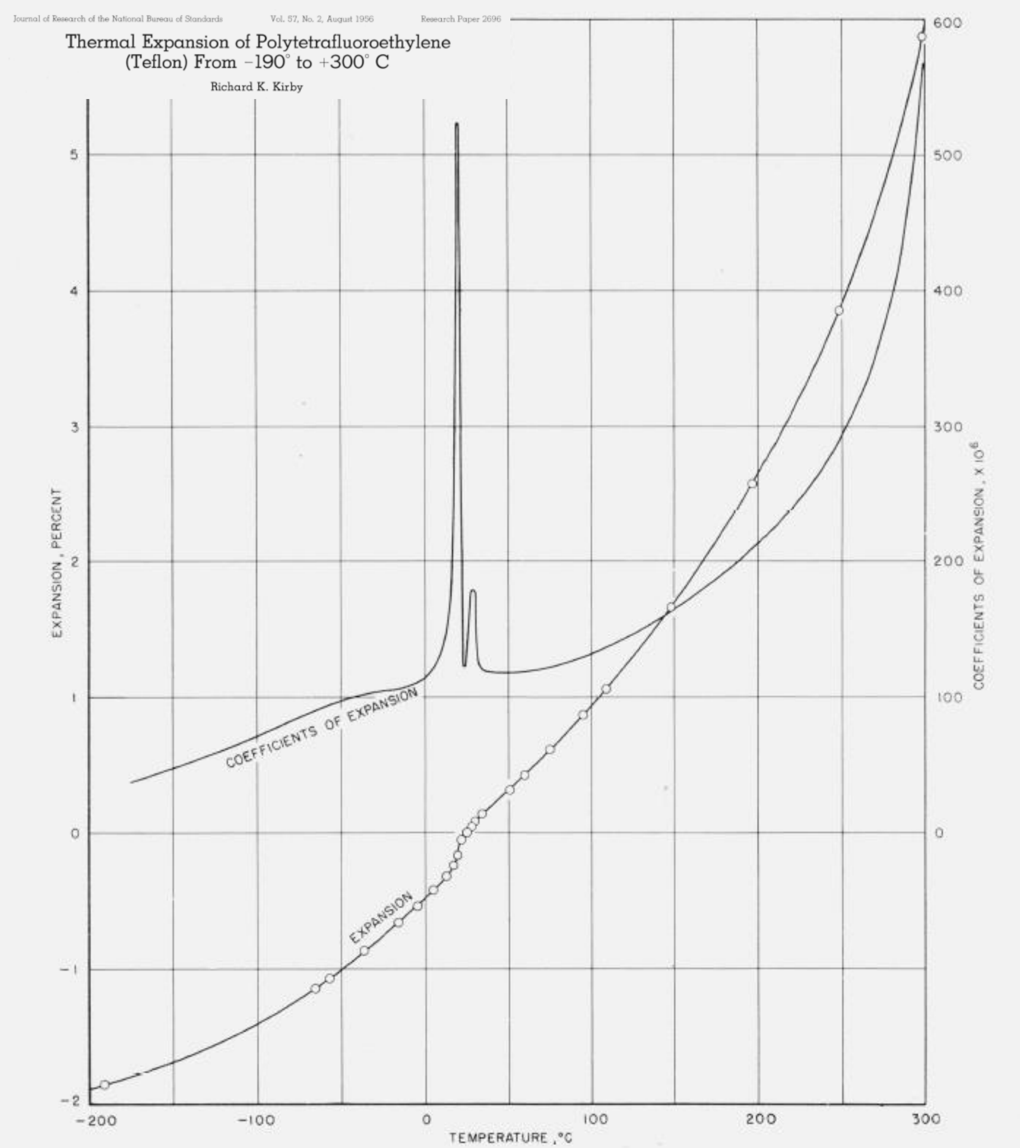
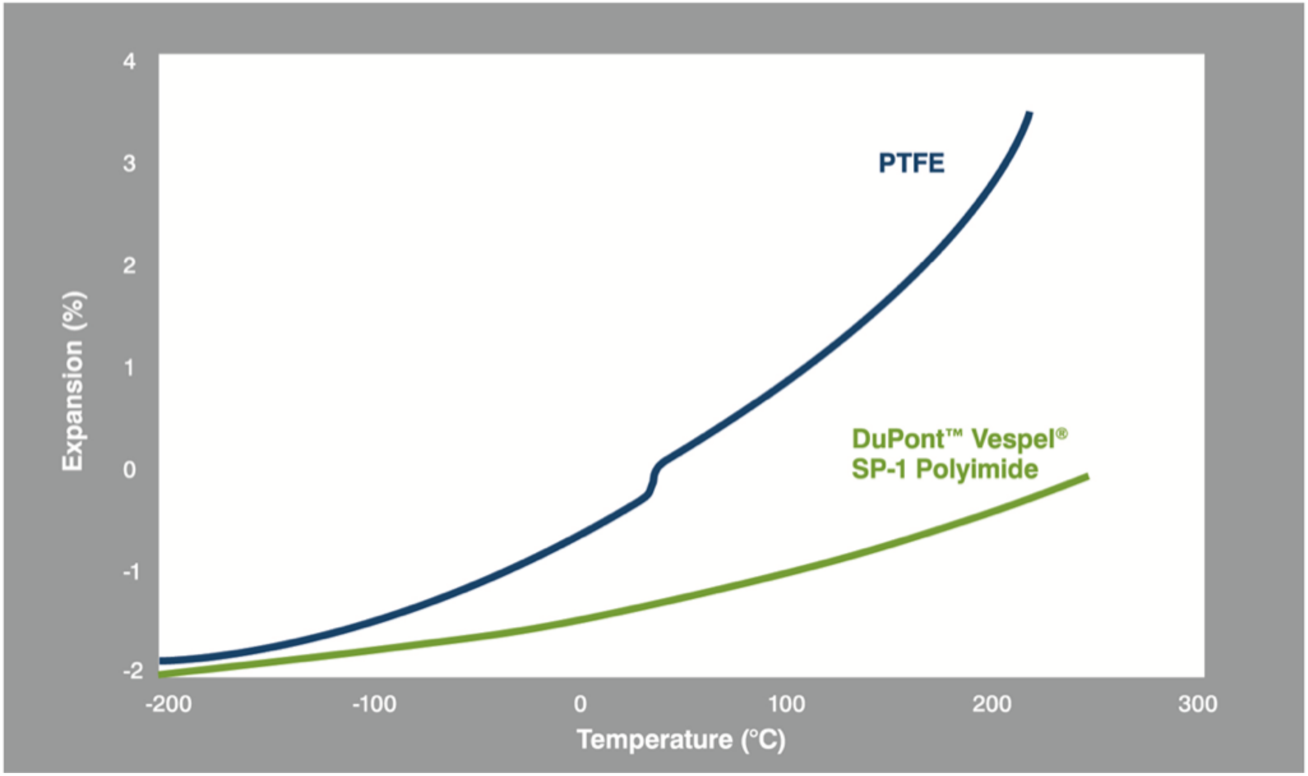


FIGURE 1. *Linear thermal expansion and coefficients of linear thermal expansion of annealed Teflon (sample A).*

Source: Richard Kirby, 1956

Thermal Expansion of PTFE and DuPont™ Vespel® SP-1

Thermal Expansion of PTFE and DuPont™ Vespel® SP-1 Polyimide



Source: Kirby, DuPont, McDonald and Rao

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Permeation Resistance of Various Fluoropolymers

Published data

Two definitive data tables have been published showing the permeation resistance of various polymers to specific gases and liquid:

Gas permeability of fluoropolymers*

Data based on 100 µm film thickness at 23°C. Method: ASTM D1434 for gases. Water vapor according to DIN 53122.

	PTFE	PFA	FEP	ETFE	CTFE	ECTFE	PVDF	PVF
Water Vapor g/m².d.bar	5	8	1	2	1	2	2	7
Air cm³/m².d.bar	2000	1150	600	175	x	40	7	50
Oxygen cm³/m².d.bar	1500	x	2900	350	60	100	20	12
Nitrogen cm³/m².d.bar	500	x	1200	120	10	40	30	1
Helium cm³/m².d.bar	3500	17000	18000	3700	x	3500	600	300
Carbon Dioxidecm³/m².d.bar	15000	7000	4700	1300	150	400	100	60

* Data published in 1980 Kunststoffe paper entitled Fluorocarbon Films–Present Situation and Future Outlook.
x = Not tested

Various liquid permeation rates in corrosive chemicals

(Source Southwest Research Institute) (test 30mil tubes static 28 days/672 hours)

Ambient Permeation Rates (g-cm/hr/m)						
	Chloroform	Methanol	Toluene	HCL	Hydrochloride	Bromine
Kynar Flex® 2800	$<1x10^{-5}$	$<1x10^{-5}$	$<1x10^{-5}$	$<1x10^{-5}$	$<1x10^{-5}$	$<1x10^{-5}$
Kynar Flex® 2850	$<1x10^{-5}$	$<1x10^{-5}$	0.00004	$<1x10^{-5}$	$<1x10^{-5}$	$<1x10^{-5}$
Kynar® 740	$<1x10^{-5}$	$<1x10^{-5}$	$<1x10^{-5}$	$<1x10^{-5}$	$<1x10^{-5}$	0.00026
66°C Permeation Rates (g-cm/hr/m)						
Kynar Flex® 2800	0.177716	0.16340	0.05972	0.01621	0.00347	
Kynar Flex® 2850	0.09386	0.11966	0.03488	0.01226	0.00258	
Kynar® 740	0.02142	0.00063	0.00966	0.02930	0.00170	

Source: Arkema Kynar® PVDF Permeation Brochure

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Purity

- Low leaching
- Low outgassing
- Low particulate contamination
- Agency Compliance (FDA, USP Class VI, etc.)

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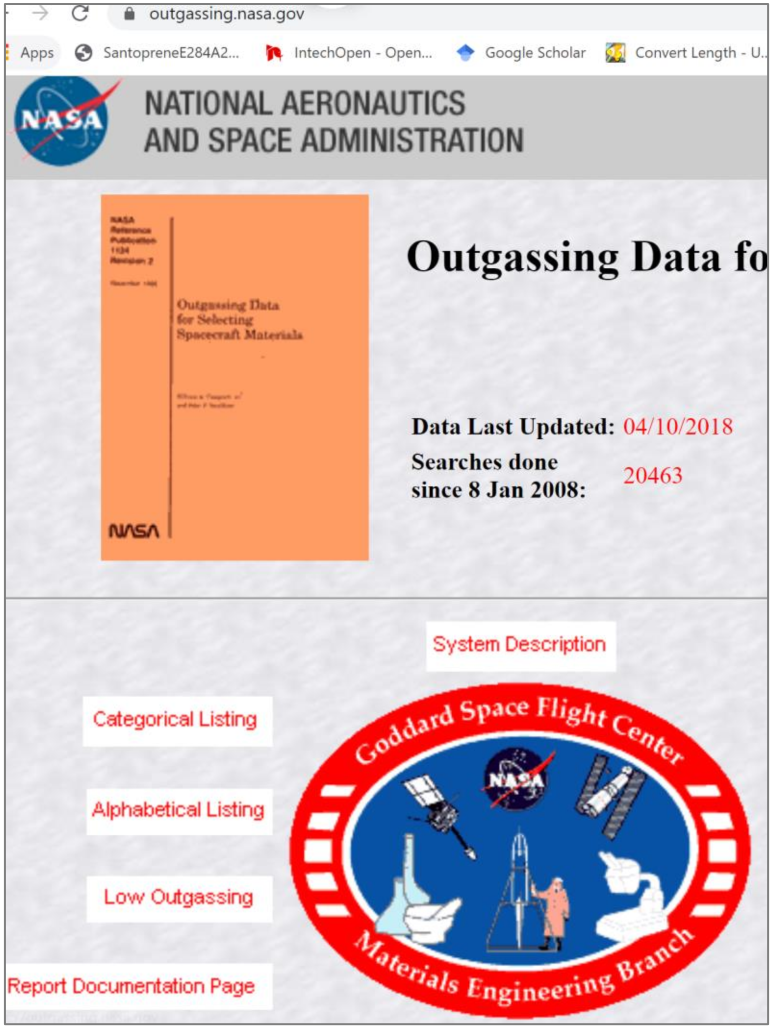
Purity



BioPharm International DECEMBER 2002

Evaluation of Extractables from Product-Contact Surfaces

John Bennan

Materials Expected to Meet or to Fail Acceptance Criteria	
Materials Expected to MEET the listed acceptance criteria when extracted at 3,000 cm^2/L, at 70 °C, for 24 hours in purified water.	**Materials Expected to FAIL** the listed acceptance criteria when extracted at 3,000 cm^2/L, at 70 °C, for 24 hours in purified water.
Fluorinated ethylene propylene (FEP)	Amorphous nylon (other than filter membranes)
Perfluoroalkoxy resin (PFA)	Neoprene
Peroxide cured, postcured EPDM	Peroxide cured, nonpost cured EPDM
Platinum cured silicone	PVC plasticized with DEHP
Polycarbonate	Rigid PVC with organotin stabilizers
Polyester	Sulfur-cured elastomers of all types including natural rubber, Buna N (nitrile), EPDM, and styrene-butadiene
Polyethylene	Viton, lead oxide filled
Polymethylpentene (TPX)	
Polypropylene	

Source: Bennan, 2002

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Resistance to Stress Relaxation

Resistance to Stress Relaxation

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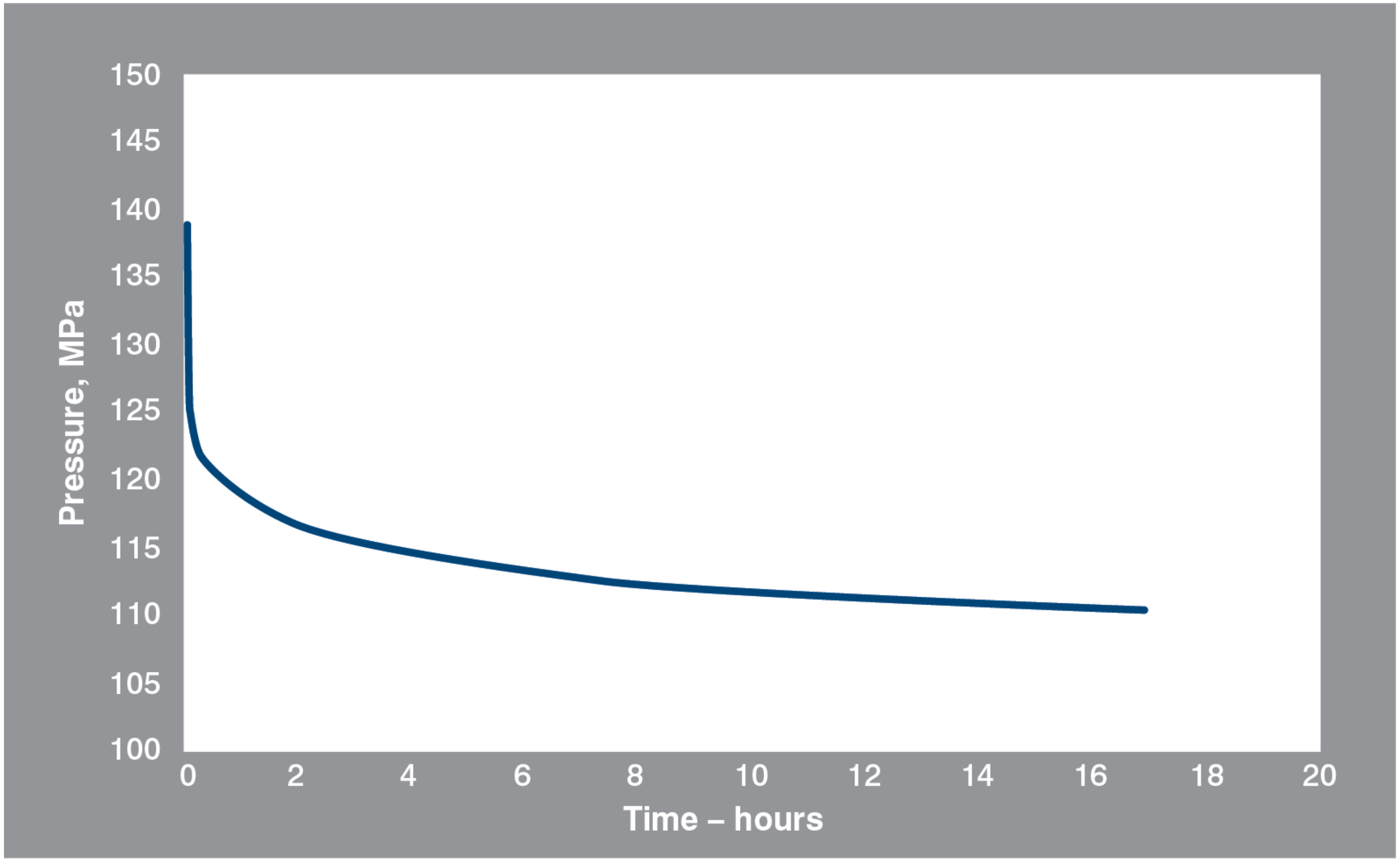
Stress Relaxation

Stress Relaxation of DuPont™ Vespel® SP-1 at 68° F
Pressure vs. Time at 15% Constant Compression



Source: McDonald and Rao, 1987

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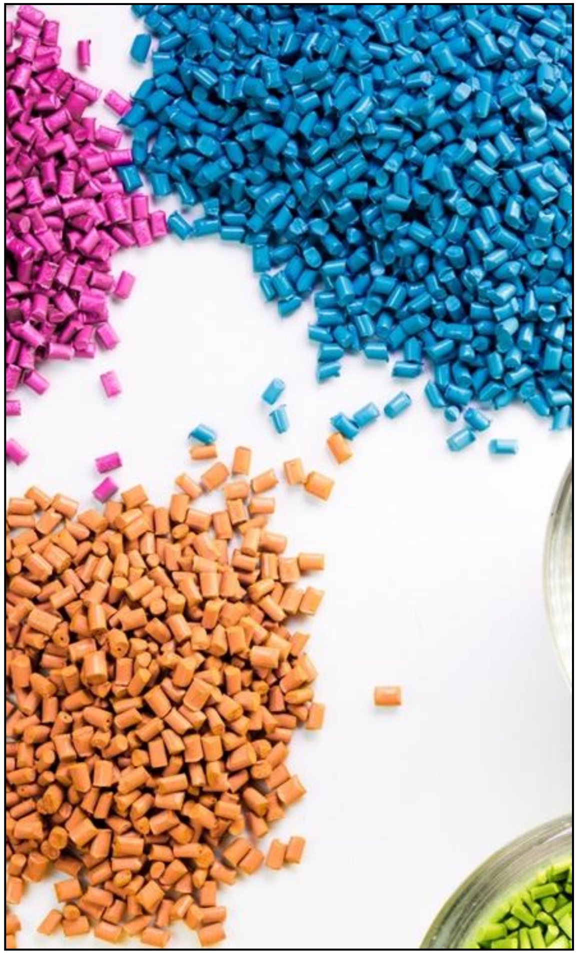
Correct Coefficient of Friction to Achieve the Desired Actuation Torque (without lubrication)

- Low friction without external lubrication
- Low wear rate
- Low wear on mating metal parts

Friction and Wear Additives to Control Actuation Torque

- "Wear" is a complex behavior. It is a system property, not a material property.
- The COF of base polymers varies considerably
- Additives can reduce COF, improve wear, and increase limiting PV
- Mating metal surface is very important
  - Chemistry
  - Hardness
  - Surface roughness



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Environmental Factors that Affect Friction and Wear Additives

- Temperature (cryogenic to elevated temperatures)
- Water / humidity
- Vacuum

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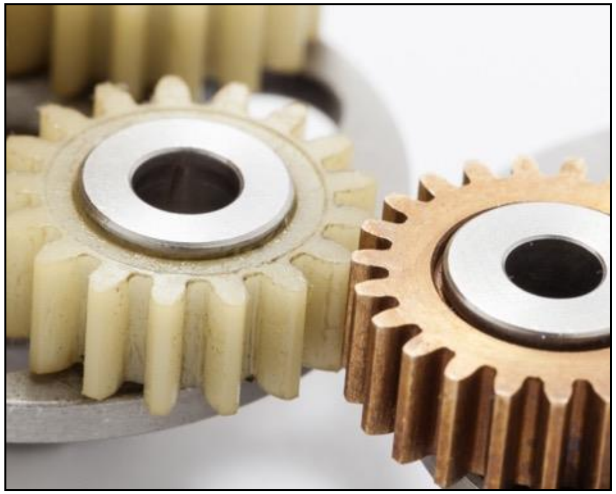
Friction and Wear Additives

- MoS2 -
  makes nylon harder and more crystalline.
- PTFE -
  creates a wear film on the mating metal surface.
- Oil -
  separates sliding surfaces with a liquid film.
- Graphite -
  molecules slide over each other in humid environments. Is not good for dry or vacuum environments.
- Carbon fibers -
  lowers friction and increases thermal conductivity.



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Effect of PTFE Additives on Sliding Wear Against Hardened Steel

Material:	Specific Wear Rate ($x10^{-15}m^3N^{-1}m^{-1}$)	Coefficient of Friction
Nylon 6/6	15.9	0.57
Nylon 6/6 with 15% PTFE	0.6	0.14
Acetal	2.1	0.45
Acetal with 15% PTFE	0.4	0.22

Source: J. Mens, 1991

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Deposition of a Polymer Film on the Mating Metal Surface

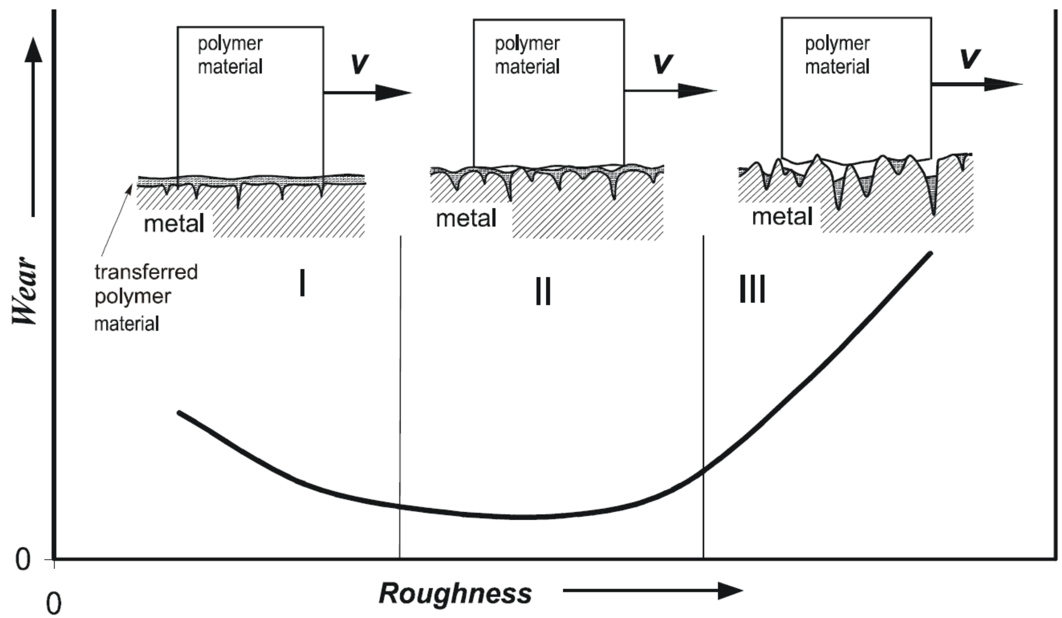
ARCHIVES OF CIVIL AND MECHANICAL ENGINEERING

Vol. VII 2007 No. 4

The Mechanism of Tribological Wear of Thermoplastic Materials

W. WIELEBA

Figure 3 shows differences in the formation process and retaining of a polymer layer depending upon the surface roughness of the steel element.



Source: Wieleba, 2007

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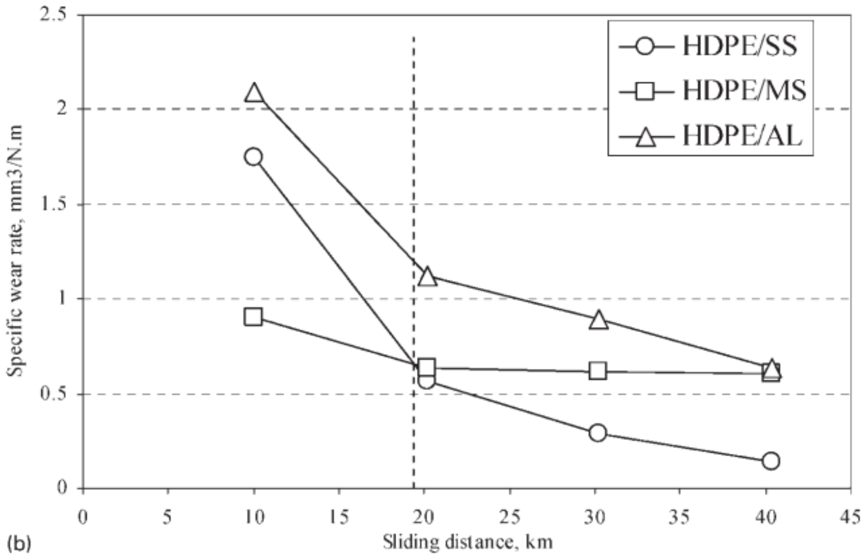
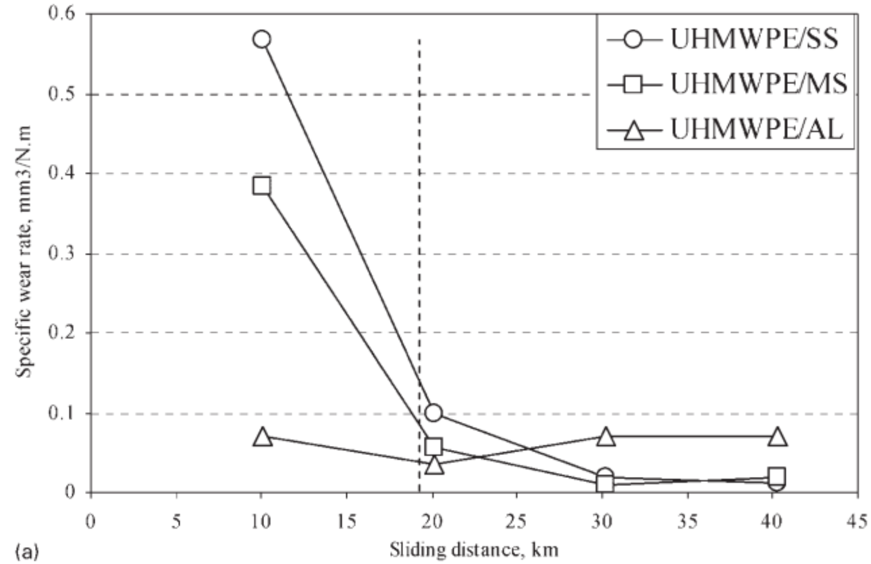
Sliding Wear of HDPE and UHMW-PE Against Stainless Steel, Mild Steel, and Aluminum





Note the importance of counterface metal and the molecular weight of the polymer.

Source: Belal Yousif, 2010

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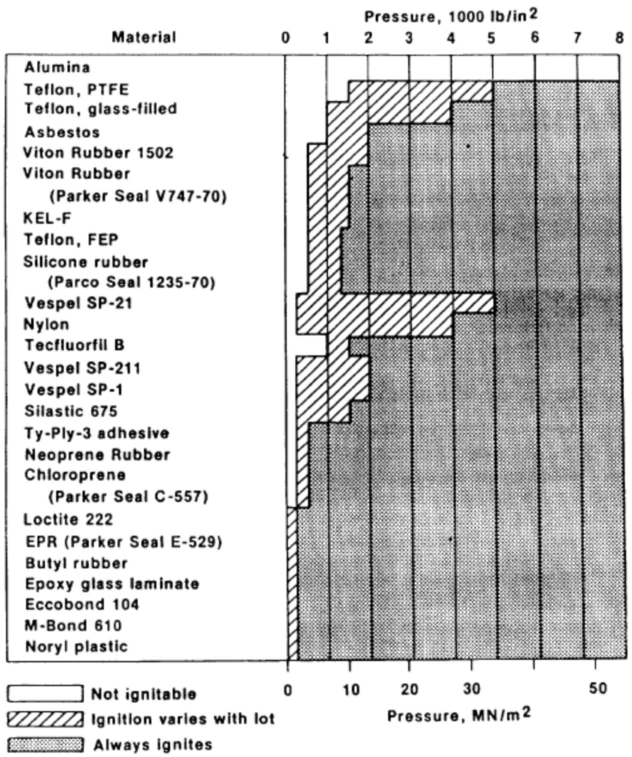
Oxygen Compatibility/Flammability

Final Report Oxygen Materials Compatibility Testing



Source: Schoenman, 1989

Liquid Oxygen Compatibility of Materials for Space Propulsion Needs

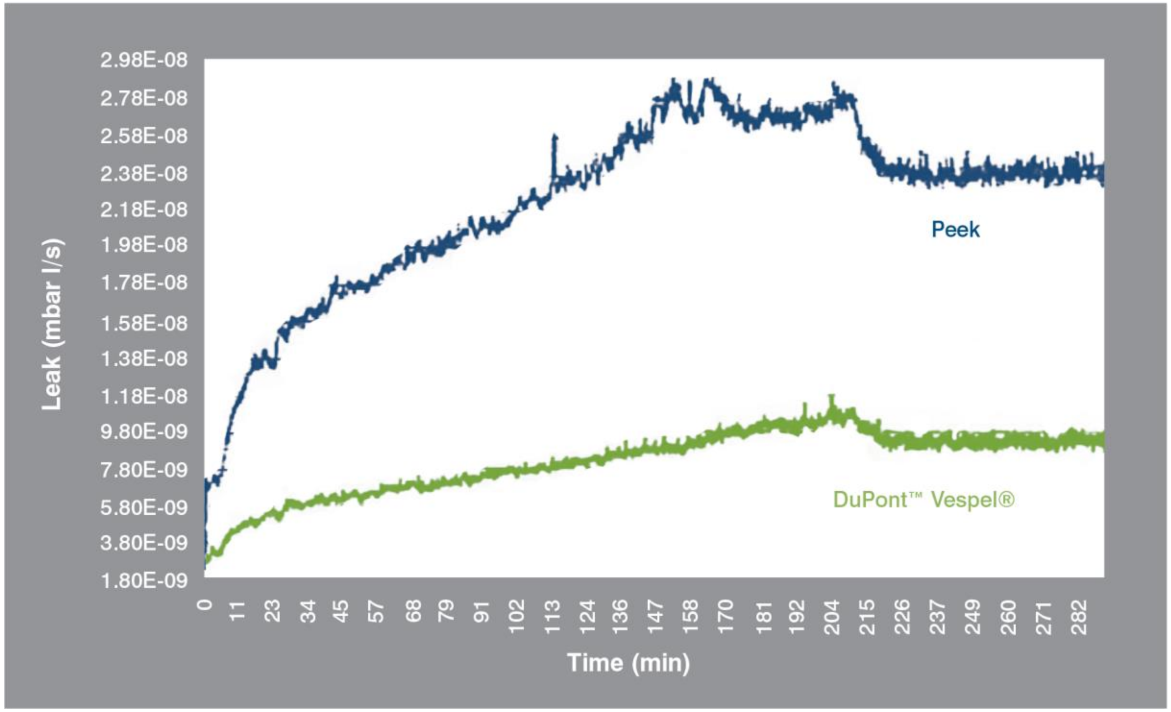
Table 1: Bomb test results

Materials	Auto ignition temperature (°C)
Polyethylene	201
PVC	259
Nylon 66	202
Nylon 66 + 30 % glass fibres	272
Polyacetal DELRIN 100AF	209
Polyacetal DELRIN 500CL	196
PFA	458
PTFCE	429
PTFCE 302	440
Polyimide VESPEL SP-3	366
Polyimide VESPEL SP-21	366
Bronze sintered PTFE	>500

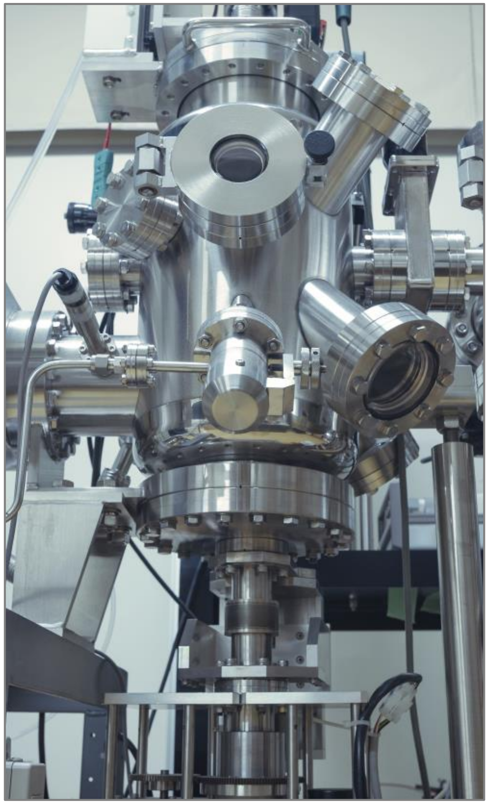
4TH EUROPEAN CONFERENCE FOR AEROSPACE SCIENCES

Source: Bozet, 2011

Vacuum Compatibility



Source: Adapted from Murari and Barzon



Note: Vacuum also affects friction and wear performance.

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Operating Temperature

- Change in modulus
- Change in elongation
- Creep behavior
- Thermal expansion
- Degradation

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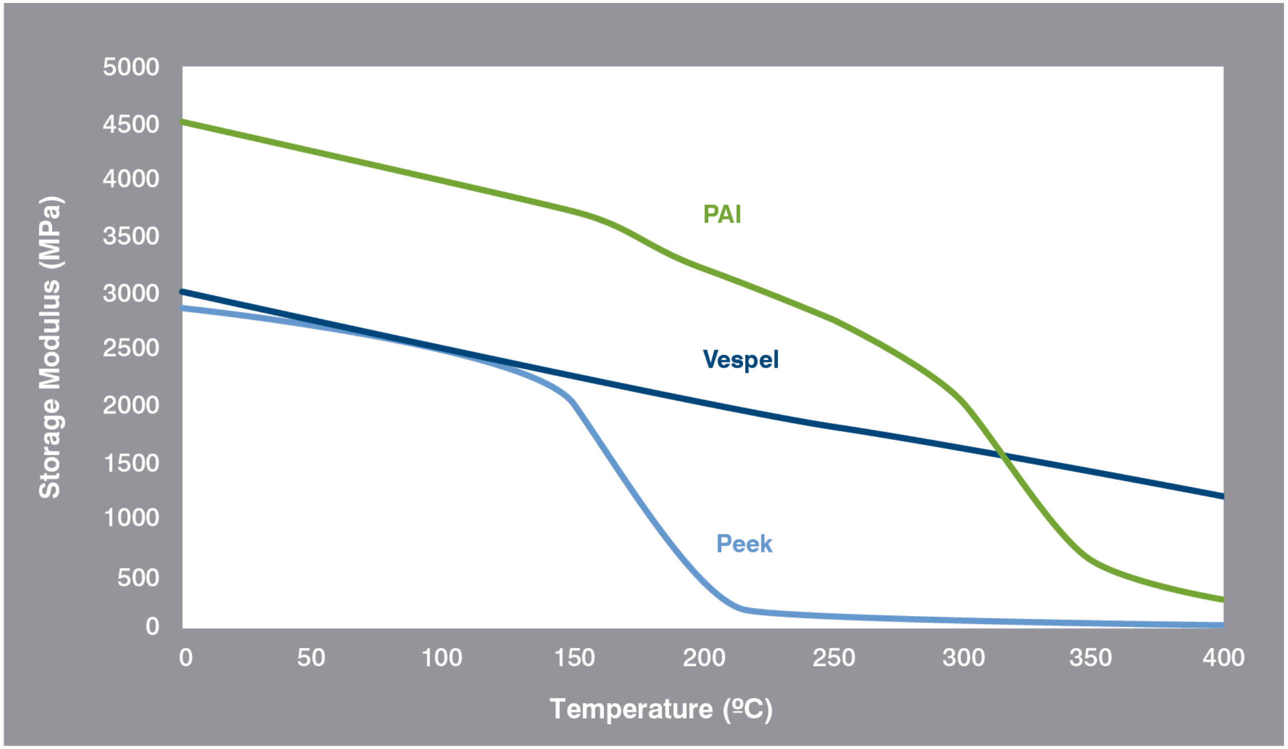
Modulus Changes as a Function of Temperature

Flexural Stiffness by Dynamic Mechanical Analysis
DuPont™ Vespel® SP-1, PEEK, PAI



Source: Adapted from Parvaiz, 2010 and Kane, 2004.

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Thermal Degradation

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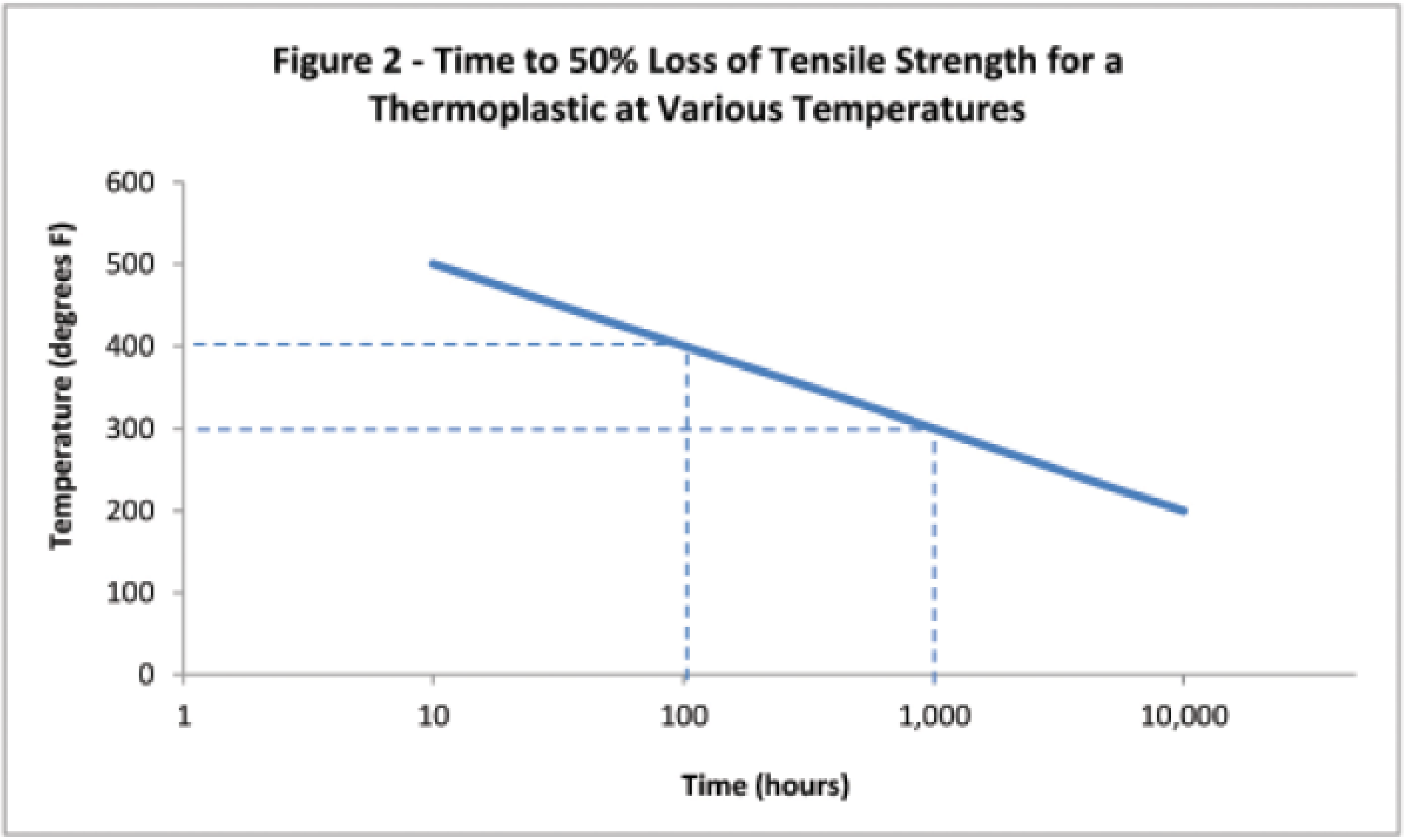
Thermal Degradation

Time to 50% Loss of Tensile Strength for a Thermoplastic at Various Temperatures



Source: Hechtel, 2014

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Cold Temperatures

- Thermal conductivity
  Low thermal conductivity sometimes required – insulators, cryogenic fixtures
- Hardness, strength and modulus increase
  Conformability is important for seals
- CTE mismatch between polymer and mating metal part
- Loss of elongation/toughness
- Decreased coefficient of friction

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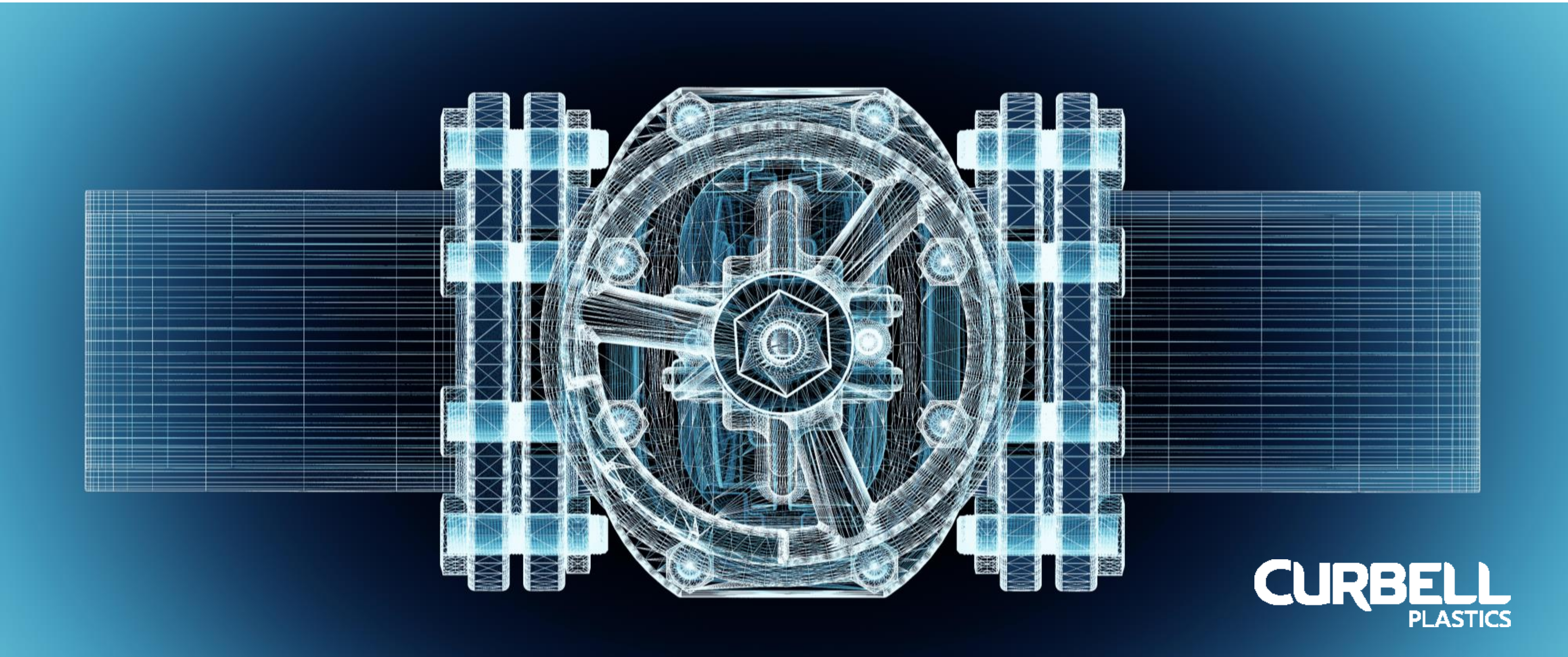
Assuring Consistent Quality of Plastic Materials



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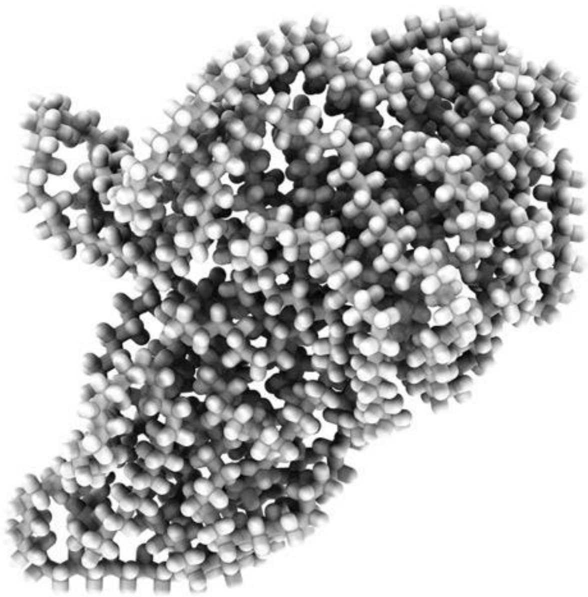
Significance of Molecular Weight

- Improves impact resistance
- Lowers brittleness temperature
- Increases melt viscosity
  - Ketchup ⟷ Tomato Paste
  - Limits processability at both the upper and lower end of the range
- Improves long-term performance
  - Fatigue (also affected by surface finish and microheterogeneity)
  - ESCR (environmental stress crack resistance)
  - Chemical resistance
  - Wear performance



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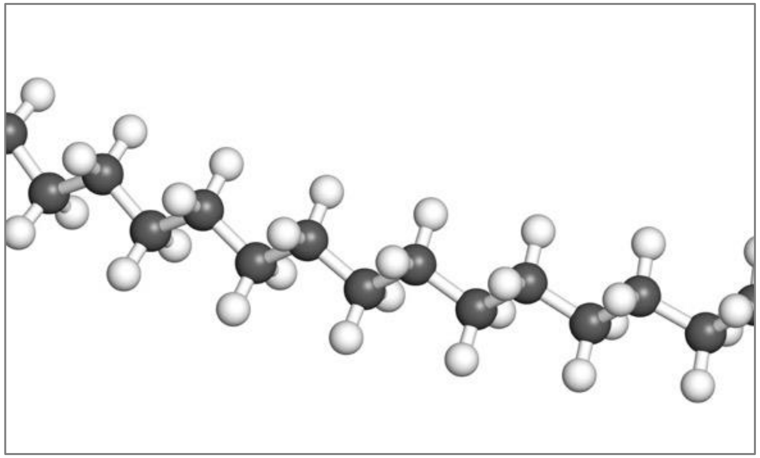
Significance of Molecular Weight

- Some degradation through normal processing
- UV light or other radiation
- Chemical attack
- Hydrolytic degradation
  - Exposure to steam
  - Improper drying of resin
- Thermal degradation
  - Excessive temperature during processing
  - Multiple heat histories, use of regrind
  - Long-term exposure to elevated temperatures
- Use of incompatible colorants



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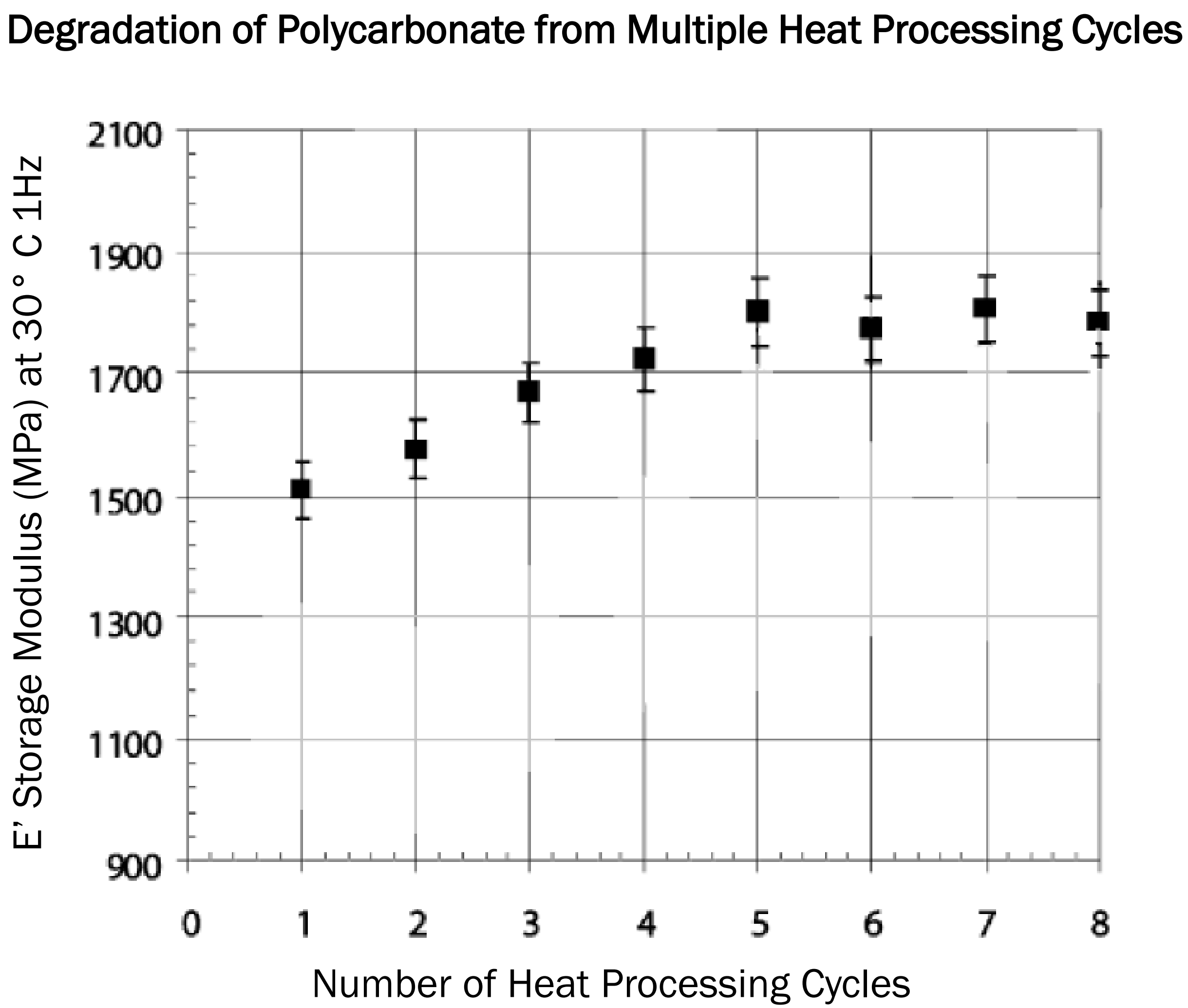
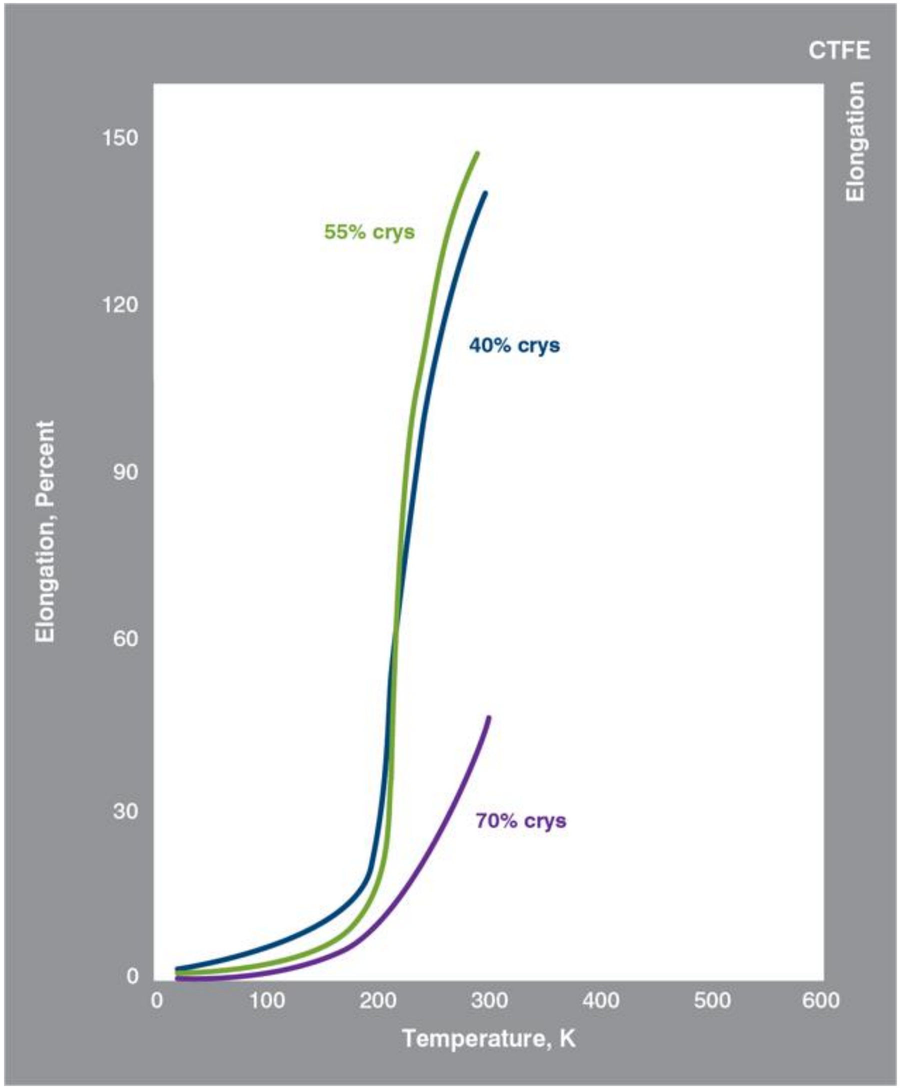
Effect of Regrind



Source: Adapted from Feller, 2003

Effect of Crystallinity

Crystallinity of PCTFE



Source: Schram, 1973

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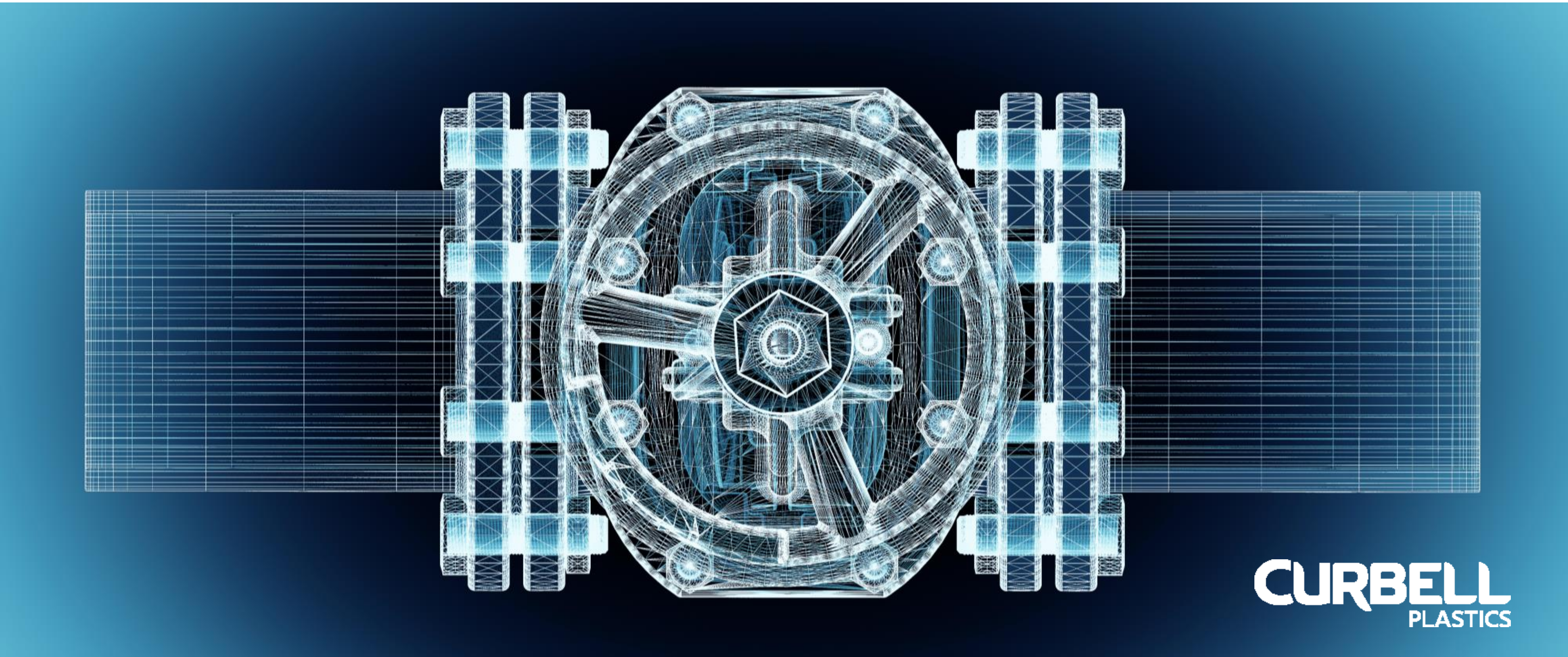
Plastic Materials for Valves and Regulators



PVC

- Advantages
  - Inexpensive
  - Easy to weld via thermoplastic welding and easy to bond with solvent cements
  - Moderately strong and stiff

- Limitations
  - Limited resistance to aggressive chemicals
  - Somewhat brittle
  - Not suitable for elevated temperature applications

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High Density Polyethylene (HDPE)

- Advantages
  - Inexpensive
  - Outstanding chemical resistance
  - Easy to weld via thermoplastic welding

- Limitations
  - Relatively low strength and stiffness
  - High CTE makes it difficult to hold tight tolerances
  - Not suitable for elevated temperature applications
  - Very difficult to bond with adhesives or solvent cements

- Properties vary based on density and molecular weight

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Polypropylene

- Advantages
  - Inexpensive
  - Outstanding chemical resistance
  - Easy to weld via thermoplastic welding
  - Slightly stronger and stiffer than HDPE
  - Slightly higher operating temperature than HDPE

- Limitations
  - Relatively low strength and stiffness
  - Less ductile than HDPE
  - Not suitable for elevated temperature applications
  - Very difficult to bond with adhesives or solvent cements

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Acetal (including Delrin®)

- Advantages
    - Easy to machine
    - Stronger and stiffer than polyethylene or polypropylene
    - Excellent friction and wear characteristics
    - PTFE filled grades available

- Limitations
    - Moderately high CTE makes it challenging to hold tight tolerances

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Nylon

- Advantages
  - Can be cast into large sheets, rods, tubes, and near net shapes
  - Available in many different colors and grades
  - Good friction and wear characteristics
  - Stronger than polyethylene, PP, or acetal

- Limitations
  - High water absorption makes it challenging to hold tight tolerances
  - Becomes softer when it absorbs moisture

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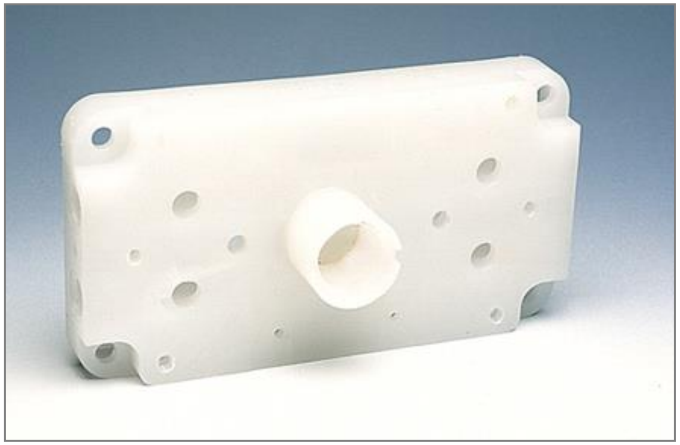
Fluoropolymers

- Good chemical resistance
- High purity
- Some have great stain resistance
- Stable at elevated temperatures
- Unfilled PTFE has poor creep characteristics and high CTE. Can use fillers to improve these characteristics.
- Unfilled PTFE can have porosity issues (Note: TFM has low porosity)
- Melt processable fluoropolymers vary based on mechanical properties, service temperature, electrical properties, permeability, and cost.



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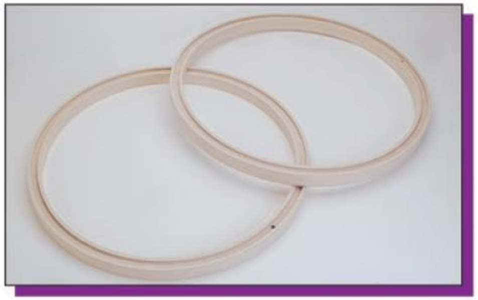
Fluoropolymers

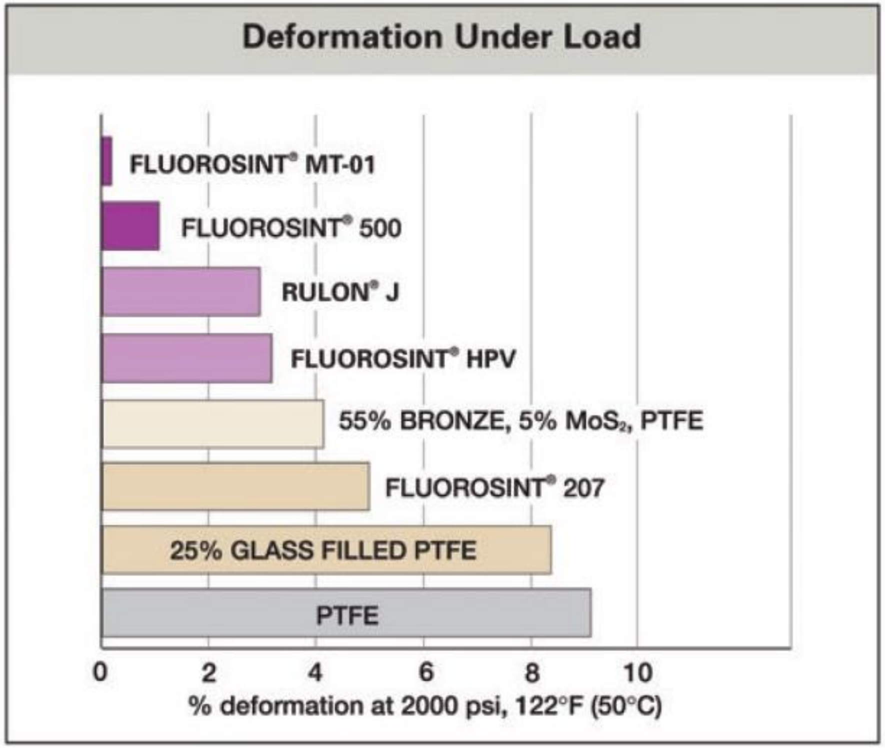
Fluoropolymer	Starting Year	Melting temperature (°C)	Tensile Modulus (MPa)	Break Elongation (%)	Dielectric Strength (kV/mm)	Appl. Temp (°C)
PTFE	1947	317–337	550	300-550	19.7	260
PCTFE	1953	210-215	60-100	100-250	19.7	200
FEP	1960	260-282	345	~300	19.7	200
PVF	1961	190-200	2000	90-250	12–14	110
PVDF	1961	155–192	1,040-2,070	50-250	63–67	150
ECTFE	1970	235–245	240	250-300	80	150
PFA	1972	302–310	276	~300	19.7	260
ETFE	1973	254–279	827	150-300	14.6	150
THV	1996	145–155	82–207	500-600	48–62	93

Source: Teng, 2012

Fluorosint®

- Family of filled PTFE materials manufactured by Mitsubishi Chemical Advanced Materials
- Stronger and stiffer than PTFE
- Better dimensional stability and creep resistance than PTFE
- FDA compliant grades available





Source: Mitsubishi Chemicals Advanced Materials.
Fluorosint® PTFE Family of Advanced Fluoropolymer Materials

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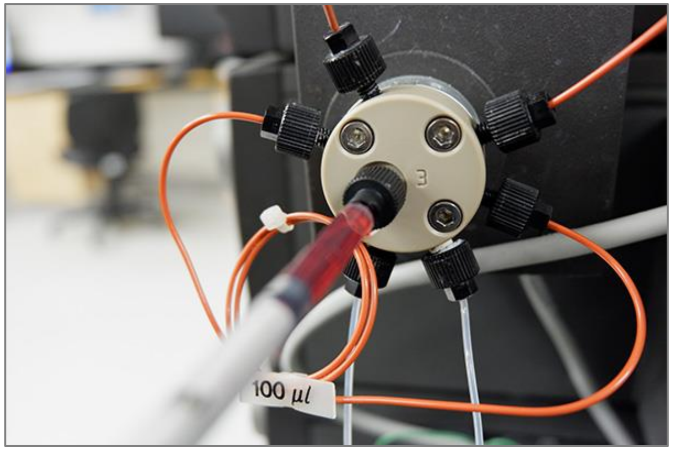
PEEK

- Good mechanical properties throughout a broad temperature range
- Good chemical resistance including resistance to steam
- High purity
- FDA compliant grades available
- Stain resistant
- Dimensional stability
- Glass filled and friction and wear grades available
- Relatively expensive



Spin Molded PEEK Manufactured by Ensinger

- Better Yields
- Lower Stress (especially important for glass filled grades)
- Higher Elongation

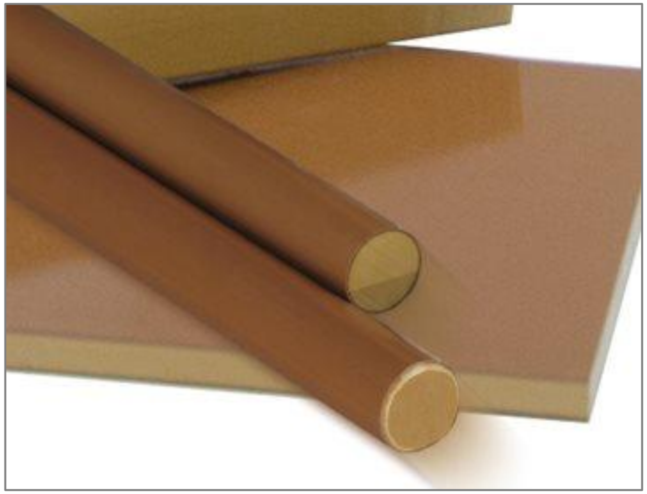
Compression Molded Tube

Spin Molded Tube

CURBELL PLASTICS

Torlon® PAI

- Advantages
  - Very high strength and stiffness
  - Higher operating temperature than PEEK
  - Filled grades available
- Limitations
  - Expands in humid conditions
  - Very expensive
  - Limited resistance to steam



CURBELL PLASTICS

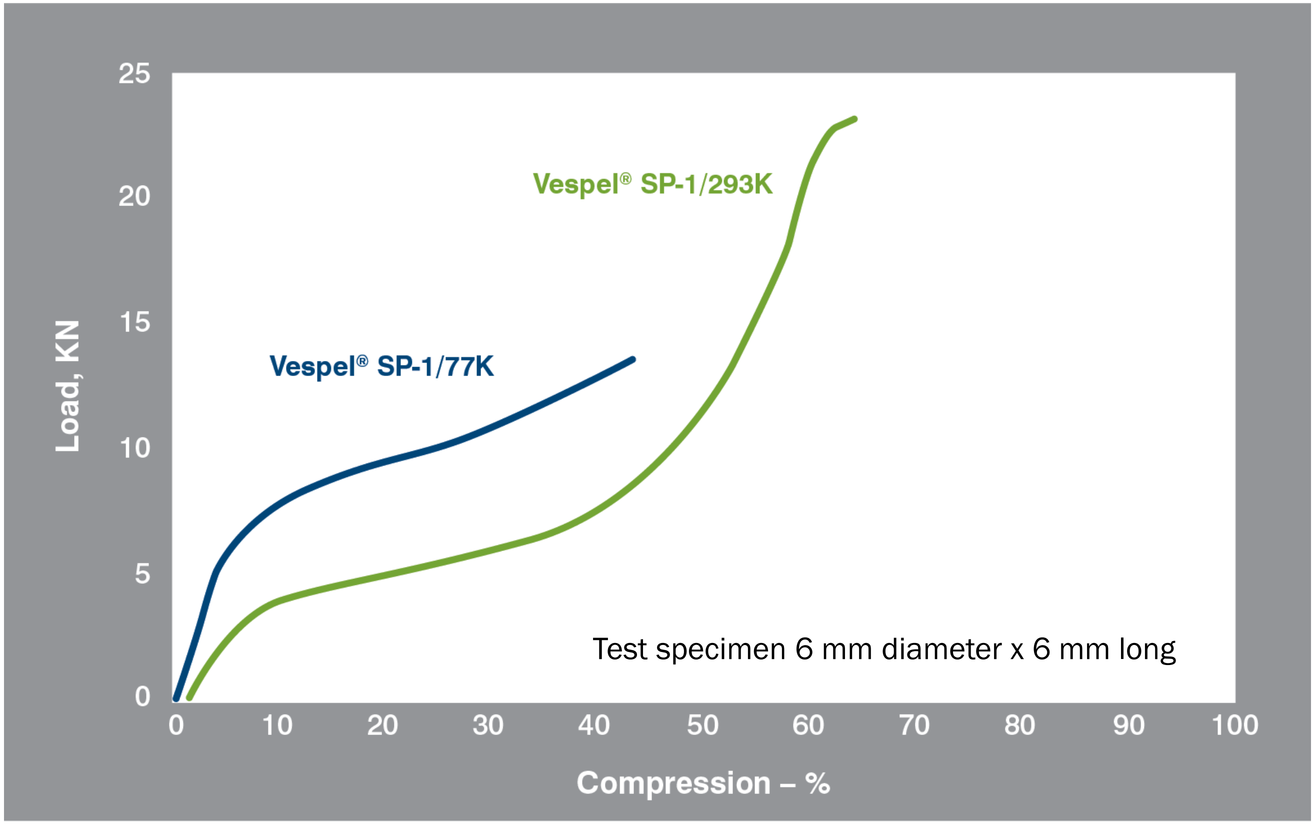
DuPont™ Vespel® Polyimide

- Advantages
  - Good mechanical properties throughout a broad temperature range
  - Higher operating temperature than PEEK or Torlon®
  - Dimensional stability - CTE, creep, stress relaxation
  - Outstanding friction and wear properties (certain grades)
- Limitations
  - Very expensive
  - Limited resistance to steam
- Very important to have authentic material

CURBELL PLASTICS

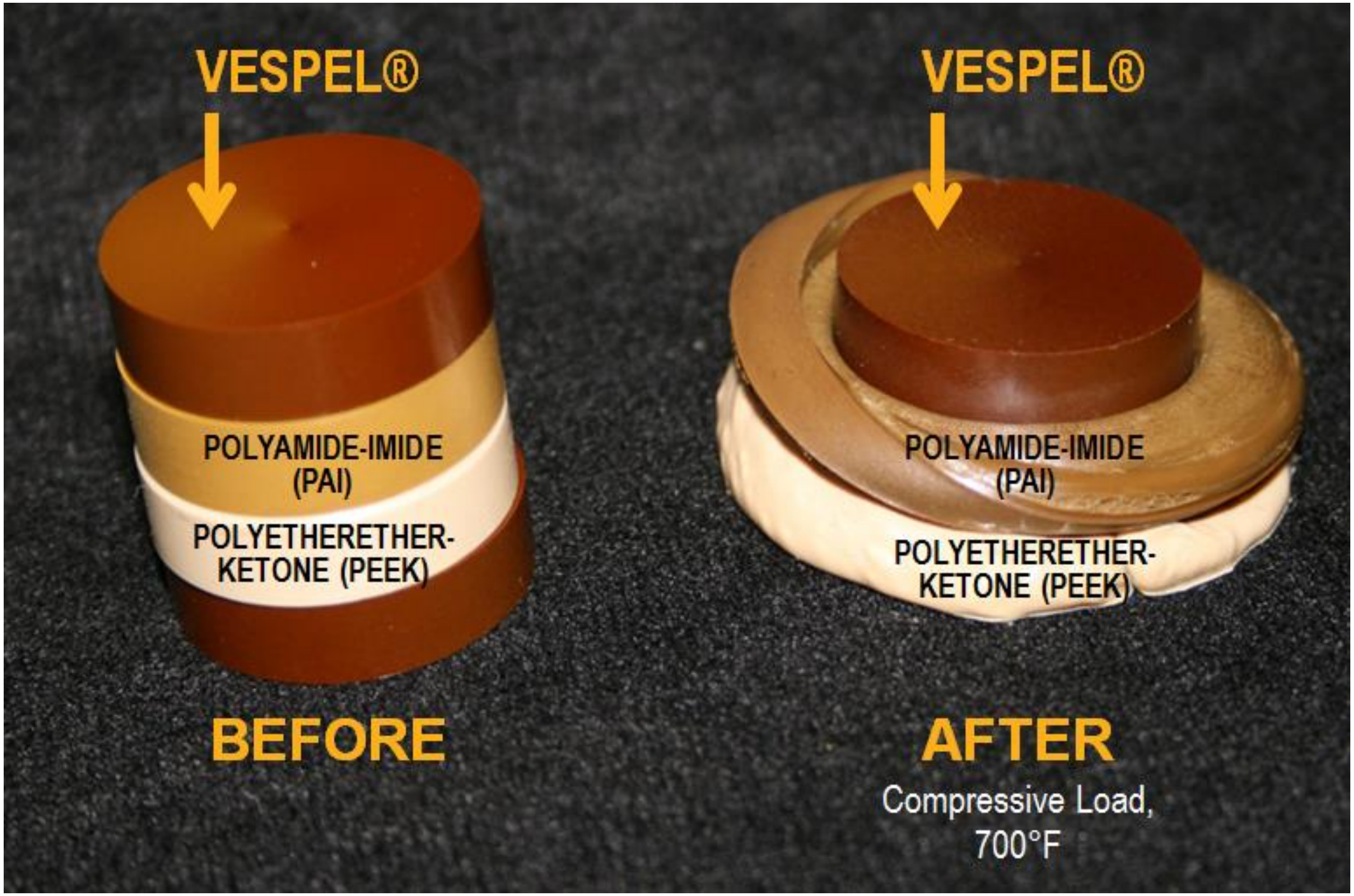
Low Temperature Performance of DuPont™ Vespel® Polyimide

Compressive Stress and Compressive Strain of Vespel® SP-1 at 77K and 293K



Source: McDonald and Rao (1987)

High Temperature Performance of DuPont™ Vespel® Polyimide



Case Study - Thermal Stability of DuPont™ Vespel® Polyimide

Dynamic Mechanical Analysis (DMA) to Help Characterize Vespel SP-211 Polyimide Material for Use as a 750°F Valve Seal on the Ares I Upper Stage J-2X Engine

Source: Wingard, 2013

Thank you for your time today! Questions?

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