

12 High-Temperature/High-Performance Polymers

This chapter covers several high-temperature, high-performance plastics. They might be classified or been appropriate to include in another chapter, but they are grouped in this chapter because of their performance levels.

12.1 Polyaryl Ether Ketone

Polyketones or polyaryl ether ketones (PAEKs) are a family of semicrystalline thermoplastics with high-temperature stability and high mechanical strength. Some of the commercial plastics that fall within this family include those listed with their structures in [Table 12.1](#).

The good strength of the semicrystalline aromatic polymers is maintained even at high temperatures. In addition, PAEK materials show very good impact strength at low temperatures, high mechanical fatigue strength, and a very low tendency to creep as well as good sliding and wear properties. The chemical resistance is also very good. Due to their unusual characteristics, PAEKs are used for particularly demanding applications.

- High mechanical strength, even at high temperatures
- Very good impact strength
- Low tendency to creep
- Good chemical resistance
- Good sliding and wear properties
- Low-moisture absorption
- Very good dielectric strength, volume resistivity, and tracking resistance
- Good radiation resistance
- Poor resistance to weathering

Weathering Properties

Victrex PEEK, like most linear polyaromatics, suffers from the effects of ultraviolet (UV) degradation during outdoor weathering. However, testing has shown this effect to be minimal over a 12-month period for both natural and pigmented moldings. In more extreme weathering conditions, painting or pigmenting will protect the polymer from excessive property degradation.

Manufacturers and trade names: PEEK: Victrex PLC Victrex and APTIV, Greene, Tweed & Co. Arlon, Solvay Advanced Polymers GATONE and KetaSpire; **Modified PEEK:** Solvay Advanced Polymers AvaSpire; **PEKK:** Polymics, LTD. Arylmax K, Arkema Kepstan; **PEKEEK:** Victrex PLC Victrex ST; **PEK:** Victrex PLC Victrex HT; **PAEK** (unspecified): Solvay Advanced Polymers AvaSpire, Polymics, LTD. Arylmax P

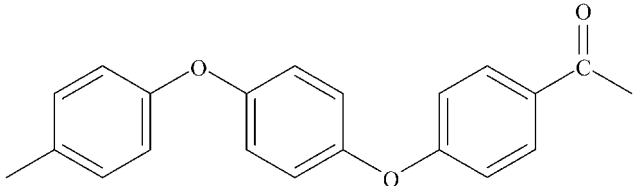
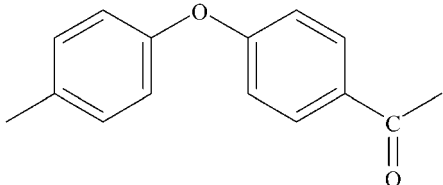
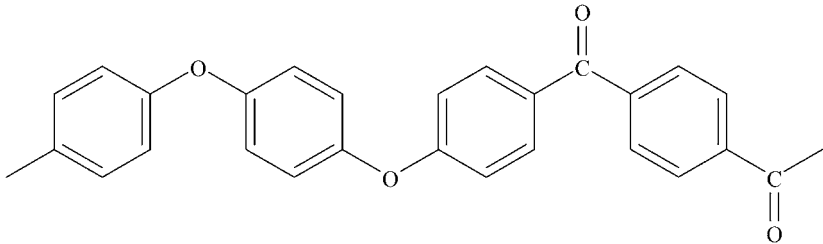
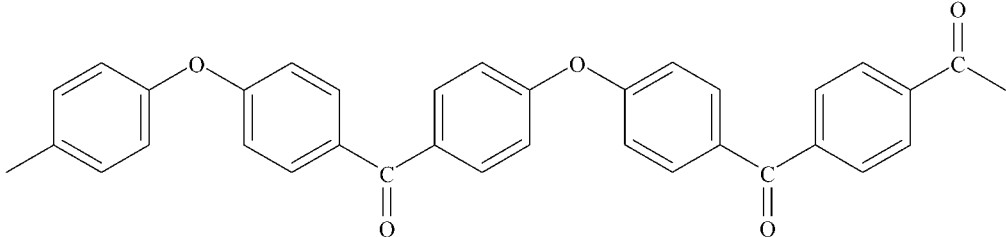
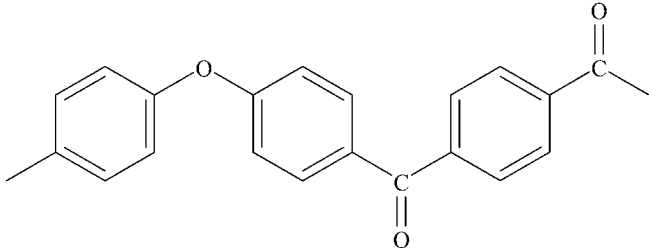
Applications and uses: Medical implants, sealing rings, bearings, piston parts, pumps, high pressure liquid chromatography columns, compressor plate valves, and cable insulation

The data for PAEK based plastics are in [Tables 12.2–12.4](#) and [Fig. 12.1](#).

12.2 Polyphenylene Sulfide

Polyphenylene sulfide (PPS) is a semicrystalline material. It offers an excellent balance of properties, including high-temperature resistance, chemical resistance, flowability, dimensional stability, and electrical characteristics. PPS must be filled with fibers and fillers to overcome its inherent brittleness. Because of its low viscosity, PPS can be molded with high loadings of fillers and reinforcements. Because of its outstanding flame resistance, PPS is ideal for high-temperature electrical applications. It is unaffected by all industrial solvents. The structure of PPS is shown in [Fig. 12.2](#).

Table 12.1 The Structures of Several Commercial Polyaryl Ether Ketone Polymers

Polymer	Approximate T_g/T_m (°C)	Structure
PEEK	151/338	
PEK	160/372	
PEEKK	160/360	
PEKEKK	165/384	
PEKK	156/338	

PEEK, Polyether ether ketone; PEK, Polyether ketone; PEEKK, Polyether ether ketone ketone; PEKEKK, Polyether ketone ether ketone ketone; PEKK, Polyether ketone ketone.

Table 12.2 Tensile Strength Retained After United Kingdom Outdoor Weathering Exposure of Natural, Black, and White Pigmented Victrex PEEK [1]

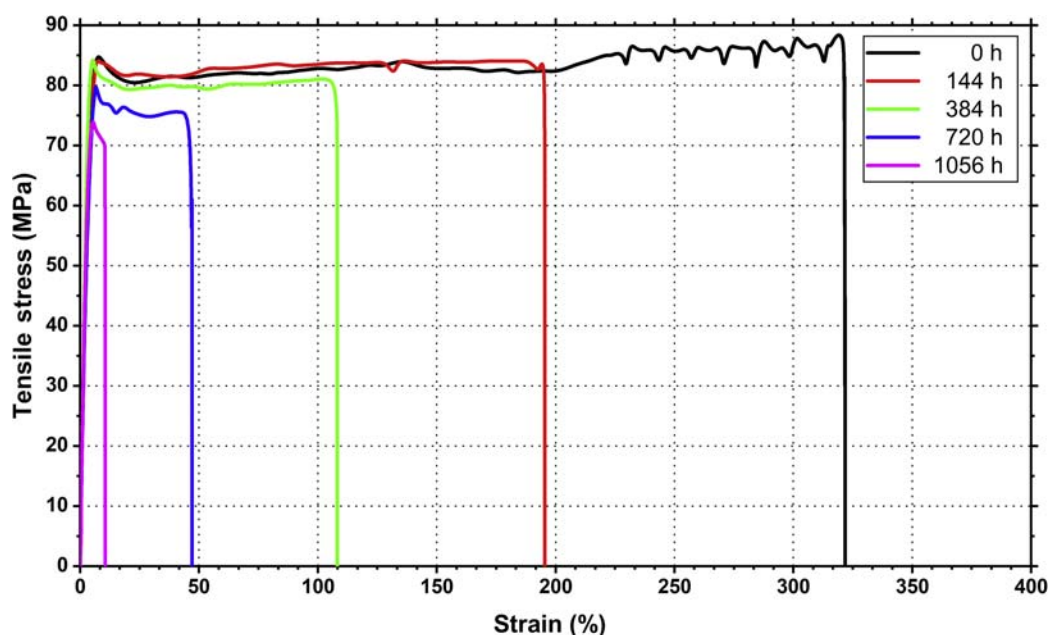
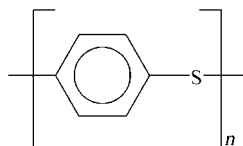
Material Grade	Victrex PEEK 450G				Victrex PEEK 450G				Victrex PEEK 450G			
Features	Natural resin				Black color				White color			
Material Composition												
Black pigment (wt%)					1–2	1–2	1–2	1–2				
White pigment (wt%)									1–2	1–2	1–2	1–2
Exposure Conditions												
Exposure time (days)	91	182	273	365	91	182	273	365	91	182	273	365
Properties Retained (%)												
Tensile strength	100.7	100.7	96.5	96.5	100.7	98.6	100	100	100	100.7	98.6	100.7

Table 12.3 Tensile Strength Retained After United Kingdom Outdoor Weathering Exposure of Pigmented Victrex PEEK [1]

Material Grade	Victrex PEEK 450G				Victrex PEEK 450G				Victrex PEEK 450G			
Features	Yellow color				Green color				Blue color			
Material Composition												
Blue pigment (wt%)	1–2	1–2	10.2	10.2								
Green pigment (wt%)					1–2	1–2	10.2	1–2				
Yellow pigment (wt%)									1–2	1–2	1–2	1–2
Exposure Conditions												
Exposure time (days)	91	182	273	365	91	182	273	365	91	182	273	365
Properties Retained (%)												
Tensile strength	100	100	97.9	96.5	98.6	98.6	95.8	96.5	100.7	100	97.9	98.6

Table 12.4 Tensile Properties of UV Irradiated Victrex 151G Easy Flow Unstabilized PEEK Fibers (Q-Lab UVA-340 bulbs \times 4) [2]

Time (h)	Yield Strength (MPa)	Tensile Strength at Rupture (MPa)	Elongation at Rupture (%)	Modulus (MPa)
0	83.2 \pm 2.0	87.6 \pm 1.9	311 \pm 9	2340 \pm 55
144	80.5 \pm 1.0	78.6 \pm 0.8	173 \pm 25	2290 \pm 95
384	78.7 \pm 1.5	78.0 \pm 1.3	137 \pm 23	2400 \pm 71
720	79.6 \pm 1.0	74.4 \pm 1.0	49 \pm 8	2200 \pm 50
1056	77.8 \pm 2.0	72.3 \pm 1.6	13 \pm 1	1980 \pm 80

**Figure 12.1** Typical tensile testing curves for UV irradiated Victrex 151G easy flow unstabilized PEEK fibers (Q-Lab UVA-340 bulbs \times 4) [2]. UV, Ultraviolet; PEEK, Polyether ether ketone.**Figure 12.2** Structure of PPS. PPS, Polyphenylene Sulfide.

The Chemical Abstracts Service (CAS) number is 26125-40-6.

There are several variants to regular PPS that may be talked about by suppliers or may be seen in the literature. There are

- Regular PPS is of “modest” molecular weight. Materials of this type are often used in coating products.
- Cured PPS is PPS that has been heated to high temperature, above 300°C, in the presence of air or oxygen. The oxygen causes some cross-linking and chain extension called oxidative crosslinking. This results in some thermoset-like properties such as improved thermal stability, dimensional stability, and improved chemical resistance.
- High molecular weight (HMW) linear PPS has a molecular weight about double of that of

regular PPS. The higher molecular weight improves elongation and impact strength.

- HMW branched PPS has higher molecular weight than regular PPS, but it also has polymer chain branches along the main molecule backbone. This provides improved mechanical properties.

PPS properties are summarized:

- Continuous use temperature of 220°C
- Excellent dimensional properties
- Transparent
- Improved impact strength and toughness as compared to polyethersulfone (PES)
- Excellent hydrolytic stability
- High stress cracking resistance
- Good chemical resistance
- Good surface release properties
- Expected continuous temperature of 180°C

Weathering

It should be noted that Celanese Fortron will discolor or show glass fibers on the surface, when it is used in outdoor conditions and exposed to UV rays or under a

fluorescent lamp. As compared with the changes in appearance, less influences of UV on the mechanical properties are found, so it shows mechanical properties are nearly equal to those of unexposed materials [3].

Products of photodegradation include cross-linking, chain scission, and conjugated double-bond formation. The molecular weight of PPS decreases on Weather-Ometer exposure as shown in Fig. 12.3. Photodegradation results in discoloration (yellowing).

Stabilization

Most important stabilizers:

UVA: Benzotriazole (derivative of Tinuvin 327 in which chlorine atom is replaced by phenylthio or phenylsulfonyl groups)

Screener: Carbon black

Stabilizers need to be used in high concentration in PPS as shown in Fig. 12.4.

Manufacturers and trade names: DIC (formerly Dainippon Ink and Chemicals); Solvay Ryton (Acquired from Chevron Phillips); Celanese Fortron; Toray Torelina

Applications and uses: Automotive: Coolant, fuel, braking, transmission, engine, electrical, and lighting components engine mounts. Electrical:

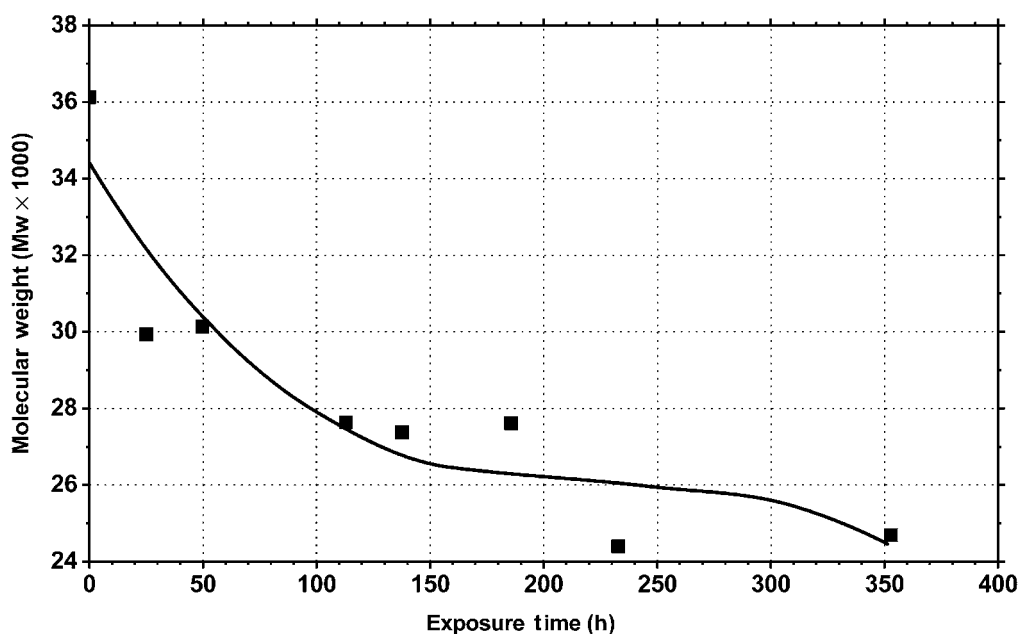


Figure 12.3 PPS weight average molecular weight vs exposure time in Weather-Ometer [4]. PPS, Polyphenylene Sulfide.

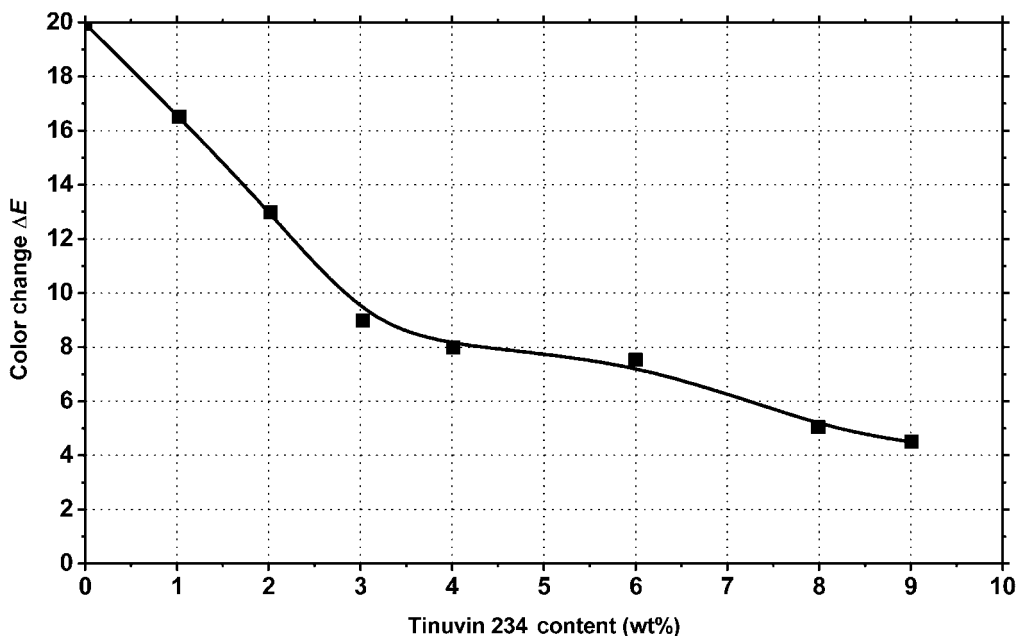


Figure 12.4 PPS color change at different levels of UV absorber [4]. PPS, Polyphenylene Sulfide; UV, Ultraviolet.

Table 12.5 Material Properties Retained and Surface Erosion After Atlas Weather-Ometer Accelerated Weathering of Solvay Ryton R4 Polyphenylene Sulfide [5]

Exposure time (days)	83.3	250	333	417	83.3	250	333
Properties Retained (%)							
Tensile strength	91.3	922	86.1	63.5	992	992	96.7
Elongation	109.1	125.5	111.8	54.5	87.5	77.5	792
Surface and Appearance							
Surface erosion (mm)				0.33			0.51

Note: Composition—carbon black 2%, glass fiber reinforcement 40%.

Table 12.6 Material Properties and Surface Erosion After 10,000 h of Atlas Weather-Ometer Accelerated Weathering of Solvay Ryton R4 Neat and With 2% Carbon Black Polyphenylene Sulfide [6]

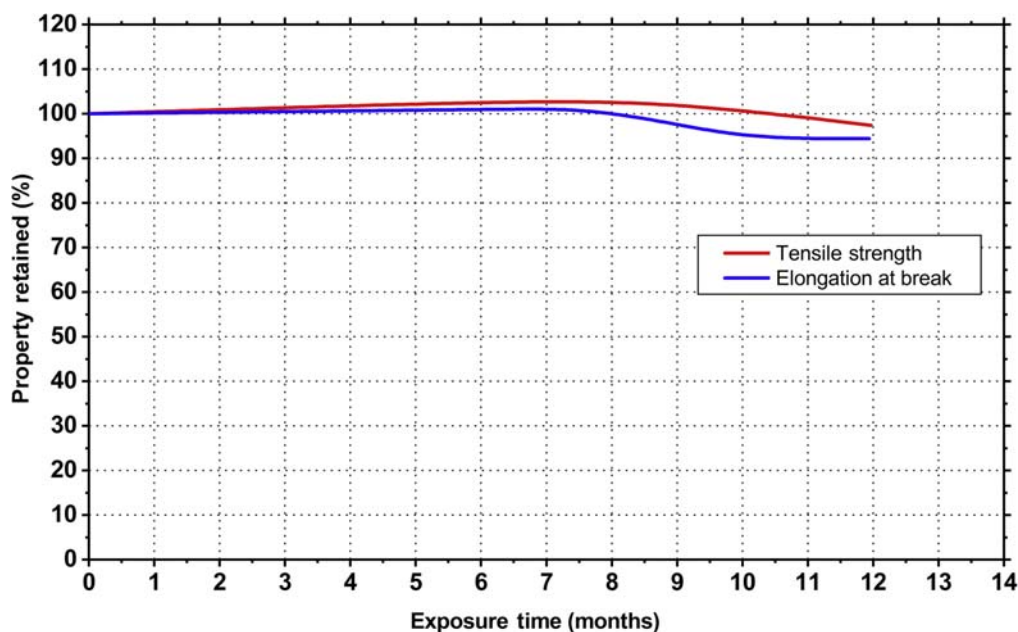
	Ryton PPS R-4		Ryton PPS R-4 with 2% Carbon Black	
Hours Exposed	Tensile (MPa)	% Elongation	Tensile (MPa)	% Elongation
0	2120	1.1	2210	1.2
2000	1940	1.2	2200	1.1
6000	1970	1.4	2200	0.9
8000	1830	1.2	2130	1.0
10,000	1350	0.6	—	—
% Retention at 10,000 h	63	55	97	79
Erosion, Mills at 10,000 h	13		2	

Table 12.7 Change in the Mechanical Properties of Celanese Fortron PPS After UV Exposure in an Atlas Weather-Ometer [3]

Fortron Grade	Exposure Time (h)	Tensile Strength (MPa)	Strain at Break (%)	Tensile Modulus (MPa)	Notched Impact Strength (Izod) (J/m)
1140L4 natural*	0	181	1.7	15,200	85
	200	181	1.7	15,200	85
	500	179	1.6	15,200	85
	1000	177	1.7	14,500	85
	2000	176	1.6	14,500	85
1140L4 brown*	0	185	1.7	15,900	91
	200	184	1.7	15,200	85
	500	184	1.7	15,200	91
	1000	183	1.7	15,200	85
	2000	183	1.6	15,200	91
1140L4 black*	0	176	1.7	13,800	80
	200	176	1.7	14,500	75
	500	178	1.6	15,200	80
	1000	176	1.7	14,500	80
	2000	175	1.6	15,200	80

*The tests used injection molded specimens according to ASTM G 23, Method 3, without water spray. It also involved a black standard temperature of 60°C and a radiation intensity of 0.35 W/m² nm at a 30% relative humidity under a xenon arc lamp according to ASTM G 26. Mechanical properties were tested according to ASTM standards. None of the test specimen showed signs of erosion.

Note: Tensile test according to ASTM D 638 ASTM D 256.

**Figure 12.5** The effect of outdoor weathering exposure in Fuji City, Japan, on the properties retention of Celanese Fortron 1140A1 Black PPS [3]. PPS, Polyphenylene sulfide.

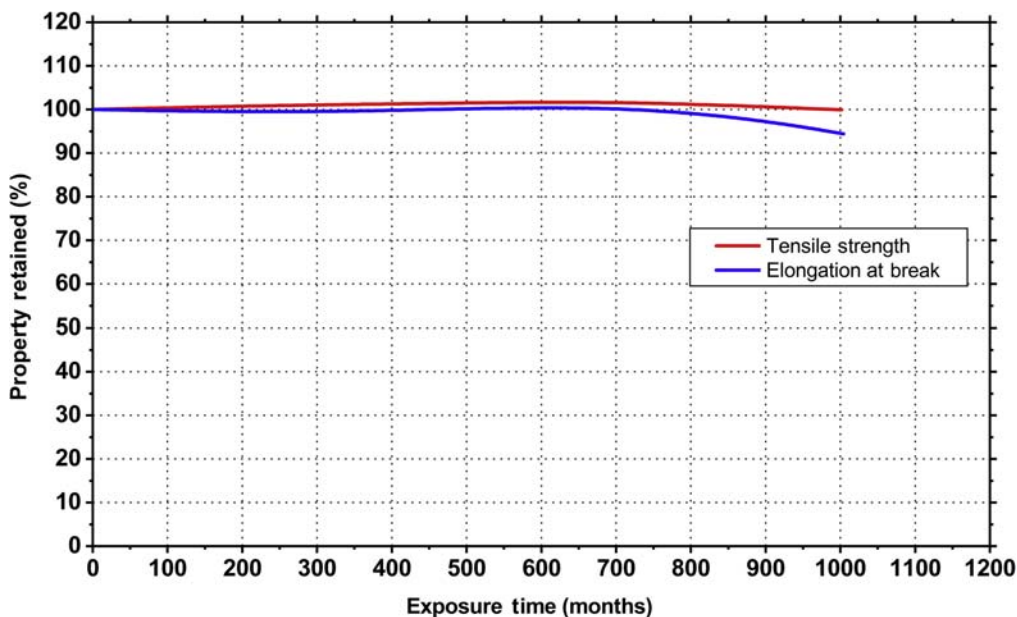


Figure 12.6 The effect of Weather-Ometer exposure on the properties retention of Celanese Fortron 1140A1 Black PPS [3].

Note: Light source: Sunshine carbon arc lamp, black panel temperature 63°C, water spray 12/60 min. PPS, Polyphenylene sulfide.

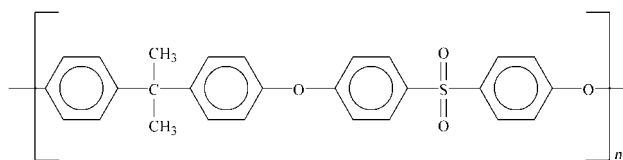


Figure 12.7 Structure of PSU. PSU, Polysulfone.

Connectors, sockets, bobbins, relays, optical pick-ups, housings. Industrial and consumer: Hair straightener housings, hard disk drive components, chemical pumps, turbo charger air ducts, piping for downhole oilfield applications, pump and motor parts, sensors, thermostats, blower housings, hot water manifolds, and nonstick cookware coatings

Data for PPS plastics are in [Tables 12.5–12.7](#) and [Figs. 12.5 and 12.6](#).

12.3 Polysulfone

Polysulfone (PSU) is a rigid, strong, tough, and high-temperature amorphous thermoplastic. The structure of PSU is shown in [Fig. 12.7](#). Its CAS number is 25135-51-7.

Its properties are summarized:

- High thermal stability
- High toughness and strength
- Good environmental stress crack resistance
- Inherent fire resistance
- Transparence

Weathering

Because of the aromatic ether backbone, PSU is susceptible to chemical degradation upon outdoor exposure. Weather resistance can be improved by the addition of carbon black. Applications of PSU involving outdoor exposure should be evaluated individually, considering the specific exposure conditions and the required material properties. Protective paints or coatings can be used to preserve the properties of PSU articles exposed to direct sunlight.

Manufacturers and trade names: Solvay Advanced Polymers Udel, BASF Ultrason S

Applications and uses: Analytical instrumentation, surgical and medical devices, and semiconductor process equipment components

Data for PSU plastics are found in [Tables 12.8 and 12.9](#) and [Figs. 12.8–12.11](#).

12.4 Polyphenylsulfone

Polyphenylsulfone (PPSU) is a rigid, strong, tough, and high-temperature amorphous thermoplastic. It has a high heat deflection temperature of 405°F (207°C); it can withstand continuous exposure to heat and still absorb tremendous impact without cracking or breaking. It is inherently flame retardant and offers exceptional resistance to bases and other chemicals. The structure of PPSU is shown in [Fig. 12.12](#).

Its properties are summarized as follows:

- High deflection temperatures, 207°C
- Inherently flame retardant
- Excellent thermal stability making films suitable
- For applications where very low shrink at high temperatures is needed

- Good electrical properties
- Superior toughness
- Exceptional hydrolytic stability
- Good chemical resistance
- Transparent

Manufacturers and trade names: Ajedum Films (a division of Solvay Solexis) Acudel, Solvay Advanced Plastics Radel R; Evonik Industries Europlex, BASF Ultrason P

Applications and uses: Electrical/Electronic, aircraft interiors, and automotive industry

Data for PPSU plastics are found in [Figs. 12.13–12.15](#).

12.5 Polyethersulfone

PES is an amorphous polymer and a high-temperature engineering thermoplastic. Even

Table 12.8 Mechanical Properties Retained After Outdoor Weathering of Sabic Innovative Plastics LNP Glass-Reinforced Polysulfone in California and Pennsylvania [7]

Exposure Conditions								
Exposure location	Los Angeles, CA				Philadelphia, PA			
Exposure time (days)	91	182	365	730	91	182	365	730
Properties Retained (%)								
Tensile strength	96	942	95	95	91	95	92	91
Notched Izod impact strength	100	90.9			100	90.9		
Unnotched Izod impact strength	100	882			98	902		

Note: Carbon black 1%, glass fiber reinforcement 30%; exposure test method ASTM D1435.

Table 12.9 Effect of Benzotriazole Type UV Absorbers on the Yellowness Index of PSU Films [8]

UV Absorber Concentration	Yellowness Index After Exposure for (h):				
	0	6	28	74	192
Without	3.7	7.7	13	21	33 ^a
0.5%	3.8	6.4	10	16	26
1.0%	3.8	5.7	9.2	16	22

^aFilm is brittle.

Note: Exposure: Xenotest 1200 without water spraying, black panel temperature ~ 53°C; solution cast films 0.1 mm thick; test method: ASTM 1925-70.

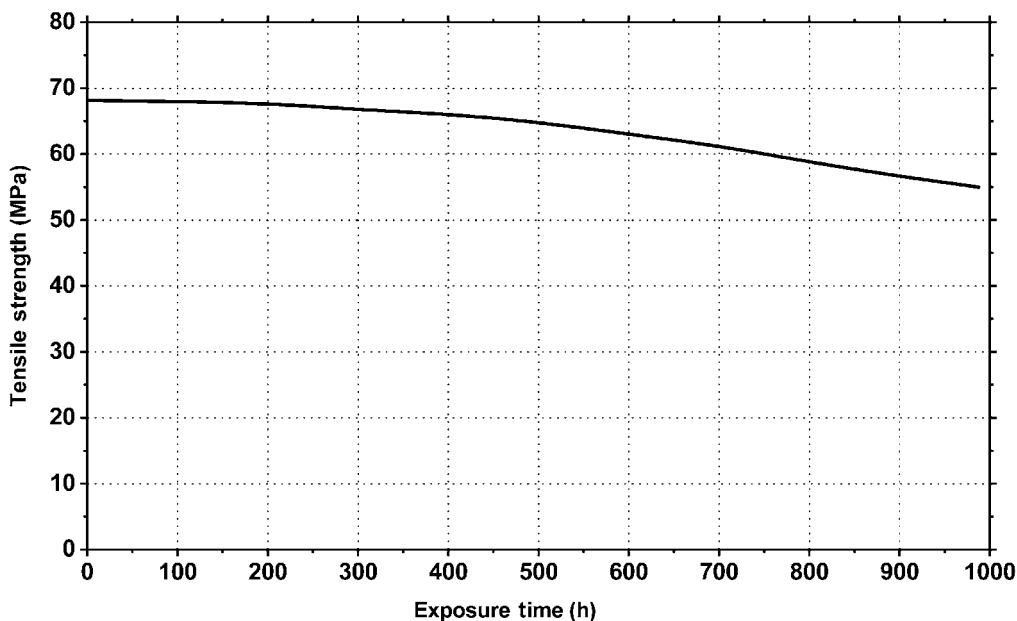


Figure 12.8 Tensile strength after xenon arc Weather-Ometer Exposure of Polysulfone [9].

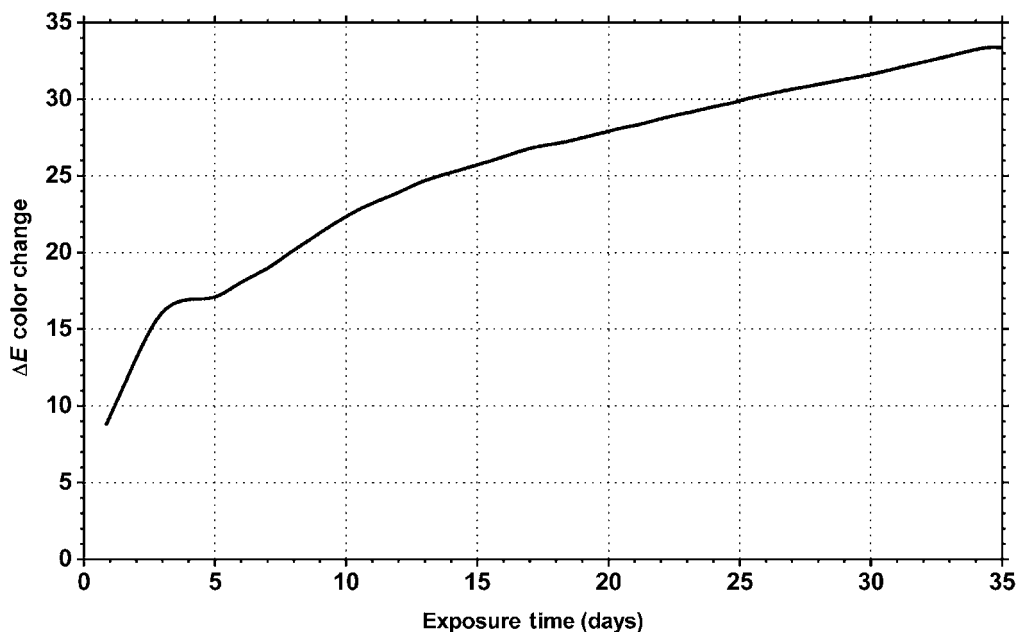


Figure 12.9 ΔE color change for natural resins 30 kJ/day xenon arc UV weathering of PSU resin [10]. *PSU*, Polysulfone; *UV*, Ultraviolet.

though PES has high-temperature performance, it can be processed on conventional plastics processing equipment. Its chemical structure is shown in Fig. 12.16. Its CAS number is 25608-63-3. PES has an outstanding ability to withstand exposure to elevated temperatures in air and water for prolonged periods.

Because PES is amorphous, mold shrinkage is low and is suitable for applications requiring close

tolerances and little dimensional change over a wide temperature range. Its properties include:

- Excellent thermal resistance— T_g 224°C
- Outstanding mechanical, electrical, flame, and chemical resistance
- Very good hydrolytic and sterilization resistance
- Good optical clarity

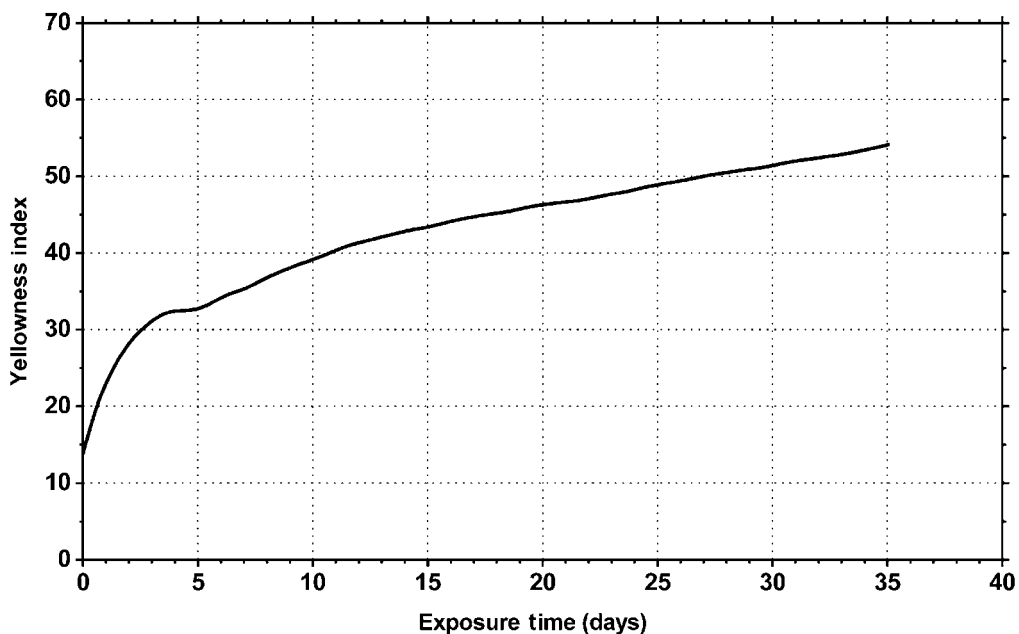


Figure 12.10 Yellowness index for natural resins 30 kJ/day xenon arc UV weathering of PSU resin [10]. *PSU*, Polysulfone; *UV*, Ultraviolet.

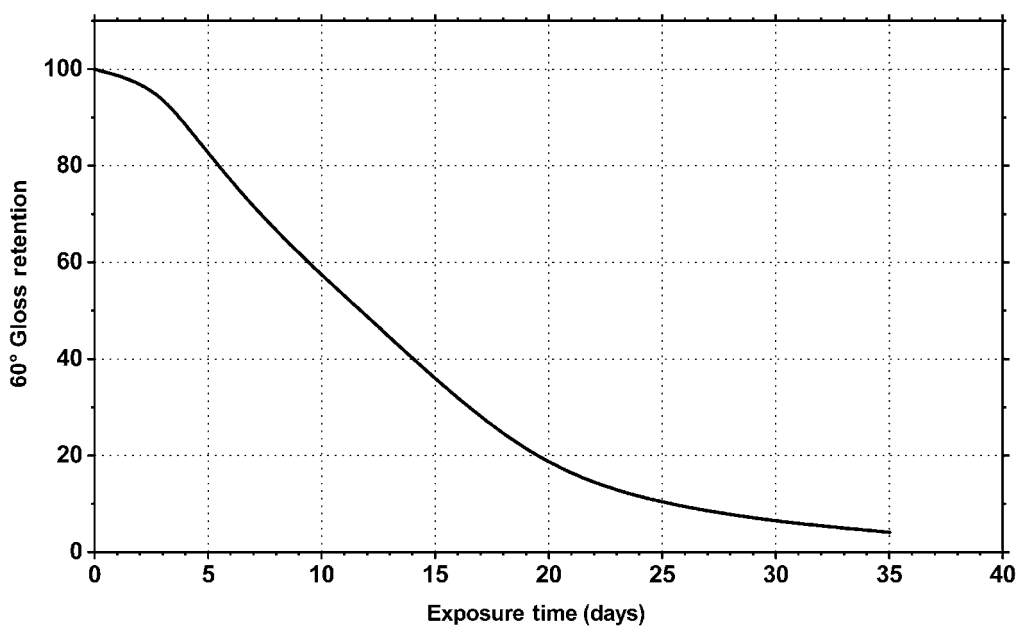


Figure 12.11 Gloss (60°) for natural resins 30 kJ/day xenon arc UV weathering of PSU resin [10]. *PSU*, Polysulfone; *UV*, Ultraviolet.

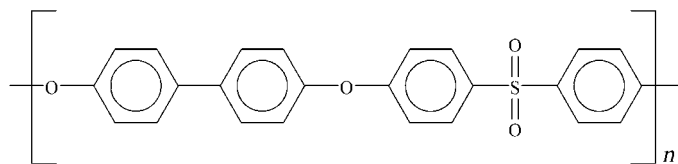


Figure 12.12 Structure of PPSU. *PPSU*, Polyphenylsulfone.

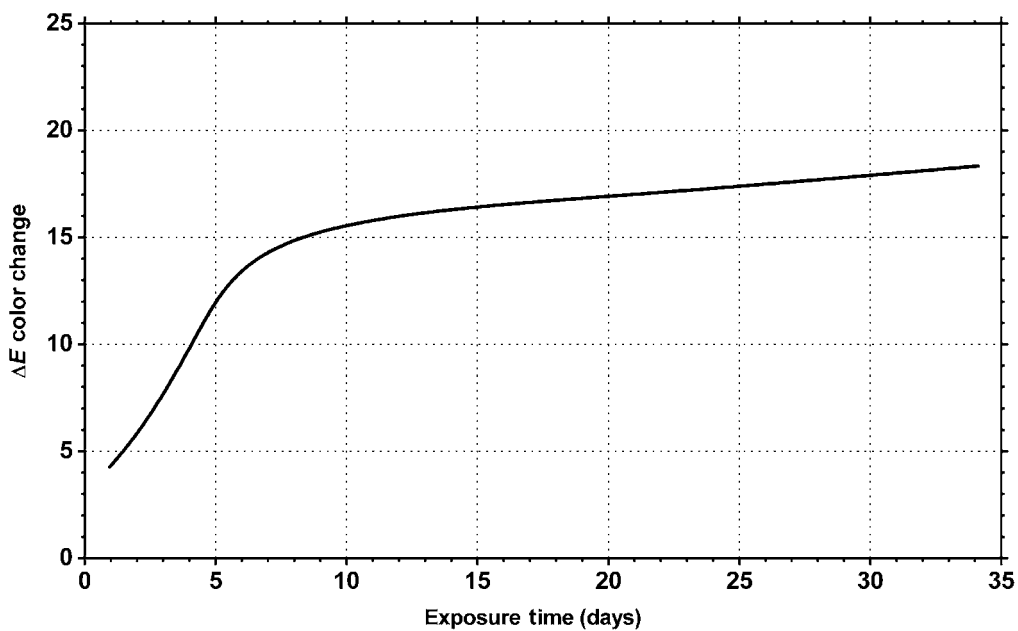


Figure 12.13 ΔE color change for natural resins 30 kJ/day xenon arc UV weathering of PPSU resin [10]. *UV*, Ultraviolet.

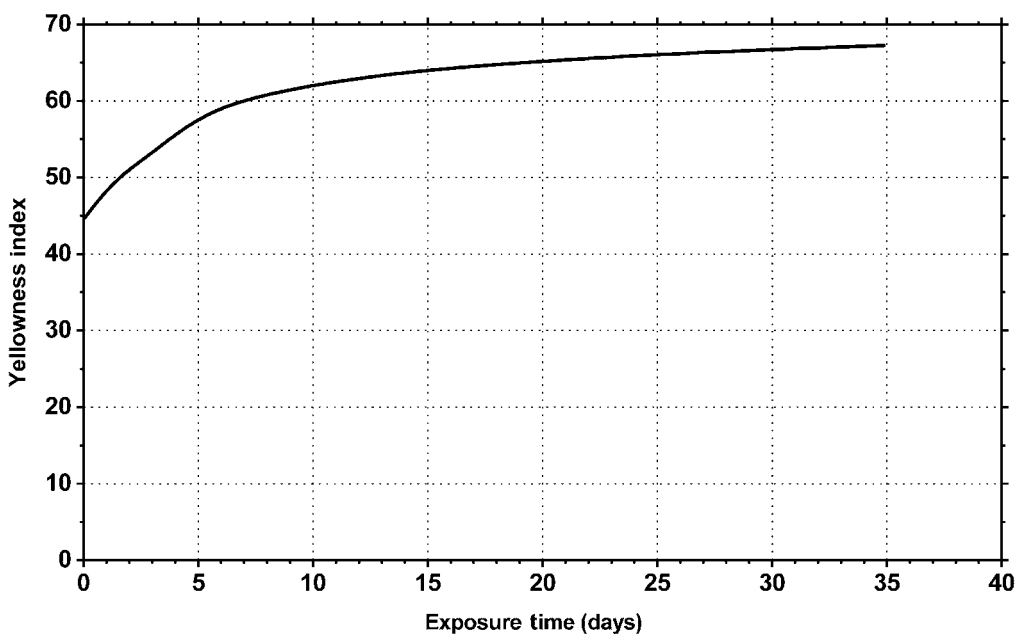


Figure 12.14 Yellowness index for natural resins 30 kJ/day xenon arc UV weathering of PPSU resin [10]. *UV*, Ultraviolet.

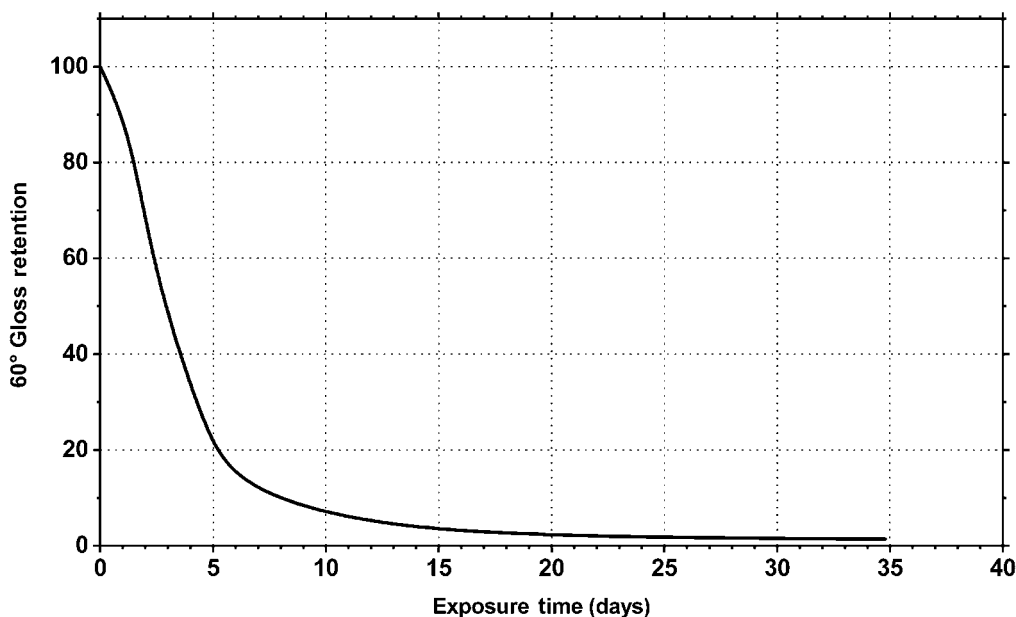


Figure 12.15 Gloss (60°) for natural resins 30 kJ/day xenon arc UV weathering of PPSU resin [10]. UV, Ultraviolet.

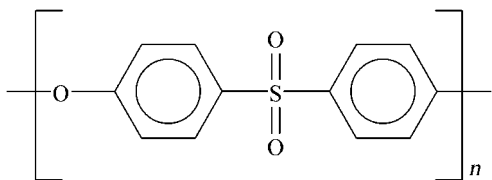


Figure 12.16 Structure of PES. PES, Polyethersulfone.

Weathering Properties

The weathering resistance of natural PES resin is not very good, and therefore, it is not suitable for outdoor use [11]. BASF Ultrason moldings yellow and embrittled quickly when exposed outdoors. The moldings can be protected from degradation by the incorporation of carbon black, surface coating, or metallizing [12].

Manufacturers and trade names: BASF Ultrason E, Sumitomo Chemical Co., Ltd. SUMIKAEXCEL PES, Solvay Advanced Polymers Veradel, Radel A

Applications and uses: Relay and switch bases, IC trays, coil bobbins, printed circuit boards, connectors, ultrafiltration devices, optical pickup parts, LCD substrates for calculators, mobile phones, lamp reflectors, brake shaft bushings, hot water pump components

Data for PES plastics are found in Table 12.10 and Figs. 12.17–12.20.

12.6 Parylene (Poly(*p*-Xylylene))

Parylene is the generic name for members of a series of polymers. The basic member of the series, called Parylene N, is poly-para-xylylene, a completely linear, highly crystalline material. The structures of four Parylene types are shown in Fig. 12.21.

Parylene polymers are not manufactured and sold directly. They are deposited from the vapor phase by a process which in some respects resembles vacuum metalizing. The Parylenes are formed at a pressure of about 0.1 torr from a reactive dimer in the gaseous or vapor state. Unlike vacuum metalizing, the deposition is not line of sight, and all sides of an object to be encapsulated are uniformly impinged by the gaseous monomer. Due to the uniqueness of the vapor phase deposition, the Parylene polymers can be formed as structurally continuous films from as thin as a fraction of a micrometer to as thick as several mils.

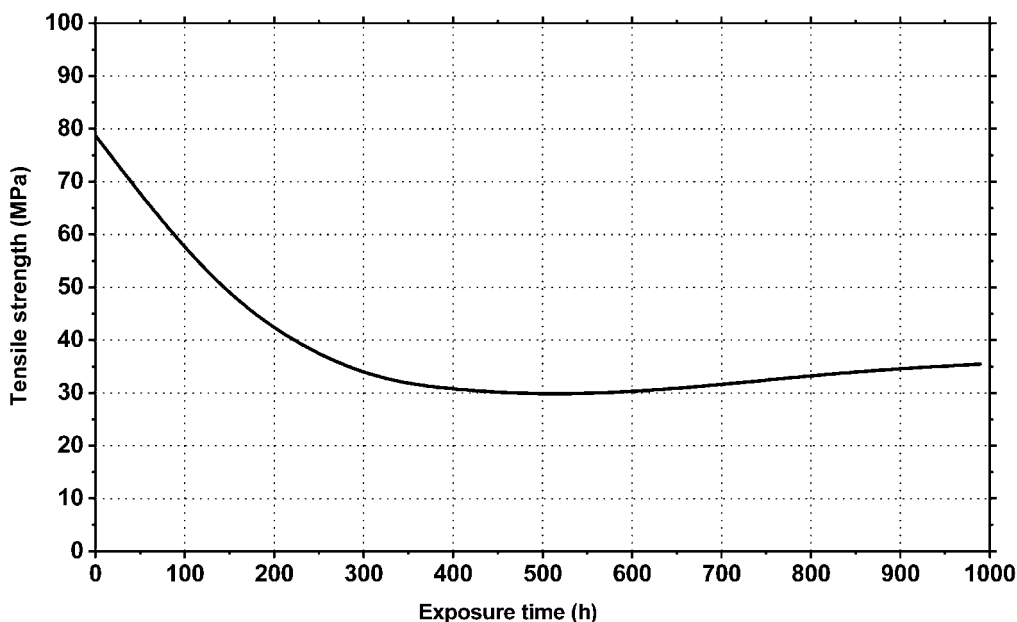
The first step is the vaporization of the solid dimer at approximately 150°C. The second step is the quantitative cleavage (pyrolysis) of the dimer vapor at the two methylene–methylene bonds at about 680°C to yield the stable monomeric diradical, para-xylylene. Finally, the monomeric vapor enters the room temperature deposition chamber where it spontaneously polymerizes on the substrate. The substrate temperature never rises more than a few degrees above ambient.

Table 12.10 Effect of Benzotriazole Type UV Absorbers on the Yellowness Index of PES Films [13]

UV Absorber Concentration	Yellowness Index After Exposure for (h):				
	0	6	28	74	192
Without	4.7	4.8	8.5	14 ^a	—
0.5%	5.5	4.2	6.1	11	16
1.0%	4.5	6.1	6.7	10	14

^aFilm is brittle.

Note: Exposure: Xenotest 1200 without water spraying, black panel temperature $\sim 53^{\circ}\text{C}$; solution cast films 0.1 mm thick; test method: ASTM 1925-70.

**Figure 12.17** Tensile strength after xenon arc Weather-Ometer exposure of PES [9]. PES, Polyethersulfone.

Parylene is used as a coating on medical devices ranging from silicone tubes to advanced coronary stents, synthetic rubber products ranging from medical grade silicone rubber to ethylene propylene diene monomer rubber.

Manufacturers and trade names: Para Tech Coating, Inc., Parylene

Applications and uses: Electronics and sensors, tire pressure monitoring systems, fuel cell technology, emissions sensors, gaskets and seals, MEMS, sensors circuit card assemblies, motor components, power supplies, backplanes, elastomeric components, LED coating applications including video displays, electronic billboards, transportation signage, aviation lighting, traffic signals, scoreboards, marine lighting, commercial refrigeration, vehicle lighting, and outdoor illumination

Weathering Resistance

Although stable indoors, the Parylenes are not recommended to use outdoors when exposed to direct sunlight [14]. Parylene films were exposed to radiation from a bank of fluorescent lamps with following details [15].

- Device used: QUV
- Test method: ASTM 154
- Type of test: Accelerated weathering
- Source: UVA 340 lamp
- Irradiance: 0.77 W/m^2
- Visual color, chalking, cracking, blistering, and flaking were characterized on the films after 100, 300, 500, 1000, 1250, 1500, and 2000 hours of UV exposure. Numerical scales

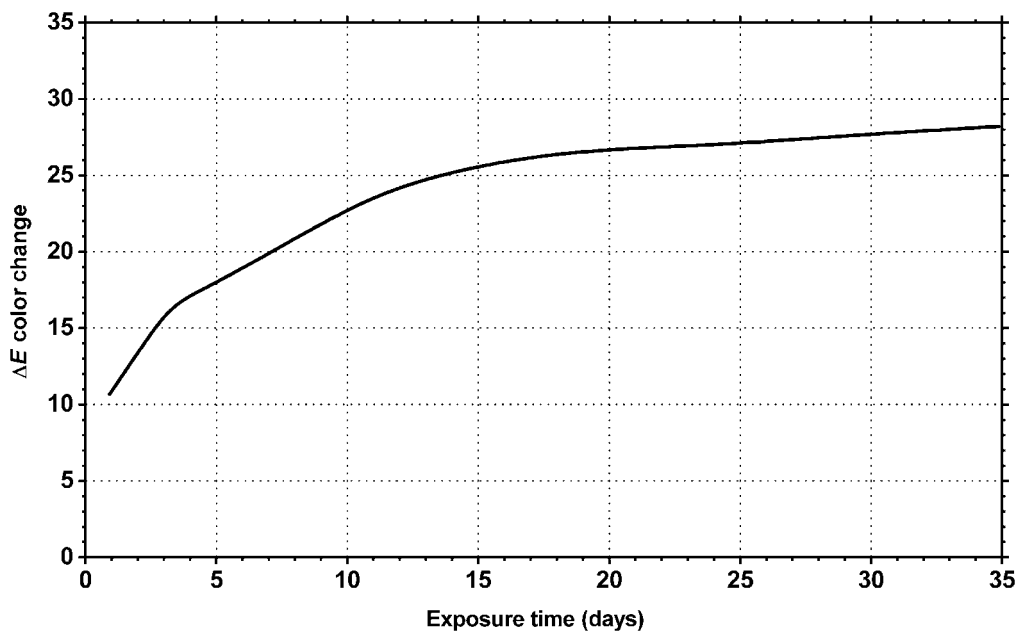


Figure 12.18 ΔE color change for natural resins 30 kJ/day xenon arc UV weathering of PES resin [10]. PES, Polyethersulfone; UV, ultraviolet.

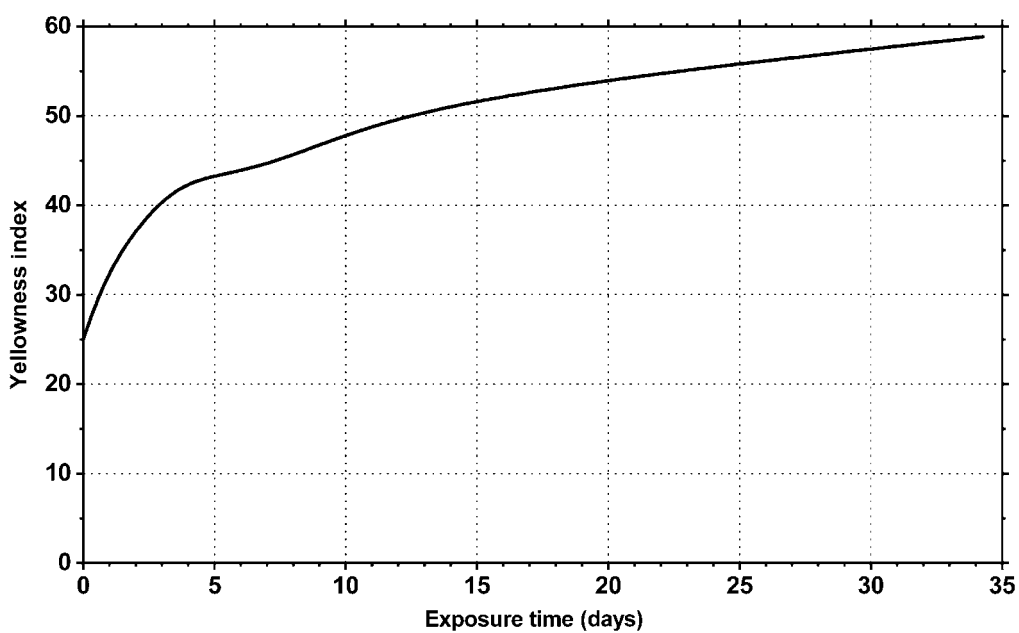


Figure 12.19 Yellowness index for natural resins 30 kJ/day xenon arc UV weathering of PES resin [10]. PES, Polyethersulfone; UV, ultraviolet.

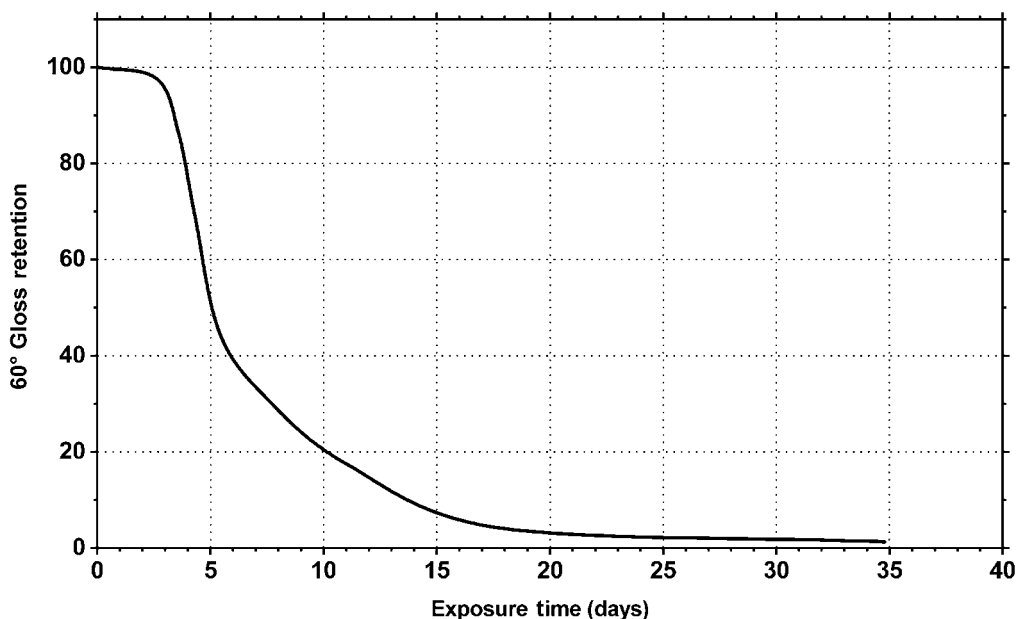


Figure 12.20 Gloss (60°) for natural resins 30 kJ/day xenon arc UV weathering of PES resin [10]. PES, Polyethersulfone; UV, ultraviolet.

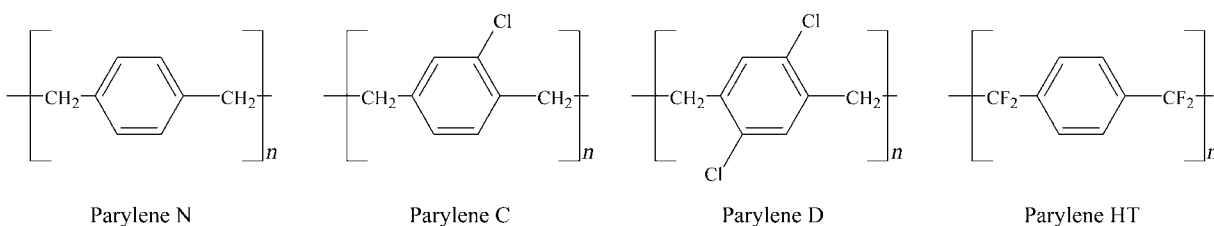


Figure 12.21 Structures of the Parylene polymer molecules.

(0–10) are used to depict the degree of effect of the exposure. The observation results are summarized below (Scale: 10—excellent (no effect), 0—very poor (very severe)).

Results were

- Parylene HT: Stability is more than 2000 hours—after 2000 hours of exposure, there was no discoloration, chalking, cracking, or blistering.
- Parylene C: Stability is less than 100 hours—after 100 hours of exposure, film turned yellow (3Y), but there was no chalking, cracking, or blistering.
- Parylene N: Stability is less than 100 hours—after 100 hours of exposure, film turned yellow (4Y), but there was no chalking, cracking or blistering.

12.7 Polyoxymethylene (POM or Acetal Homopolymer)/ Polyoxymethylene Copolymer (POM-Co or Acetal Copolymer)

There are two variations to acetal plastics: Homopolymer and copolymer.

Polyoxymethylene (POM or Acetal Homopolymer)

Acetal polymers, also known as polyoxymethylene (POM) or polyacetal, are formaldehyde-based thermoplastics that have been commercially available since the 1960s. Polyformaldehyde is thermally unstable. It decomposes on heating to yield formaldehyde gas. Two methods of stabilizing polyformaldehyde for use as an engineering polymer were developed and introduced by DuPont, in 1959, and Celanese in 1962 (now Celanese).

DuPont's method for making polyacetal yields a homopolymer through the condensation reaction of polyformaldehyde and acetic acid (or acetic anhydride). The acetic acid puts acetate groups ($\text{CH}_3\text{COO}-$) on the ends of the polymer as shown in Fig. 12.22, which provide thermal protection against decomposition to formaldehyde.

Further stabilization of acetal polymers also includes the addition of antioxidants and acid scavengers. Polyacetals are subject to oxidative and acidic degradation, which leads to molecular weight decline. Once the chain of the homopolymer is ruptured by such an attack, the exposed polyformaldehyde ends may decompose to formaldehyde and acetic acid.

Polyoxymethylene Copolymer (POM-Co or Acetal Copolymer)

The Celanese route for the production of polyacetal yields a more stable copolymer product via the reaction of trioxane, a cyclic trimer of formaldehyde, and a cyclic ether, such as ethylene oxide or 1,3-dioxolane. The structures of these monomers are shown in Fig. 12.23. The polymer structure is given in Fig. 12.24.

The improved thermal and chemical stability of the copolymer versus the homopolymer is a result of randomly distributed oxyethylene groups, which

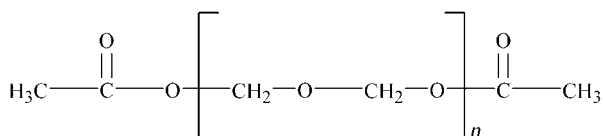


Figure 12.22 Chemical structure of acetal homopolymer.

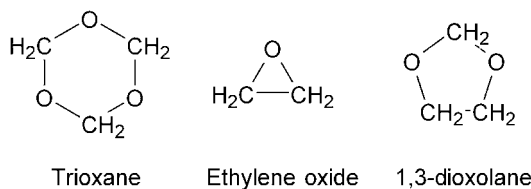


Figure 12.23 Chemical structure polyoxymethylene copolymer monomers.

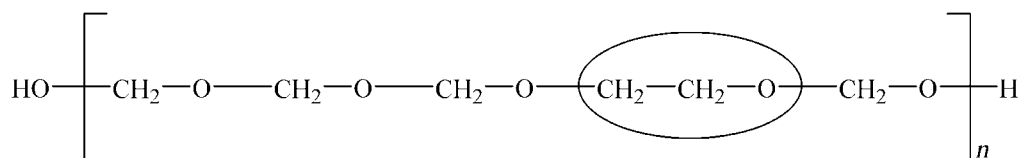


Figure 12.24 Chemical structure of acetal copolymer.

is circled in Fig. 12.24. All polyacetals are subject to oxidative and acidic degradation, which leads to molecular weight reduction. Degradation of the copolymer ceases, however, when one of the randomly distributed oxyethylene linkages is reached. These groups offer stability to oxidative, thermal, acidic, and alkaline attack. The raw copolymer is hydrolyzed to an oxyethylene end cap to provide thermally stable polyacetal copolymer.

The copolymer is also more stable than the homopolymer in an alkaline environment. Its oxyethylene end cap is stable in the presence of strong bases. The acetate end cap of the homopolymer, however, is readily hydrolyzed in the presence of alkalis, causing significant polymer degradation.

The homopolymer is more crystalline than the copolymer. The homopolymer provides better mechanical properties, except for elongation. The oxyethylene groups of the copolymer provide improved long-term chemical and environmental stability. The copolymer's chemical stability results in better retention of mechanical properties over an extended product life.

Acetal polymers have been particularly successful in replacing cast and stamped metal parts due to their toughness, abrasion resistance, and ability to withstand prolonged stresses with minimal creep. Polyacetals are inherently self-lubricating. Their lubricity allows the incorporation of polyacetal in a variety of metal-to-polymer and polymer-to-polymer interface applications such as bearings, gears, and switch plungers. These properties have permitted the material to meet a wide range of market requirements.

The properties of polyacetals can be summarized as follows:

- Excellent wear resistance
- Very good strength, stiffness
- Good heat resistance
- Excellent chemical resistance
- Opaque

- Moderate to high price
- Somewhat restricted processing

Weathering

Upon exposure to light, polyacetals that are not UV stabilized display loss of gloss, a change in color, and in some cases, chalking—the formation of a white coating on the surface. This degradation process is accompanied by a decrease in strength. The wavelength of solar radiation that is harmful to polyacetals is in the range of 290–400 nm [16].

Photolysis leads to formation of radicals which may lead to the formation of formaldehyde as shown in Fig. 12.25. Thermal oxidation and photooxidation are both accelerated in the presence of water. Water can readily cleave the polymer backbone by acid-catalyzed hydrolysis as shown in Fig. 12.26.

Copolymerization increases the durability of POM over that of homopolymerization.

Stabilization

Most important stabilizers

UVA: 2-(2*H*-Benzotriazol-2-yl)-*p*-cresol; 2-(2*H*-benzotriazole-2-yl)-4,6-di-*tert*-pentylphenol;

HAS: 1,3,5-Triazine-2,4,6-triamine, *N,N'*[[1,2-ethane-diyl-bis[[[4,6-bis[butyl (1,2,6,6-pentamethyl-4-piperidiny]amino]-1,3,5-triazine-2-yl]imino]-3,1-propanediyl] bis[*N',N''*-dibutyl-*N',N''*-bis(1,2,2,6,6-pentamethyl-4-piperidiny)]-;

Phenolic antioxidant: Ethylene-bis(oxyethylene)-bis(3-(5-*tert*-butyl-4-hydroxy-*m*-tolyl)-propionate);

Optical brightener: Fluorescent brightener 378 (Clariant);

Manufacturers and trade names: DuPont Delrin, Celanese Hostaform; Celcon, BASF Ultraform; Asahi Kasei Corporation Tenac; Mitsubishi Engineering Plastics Iupital;

Applications and uses: Metal and glass replacement in many automotive (door handles/locks, seat belt buckles, fuel/fuel sending systems, gas tank caps, windshield wiper components, window hardware, and control cables) industrial equipment (gears, bearings, conveyor links, cams, bushings, valve bodies, hose connectors, pistons, pulleys, casters, and rollers), consumer goods (zippers, cosmetic applicators/containers, aerosol valves, pens, phone housing, keys, and parts), appliances (food processor blades, dishwasher soap dispensers, spray nozzles, and rollers, food containers, functional gears in washers and dryers, kettles, mixer bowls, washing machine/dryer parts, electrical, and office automation).

Data for both types of acetal plastics are found in Tables 12.11–12.17 and Figs. 12.27–12.47.

12.7.1 POM (Homopolymer)

12.7.2 POM-Co (Copolymer)

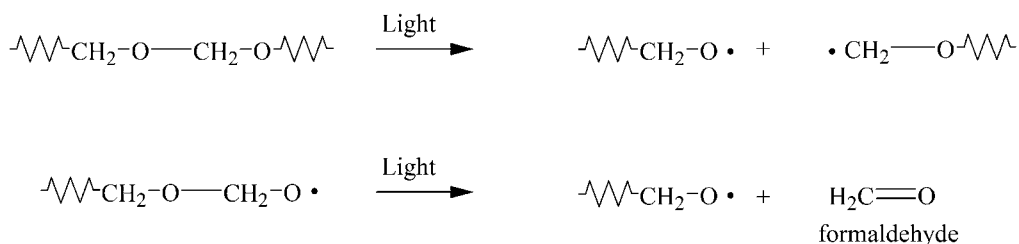


Figure 12.25 Photolysis reactions of POM. *POM*, Polyoxymethylene.

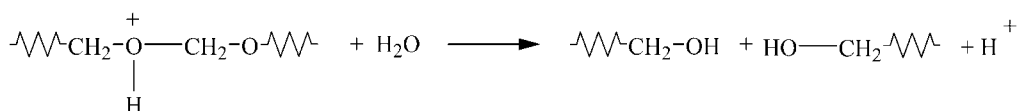


Figure 12.26 Acid catalyzed hydrolysis POM. *POM*, Polyoxymethylene.

Table 12.11 Weatherability of DuPont Delrin 507 BK601 Acetal Homopolymer [17]

Exposure Time (Year)	Arizona		Michigan	
	Tensile Strength (MPa)	Elongation (%)	Tensile Strength (MPa)	Elongation (%)
0	70.3	20	70.3	20
1	71.0	12	70.3	7
2	71.7	11	70.3	13
3	71.0	9	70.3	12
4	73.1	11	72.4	14
10	69.6	10	69.6	10
20	70.2	8	64.4	11

Samples: ASTM Tensile specimens, 216 mm \times 13 mm \times 3 mm (8 1/2 in \times 1/2 in \times 1/8 in).

Table 12.12 Color Differences, ΔE , After Light Exposure for Pigmented Celanese Celcon UV90Z (GM and Ford Automotive Colors) Acetal, POM [20]

Color	GM Standard Black	GM Garnet Red	GM Very Dark Sapphire	GM Medium Beechwood	Ford Corporate Red
Color change, ΔE	0.17	1.00	1.35	0.57	1.50

Note: Exposure conditions SAE J1885, Exposure energy 1240.8 kJ/m², Exposure time approx. 800 h.

Table 12.13 Color Differences, ΔE , After Light Exposure for Pigmented Celanese Celcon UV90Z Acetal, POM [20]

Color	Black	Light Red	Light Tan	Medium Tan	Brown	Medium Gray	Dark Blue	Flame Red	Maroon
Color change, ΔE	0.2	0.2	0.2	0.6	0.2	0.3	0.5	0.9	1.2

Note: Exposure conditions SAE J1885, Exposure energy 1240.8 kJ/m², Exposure time approx. 800 h.

Table 12.14 Color Differences, ΔE , After Light Exposure for Unpigmented Celanese Celcon M90UV Acetal, POM [20]

Exposure Conditions	Initial Value	HPUV	Xenon Arc ASTM 4459		
Exposure time		300 HP Units	200 h	600 h	1000 h
Color change, Δb	4.08	2.62	2.63	2.66	2.89

Note: Initial b value 4.08; Δb is a color value; lower values mean whiter samples.

Table 12.15 Color Differences, ΔE , After Florida Weathering for Celanese Hostaform Acetal, POM Material Grade [21]

Celanese Hostaform Product	S 27072 WS 10/1570	C 9021 10/1570	C 9021 LS 10/1570
Color change, ΔE	1.8	2.4	0.8

Note: Exposure conditions xenotest 1200 CPS (EDAG) VW PV 3920 (Florida), Exposure time 1600 h.

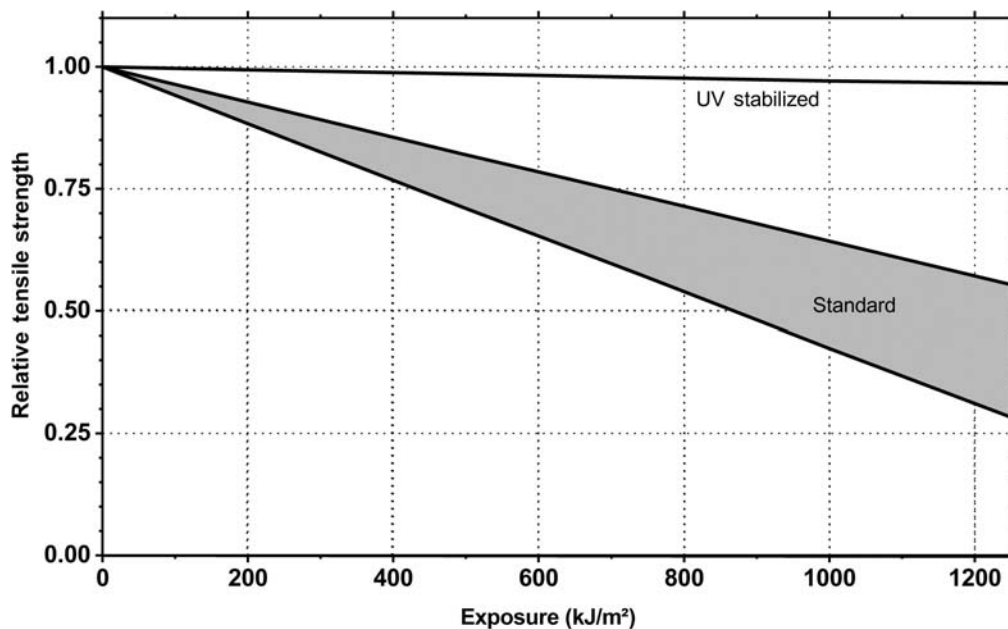
Table 12.16 Color Differences, ΔE , After Xenotest 1200 for Celanese Hostaform C 9021 LS Blue 80/4065 Acetal, POM [22]

Exposure Time	500 h	1000 h	1500 h	2000 h
Color change, ΔE	1.2	1.3	1.6	2.2

Table 12.17 Changes in Mechanical Properties After Light Exposure of Celanese Celcon UV90Z [20]

Mechanical Property	Property Retained (%)
Tensile strength	104.5
Flexural strength	100.8
Flexural modulus	96.7
Notch Izod impact	105.2

Note: Total light exposure energy 1240 kJ/m² (approximately 800 h).

**Figure 12.27** Relative tensile strength after accelerated interior weathering according to SAE J1885 for DuPont Delrin POM [17].

Note: Improved weathering performance (retention of surface appearance as well as mechanical properties) is achieved in the DELRIN x07 series by the use of a selected UV stabilizer package, as Fig. 12.28 illustrates. POM, Polyoxymethylene.

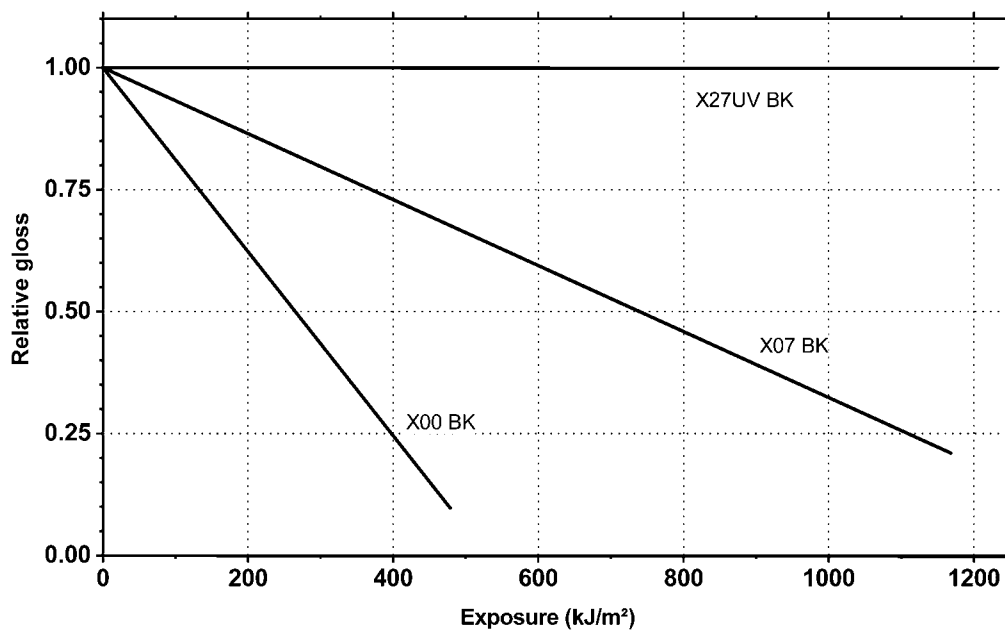


Figure 12.28 Relative gloss after accelerated interior weathering according to SAE J1885 for DuPont Delrin POM [17].

Note: Fig. 12.29 illustrates schematically how outstanding improvements in weatherability have been achieved through the selection and optimization of UV stabilizer systems for DELRIN. POM, Polyoxymethylene.

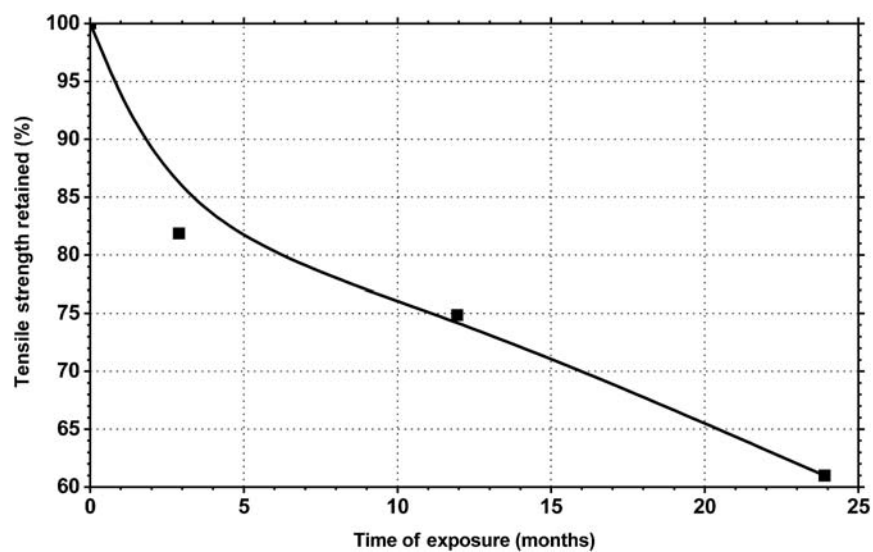


Figure 12.29 Retention of tensile strength during POM natural exposure in southern Slovakia [18].

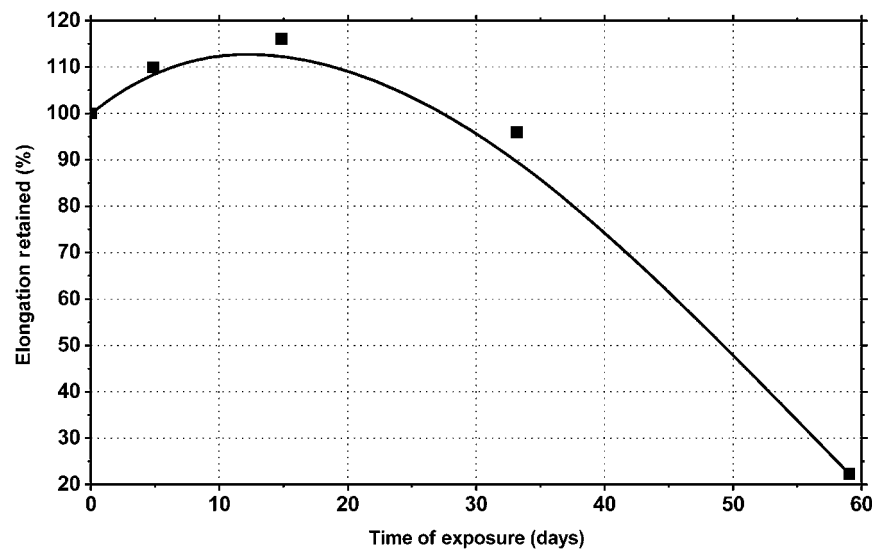


Figure 12.30 Elongation retention during POM natural exposure in rain tropics [19].

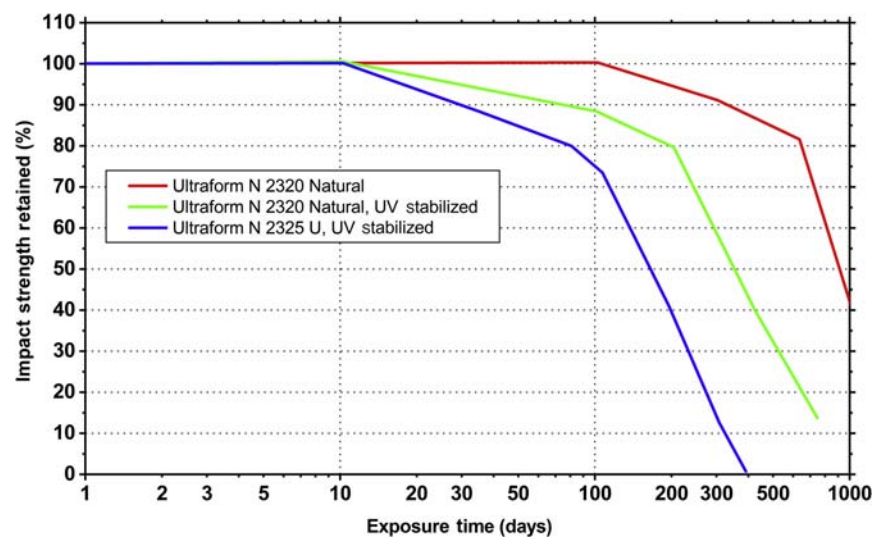


Figure 12.31 Outdoor exposure time vs impact strength retained of BASF Ultraform N 2320 and Ultraform N 2325 U acetal copolymer [23].

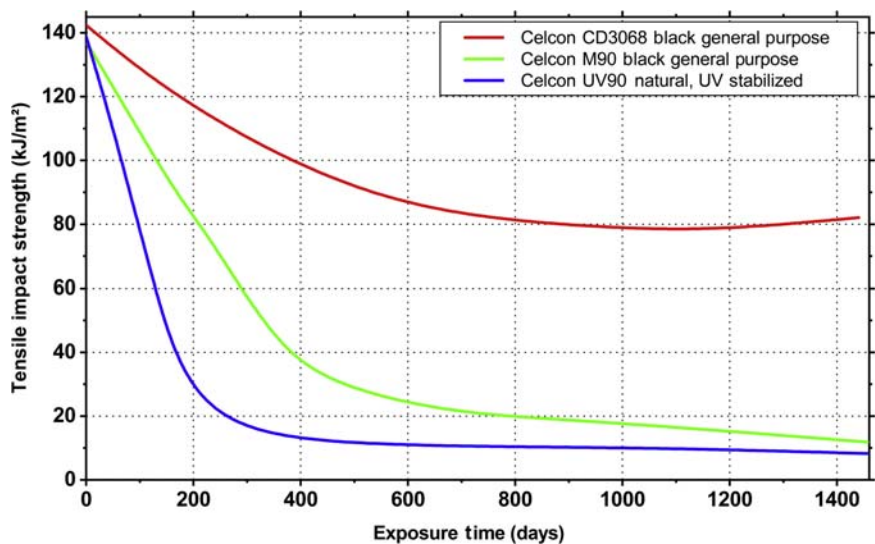


Figure 12.32 Outdoor exposure time vs tensile impact strength of Celanese Celcon M90 and UV90 acetal copolymer [24].

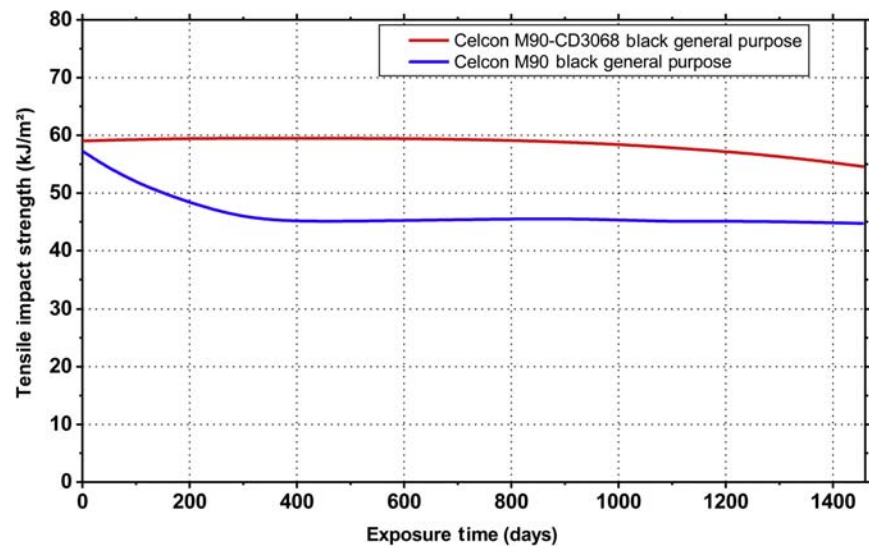


Figure 12.33 Outdoor exposure time vs tensile strength at yield of Celanese Celcon M90 acetal copolymer [24].

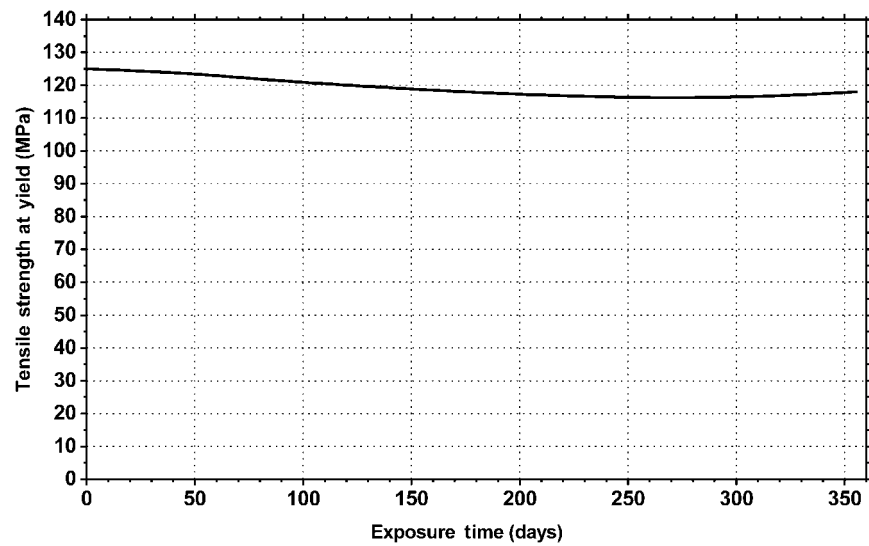


Figure 12.34 New Jersey outdoor exposure time vs tensile strength at yield of Celanese Celcon GC25A acetal copolymer [24].

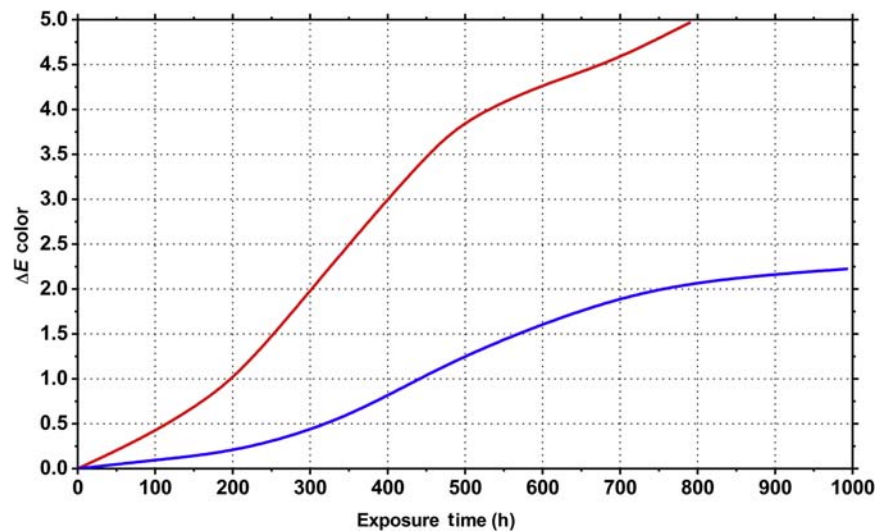


Figure 12.35 QUV exposure time vs ΔE color change of Celanese Celcon acetal copolymer [24].

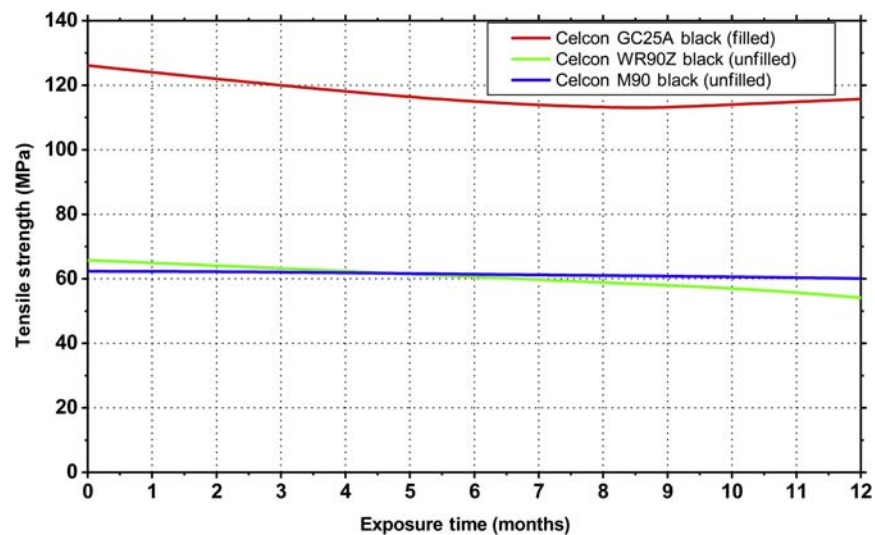


Figure 12.36 Tensile strength vs outdoor weathering of black Celcon acetal copolymers [25].
** Note: Data for Celcon WR90Z generated using SAE test method J 1960; 2000 h exposure.*

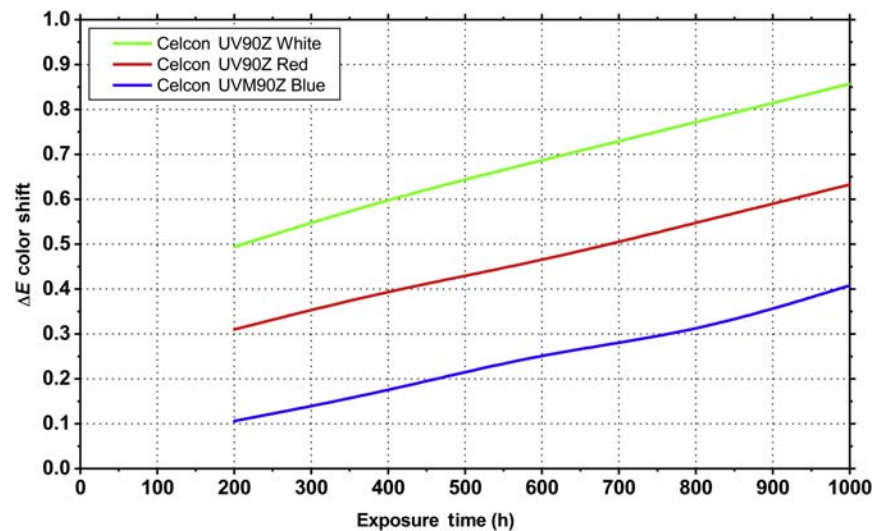


Figure 12.37 Change in color vs simulated weathering time for Celcon UV90Z UV stabilized acetal copolymer (colored grades) [25]. UV, Ultraviolet.

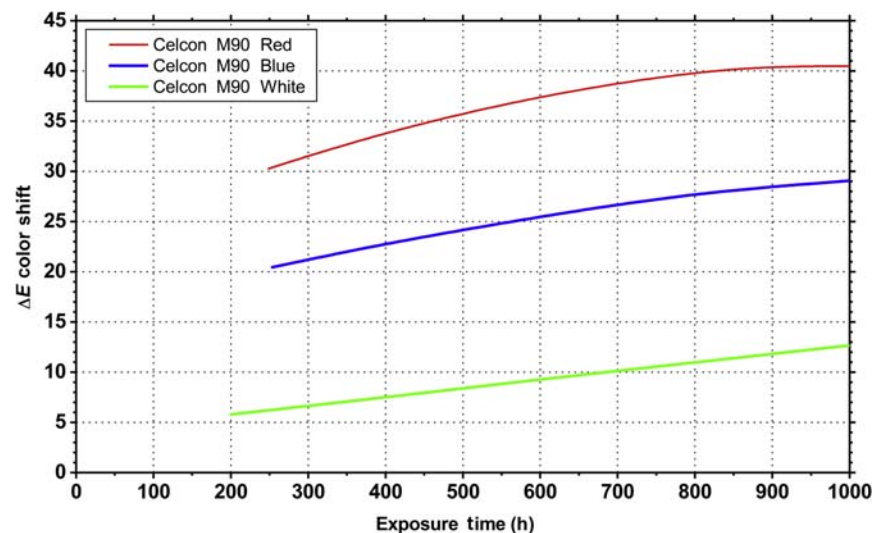


Figure 12.38 Change in color vs simulated weathering time for Celcon M90 acetal copolymer (colored grades) [25].

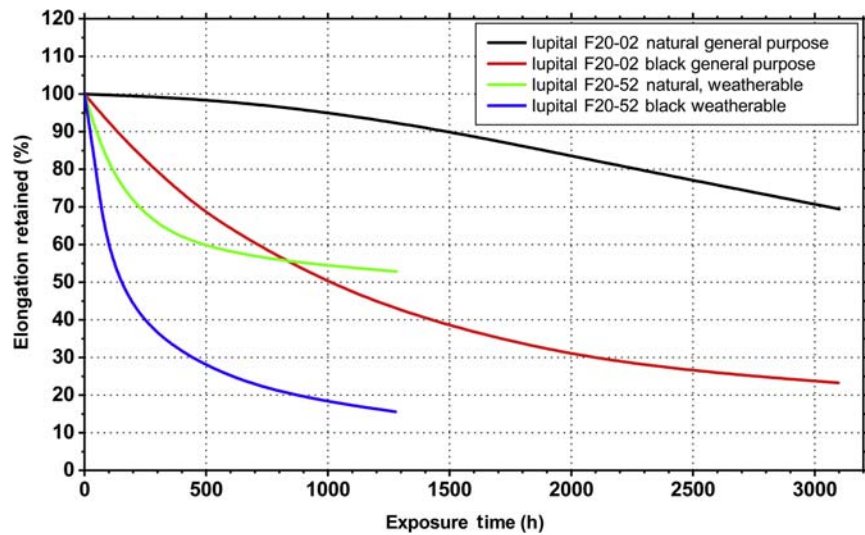


Figure 12.39 Sunshine Weather-Ometer exposure time vs elongation retained of Mitsubishi Lupital F20 acetal copolymer [26].

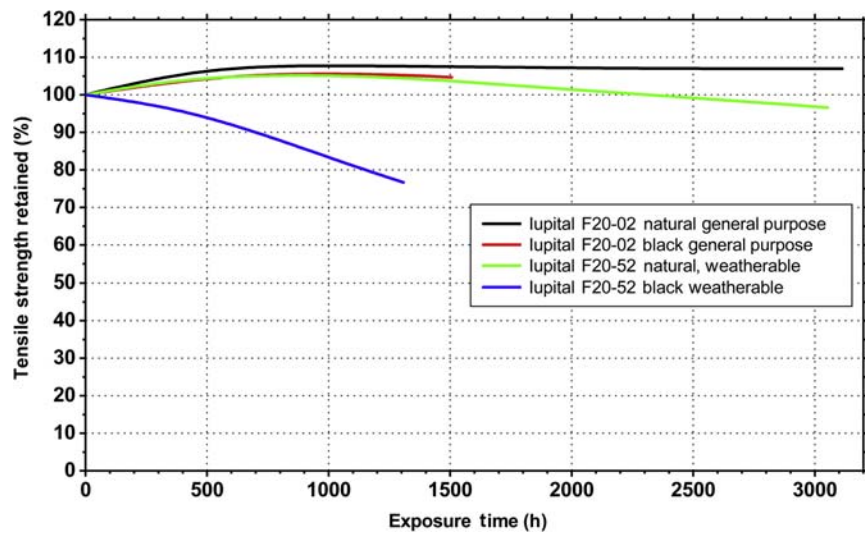


Figure 12.40 Sunshine Weather-Ometer exposure time vs tensile strength retained of Mitsubishi Lupital F20 acetal copolymer [26].

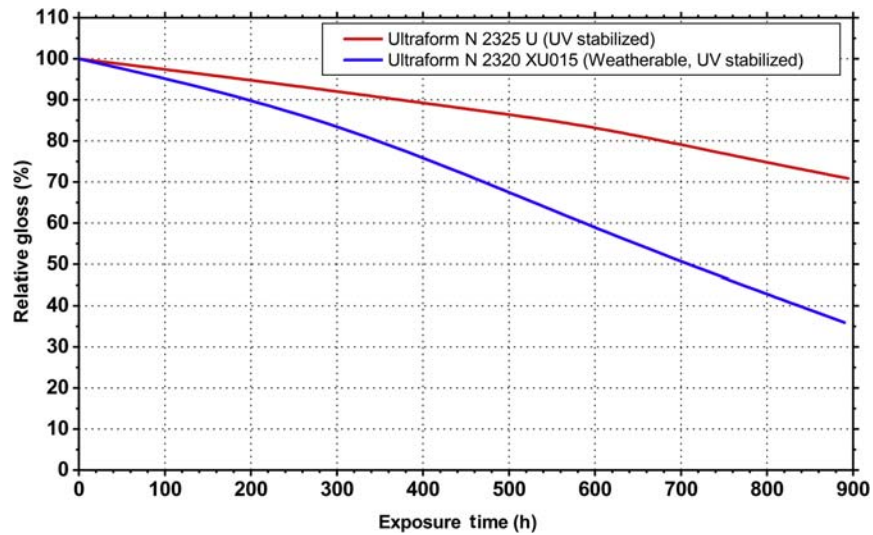


Figure 12.41 Xenon arc Weather-Ometer exposure time vs relative gloss of BASF Ultraform N acetal copolymer [27].

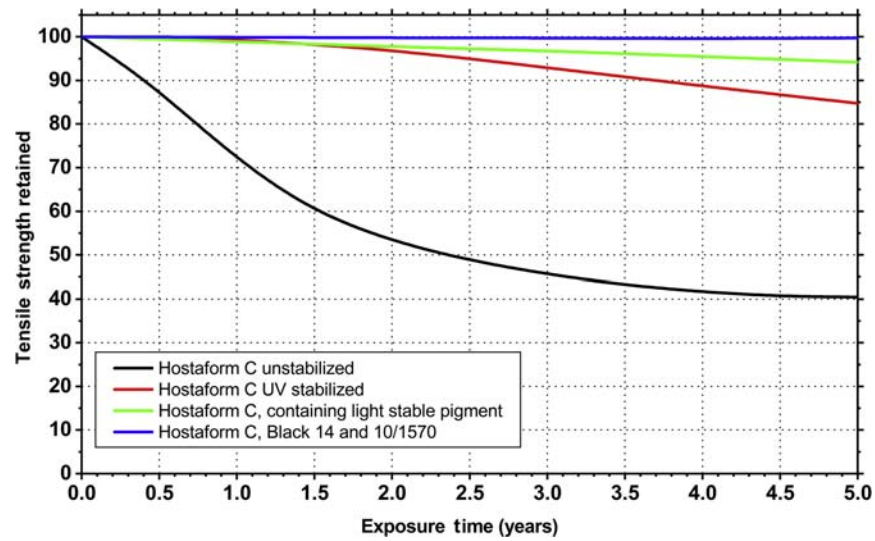


Figure 12.42 Relative tensile strength of unstabilized and UV-stabilized Hostaform C as a function of weathering time [28]. *UV*, Ultraviolet.

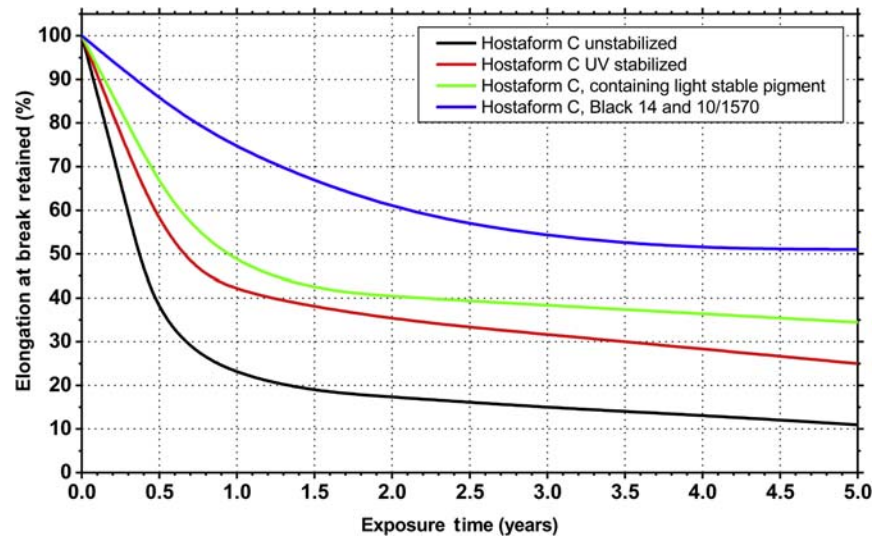


Figure 12.43 Relative elongation at break of unstabilized and UV-stabilized Hostaform C as a function of weathering time [28]. *UV*, Ultraviolet.

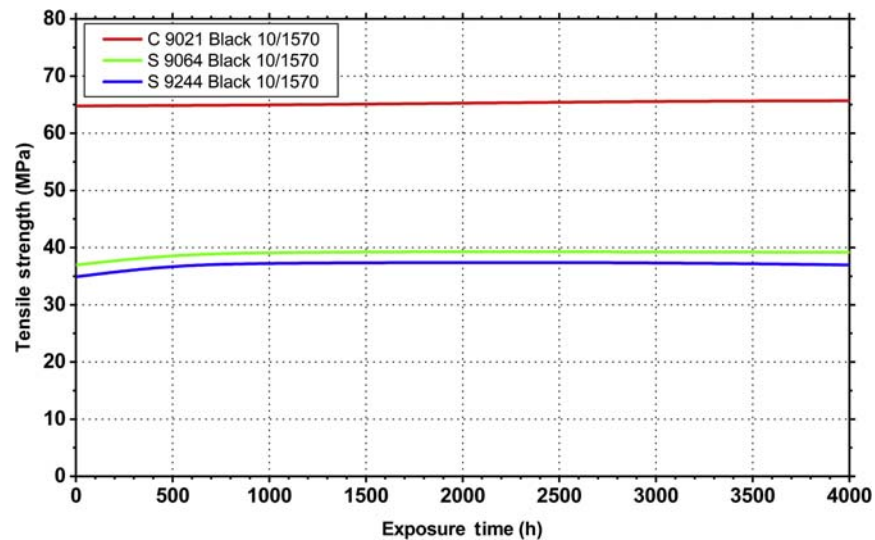


Figure 12.44 Tensile strength (ISO 1/4 tensile test bar) of Hostaform C 9021, S 9064, and S 9244 in the black 10/1570 formulation as a function of exposure time in the Xenotest 1200 [28].

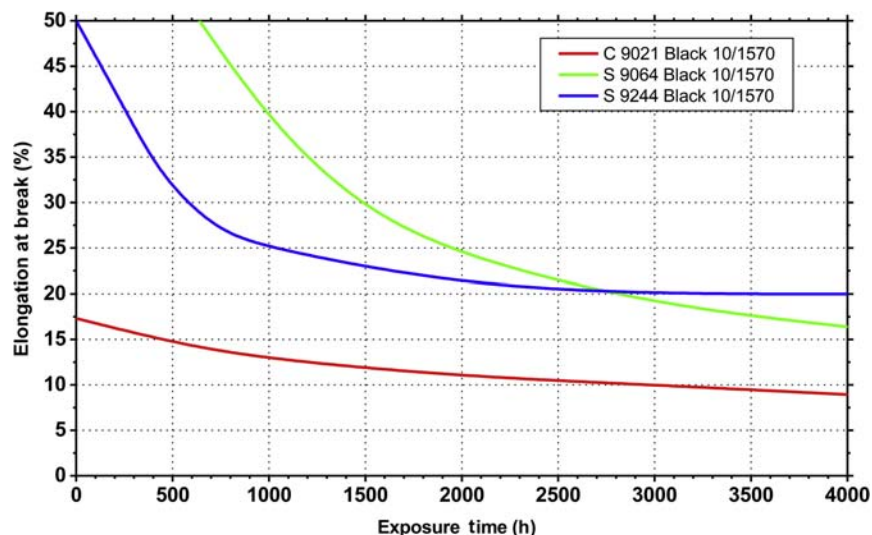


Figure 12.45 Elongation at break (ISO 1/4 tensile test bar) of Hostaform C 9021, S 9064, and S 9244 in the black 10/1570 formulation as a function of exposure time in the Xenotest 1200 [28].

12.8 Polysiloxane

Silicones are also known as siloxanes, polyorganosiloxanes, or polysiloxanes. Silicone rubber is a semi-organic synthetic. Its polymer backbone structure consists of a chain of silicon and oxygen atoms rather than carbon and hydrogen atoms, as in the case with other types of rubber. The molecular structure of silicone rubber results in a very flexible—but weak—chain. Silicones are very stable at low and high temperatures. Although fillers may improve properties somewhat, tear and tensile strengths remain relatively low. Fig. 12.46 shows four of the primary groups that

make up a typical polysiloxane, the typical structure of which is shown in Fig. 12.47. To simplify the discussion of polysiloxane composition, the monomers are identified by letters.

Some common abbreviations for the polymers include MQ, VMQ, PMQ, PVMQ, and PDMS poly (1-trimethylsilyl-1-propyne) or PTMSP.

The side groups can also be reactive moieties such as amine ($-\text{NH}_2$) or hydroxyl ($-\text{OH}$) and are typically used at small relative concentrations. Fig. 12.48 shows the reaction of an amine functionalized polysiloxane with an epoxy and with an acrylic (methyl methacrylate) in Fig. 12.49.

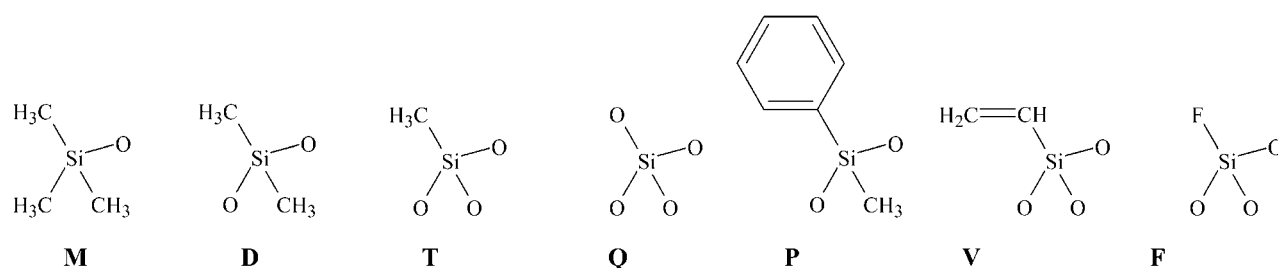


Figure 12.46 Structure of groups that make up polysiloxanes.

“M” stands for Me_3SiO

“D” for Me_2SiO_2

“T” for MeSiO_3

“Q” for SiO_4

“P” for replace Me with phenyl side groups

“V” for replace Me with vinyl side groups (typically <1%)

“F” for replace Me with fluorine.

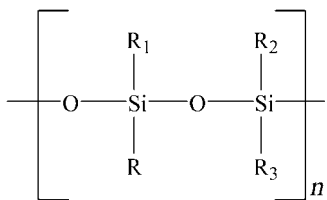


Figure 12.47 Idealized structure of polysiloxane.

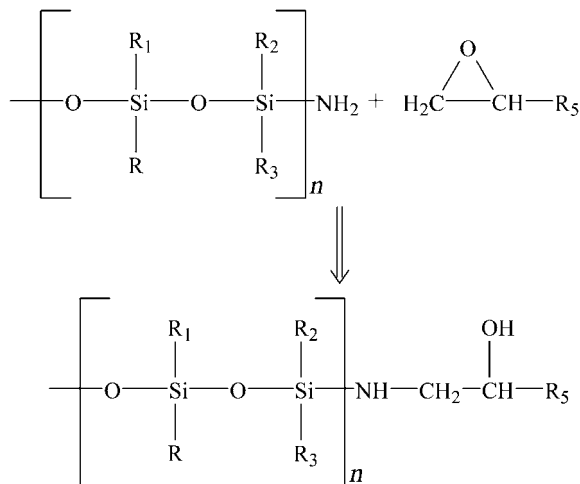


Figure 12.48 Reaction of an epoxy with an amine functionalized polysiloxane.

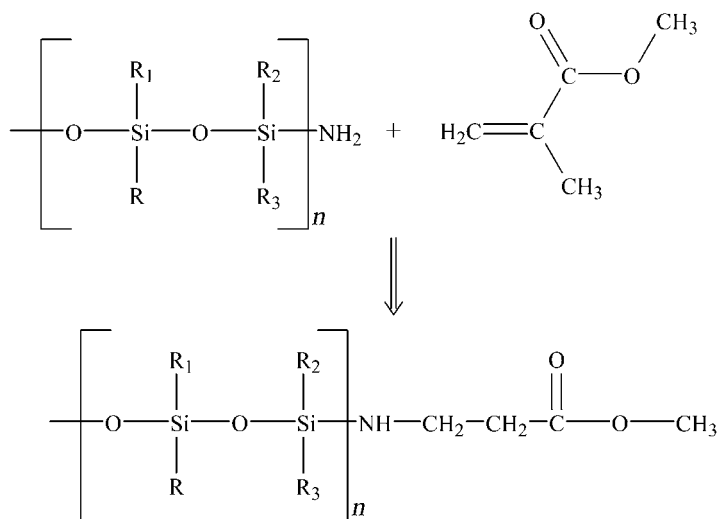


Figure 12.49 Reaction of an acrylic with an amine functionalized polysiloxane.

The elastomer materials containing silicone are discussed in [Section 10.15](#). Many siloxane materials, particularly coatings, are hybrid materials, combining polysiloxane with epoxy, acrylic, vinyl, fluoropolymer, or other molecules [29]. The hybrid materials can also be polymers. Often these materials react with reactive side groups intentionally added to the polysiloxane polymer chain such as amine or hydroxyl groups.

Manufacturers and trade names: Bayer Corporation Baysilone; Shincor Silicones KE; Dow Corning Corp. Silastic; General Electric Silplus, Tufel, and SE; Rhone-Poulenc Inc. Rhodorsil

Applications and uses: Calking, non-stick coatings

Weathering

Silicon-based polymers are uniquely resistant to photolysis and photooxidation. This can easily be rationalized when one considers that the Si—O bond is already in an oxidized state and unlike Carbon—Carbon bonds cannot be oxidized further. However, photolysis can still occur between the silicon and carbon bonds if present as shown in [Fig. 12.50](#).

The products of photodegradation include hydrogen, methane, and ethylene. Photodegradation generally leads to lower mechanical properties.

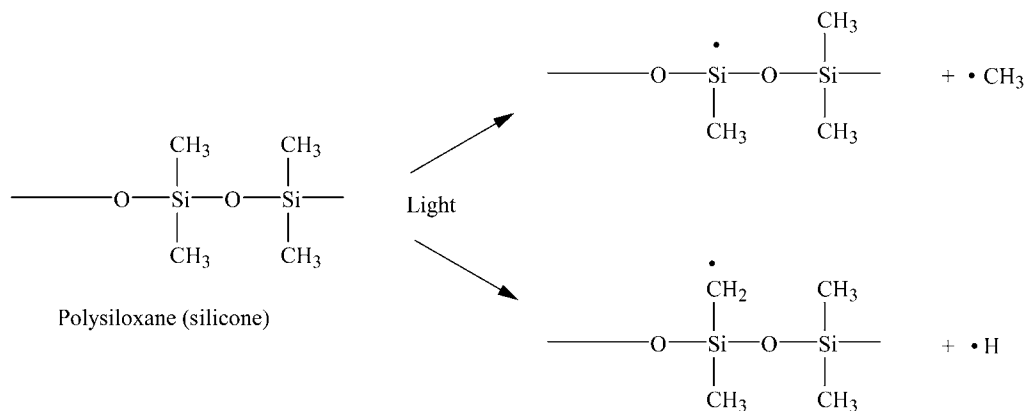


Figure 12.50 Photolysis of a polysiloxane.

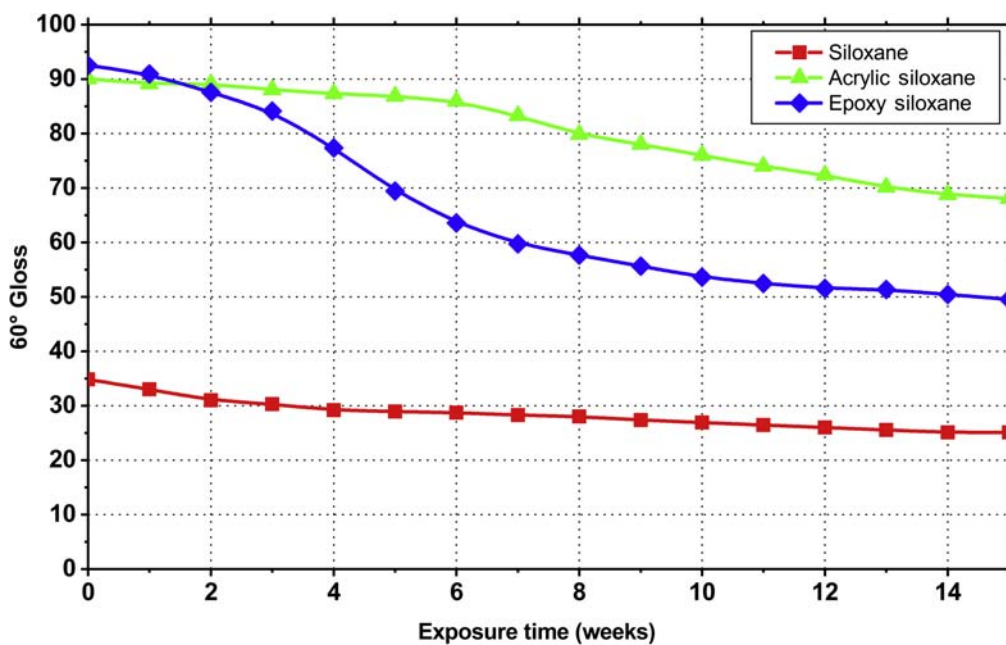


Figure 12.51 60° Gloss vs exposure time of siloxane, epoxy siloxane, acrylic siloxane after accelerated QUV-B weathering [30].

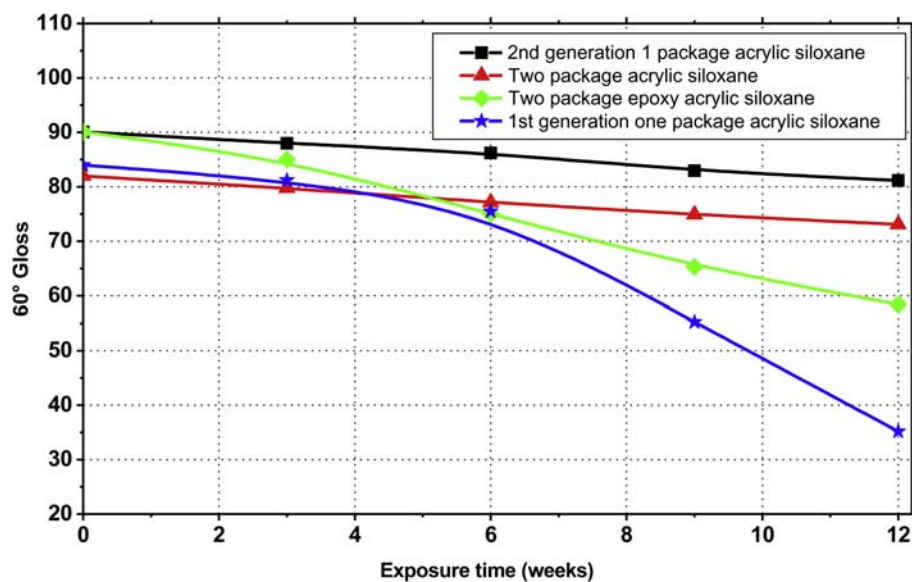


Figure 12.52 60° Gloss vs exposure time of acrylic siloxane coatings after accelerated QUV-B weathering [30].

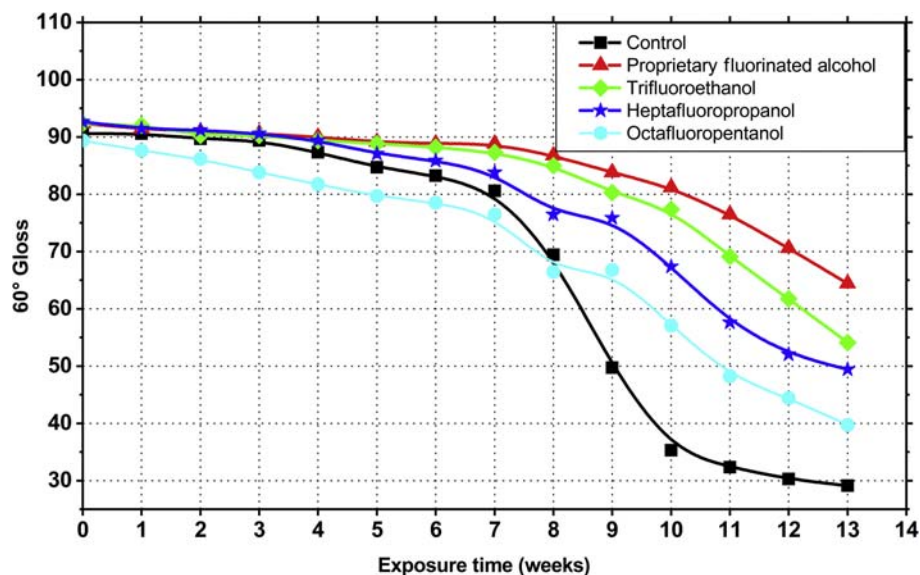


Figure 12.53 Comparative QUV-B data of pigmented fluorinated epoxy siloxane hybrids [29].

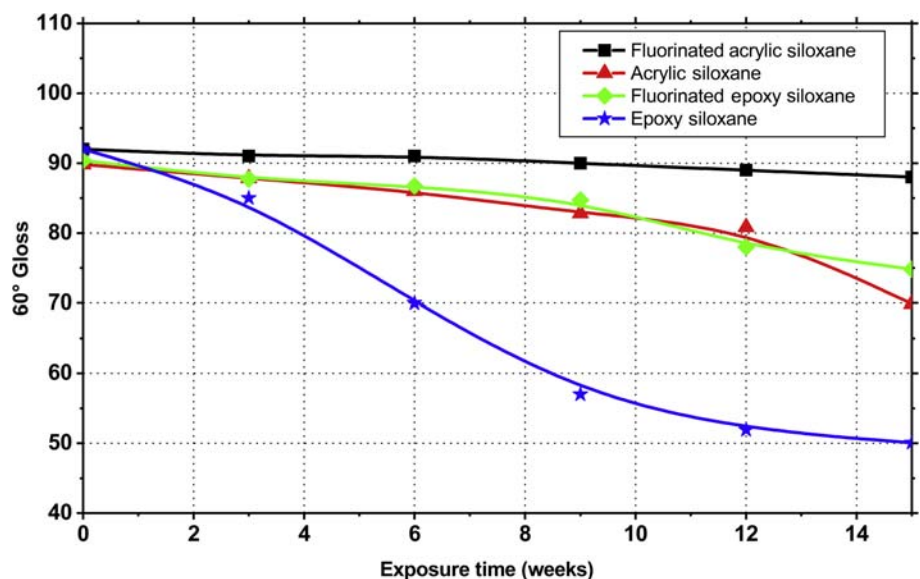


Figure 12.54 60° Gloss vs exposure time of QUV-B accelerated weathering of fluorinated siloxane hybrids [30].

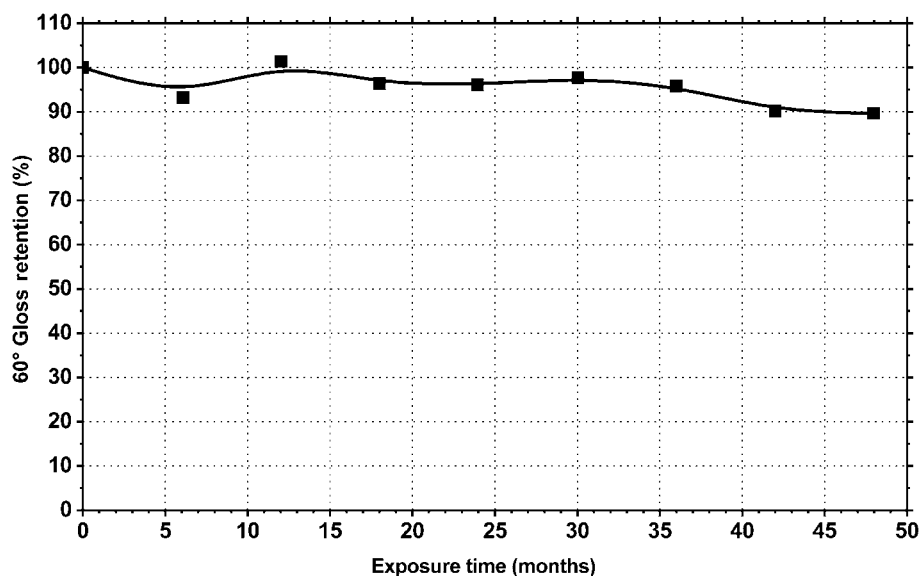


Figure 12.55 Gloss retention of epoxy-siloxane after outdoor weathering in Allunga Australia (5° north) [31].

Stabilization

Example stabilizers:

UVA: 2-(2'-Hydroxy-5'-methacryloxyethylphenyl)-2*H*-benzotriazole

HAS: *N*-Acetyl-3-dodecyl-1-(2,2,6,6-tetramethyl-4-piperidiny)pyrrolidine-2,5-*d*-ione

Data for polysiloxane materials is shown in Figs. 12.51–12.55.

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