Thioplast® G Polysulfides

SH-functionalized telechelic polymers

Thioplast®

Nouryon

Thioplast® G Polysulfides

Liquid polysulfide polymers with reactive SH-End groups

Introduction

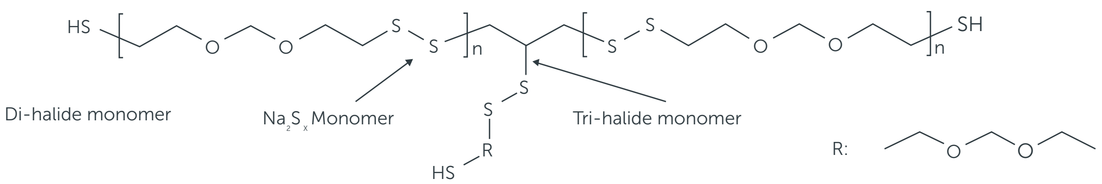
Liquid polysulfide polymers are the oldest specialty elastomers. They are low- to high-viscos polymers with highly reactive terminal thiol end- groups, characterized by outstanding solvent and chemical resistance, great electrical properties, low temperature flexibility, ultraviolet (UV) light, oxygen and ozone resistance, highly impermeable to many gases and moisture, good adhesion properties, and flex-crack resistance.

Liquid polysulfide polymers are used in the form of highly flexible joint sealants, adhesives and protective coatings.

Properties that make liquid polysulfide polymers useful are:

- Excellent oil, gasoline and solvent resistance
- Water and sewage resistance
- Low temperature and high temperature resistance

Polymer structure



Liquid polysulfide polymers are widely used in:

- sealants for insulating glass windows
- sealants in road pavement and building construction
- sealants to seal aircraft fuel tanks and fuselages
- epoxy modifiers to improve the flexibility of epoxy coatings and -adhesives
- intumescent protective coatings

On the market, liquid polysulfide polymers are well known under the brand name Thioplast® G polysulfides. Nouryon Functional Chemicals GmbH in Greiz, Germany, is the leading manufacturer of liquid polysulfide polymers under this brand name.

Nouryon offers eleven types of Thioplast® G liquid polysulfide polymers, differing in molecular weight, viscosity, SH-content and branching.

Thioplast®	Unit	G10	G 112	G 131	G 1	G 2267	G 12	G 21	G21F	G 22	G 44	G 4
Viscosity at 25°C	Pa*s	42 -48	38 - 50	80 - 140	41 - 52	22 - 38	38 - 50	10 - 15	10 - 15	10 - 15	max. 1.3	max. 1.3
Repeating units		26 - 28	26 - 28	31 - 38	26 - 28	20 - 24	24 - 28	13 - 15	13 - 15	13 - 15	< 5	< 5
Volatile ingredients	%	max. 0.3	max. 0.3	max. 0.3	max. 0.3	max. 0.3	max. 0.3	max. 0.5	max. 0.5	max. 0.5	max. 1.0	max. 1.0
Specific weight	g/cm³	1.28	1.28	1.28	1.28	1.28	1.28	1.28	1.28	1.28	1.25	1.25
Branching	mol% TCP calc.	0	0.5	0.5	2.0	0.7	0.2	2.0	1.45	0.5	0.5	2.0
SH-content	%	1.4 - 1.5	1.5 - 1.7	1.0 - 1.3	1.8 - 2.0	1.7 - 1.9	1.5 - 1.7	2.7 - 3.1	2.6 – 3.0	2.1 - 2.7	6.0 - 7.0	6.0 - 7.0
Free sulfur	%	max. 0.1										
Water content	wt%	max. 0.35										
Glass point	°C	ca. -55										
Fkashpoint	°C	> 230										
Specific heat	kJ/kg*K	ca. 1,26										
Heat of combustion	kJ/kg	ca. 24,075										
Storage stability	m	minimum 3 years in closed and original packaging at < 30°C storage temperature										

Thioplast® G polysulfides are aliphatic short chain liquid polymers with two consecutive sulfur atoms in the polymer backbone. They are functionalized by highly reactive thiol groups. Viscosity ranges from about 1.000 to 140.000 mPas.

Most common grades of Thioplast® G polysulfides have molecular weights between 2.000 to 8.000 Dalton and are widely used in highly flexible sealants in insulating glass, construction, coatings and aerospace applications.

Chain length, the molecular weight, SH-content and the level of branching respectively, expressed as the mol% of 1,2,3-Trichloropropane (TCP), are variable in order to offer suitable polymer types for different sealant or coating applications.

Branching ranges from 0 – 2 mol% TCP. The content of cross-linking agent (TCP) used in production of Thioplast® G polysulfides affect physical parameters like tensile strength, pot life, elongation and Shore-A hardness of the cured polymer.

The sulfur-sulfur bonds in the Thioplast® G polysulfides backbone will chemically interchange with themselves and with the mercaptan end groups.

It is possible, by blending two different Thioplast® G grades, to obtain a Thioplast® G polysulfide with intermediate molecular weight, SH-content and viscosity.

The same principle applies to branching. It is possible by blending two different Thioplast® G grades of the same or different molecular weight but different levels of branching to create a Thioplast® G grade with an intermediate level of branching. Heat and a basic amine catalyst will accelerate these interchange reactions.

The lower molecular weight polymers, like Thioplast® G4 and G44 polysulfides, are used as reactive diluents in sealant applications and as modifier polymer and curing partner to epoxy resins. They improve the flexibility of the resulting sealant, adhesive or coating.

Synthesis and chemical structure

The predominant monomer in the manufacture of Thioplast® G polysulfides is bis-(2-chloroethyl-) formal (diformal) and sodium polysulfide (Na2Sx) with a sulfur x- rank of 2.4 to 2.6.

Thioplast® G liquid polysulfide polymers are produced in aqueous dispersion by nucleophilic substitution polycondensation of Bis-(2-chloro-ethyl)-formal with sodium polysulfide.

During the Thioplast® G polysulfide synthesis and introducing of a tri-functional co-monomer (1,2,3-Trichloropropane, TCP) as branching agent, a high macromolecular (molecular weight of approx. 300.000 Dalton) and cross-linked polymer latex gets formed.

In order to achieve maximal chemical yield during the manufacture of the polymer, the sodium polysulfide component is applied in an excess to the organic components.

In consequence, the polymer network chains consist of organic segments which are linked by disulfide groups. There is no chlorine part of the polymer backbone.

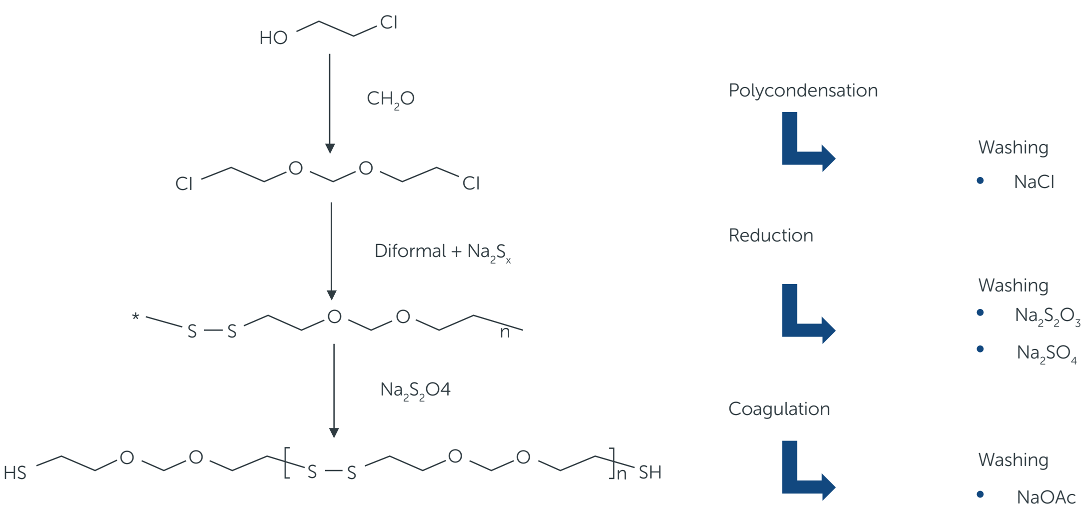
Polymerisation of mentioned monomers to Thioplast® G polysulfides takes place in an environmentally friendly water-based dispersion under the conditions of an emulsion polymerization.

The macromolecules get reduced to the required molecular weight and chain length by reductive chemical splitting with sodium dithionite and sodium sulfite. At the same time the split disulfide groups are converted into reactive thiol terminal groups and the residual high rank polysulfide groups (–RSx-) are transformed into disulfides.

The chain length, respectively the molecular weight and the level of branching of the final Thioplast® G polysulfide varied in order to offer suitable polymer types for different applications.

Schematic process descriptions can be found in the following scheme.

Schematic synthesis



Typical properties

Thioplast® G polysulfides are medium to high viscos liquids of light red-brownish color. The average molecular weight, as a measure of chain length and degree of branching, determines the viscosity. Consequently, the viscosity is the most important characteristic and accurate tested parameter of any Thioplast® G liquid polysulfide type.

Characteristics

Low / high temperature flexibility (-55 °C up to 140°C). Intermittent heat resistance to 150 °C.	High weathering and ageing stability against ozone, UV and O2.
O – 2 mol% TCP branching for increased elasticity and flexibilities. No-shrinkage during curing.	Self-healing properties of cured and uncured polymers due to exchange reactions of the di-sulfide based polymer backbone.
Exchange reactions, stress relaxation. Strength and physical resilience under dynamic conditions.	Health and Safety: No special precaution needed. Contains NO toxic tributylamine.
Best chemical resistance of all commercially available polymers against solvents, oils, jet fuels, bases etc.	Beside butyles, lowest rate of gas- and moisture vapor transmission of all commercially available polymers.
Allows polymerisation by oxidation-, NCO- and epoxy curing. michael-addition on acrylates.	Thioplast® G polysulfide and Thioplast® G polysulfide based sealants and adhesives in appropriate formulation does not corrode metals.

Thioplast® G polysulfides are soluble in solvents like benzene, toluene, dichloroethane, chloroform and in plasticizers such as phthalates, benzoates and chlorinated paraffins. They are partially soluble in aliphatic esters and Ketones, but insoluble in water, aliphatic hydrocarbons and alcohols.

Depending on temperature, up to 0.35 wt% water is soluble in Thioplast® G polysulfides, same as finely dispersed elemental sulfur.

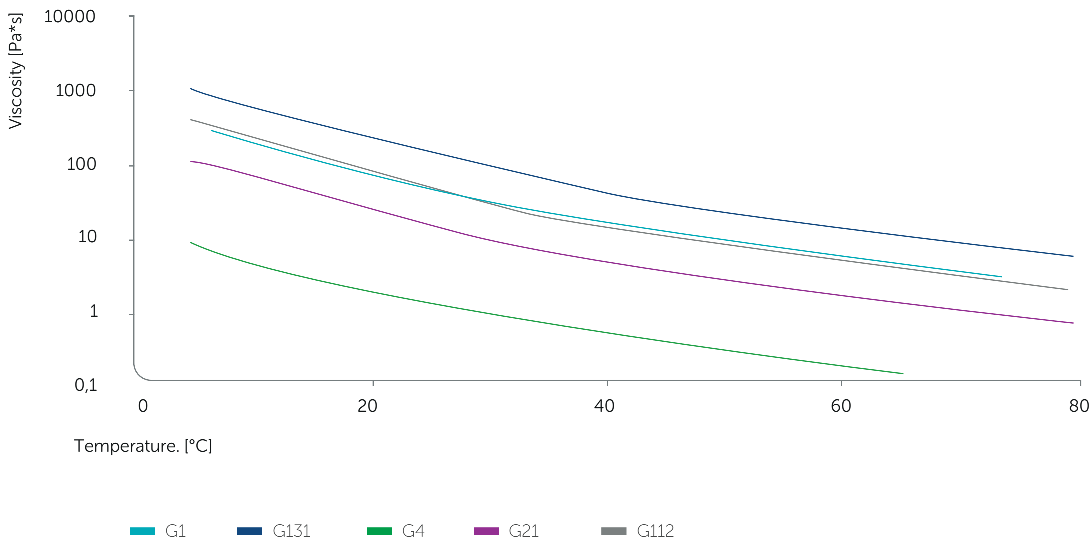
The sulfur chemically interacts with the disulfide groups of the polymer backbone and will be finally part of the polymer backbone.

Due to the highly reactive thiol end-groups, Thioplast® G polysulfides react under the influence of oxidizing agents at ambient temperature by forming a rubber-like polymeric network without shrinking effects.

Besides their high elasticity, cured Thioplast® G polysulfides

- show very good low temperature properties and excellent resistance to weathering, water, UV light, ozone, oils, fats, many chemicals, alkalis and diluted acids.
- are easy to process and therefore the ideal polymer for sealants, adhesives and coatings.
- do not get chemically attacked by most chemicals
- get destroyed by strong aqueous solutions of oxidising acids e.g. 50% sulfuric acid and 10% nitric acid. But, dilute acids and aqueous solutions of alkali metal hydroxides, chlorides, sulfates etc. will not degrade Thioplast® G polysulfides.
- get degraded by solutions of monosulfides in toluene through attack on the sulfur-sulfur bonds in the polymer backbone. This is the basis of a Thioplast® G polysulfide recycling and a useful way to remove cured Thioplast® G polysulfides based sealants from surfaces.

Viscosity vs. temperature of different grades



The resistance to serious swelling or degradation in water is one important characteristic of Thioplast® G polysulfides.

Their polymer backbone is resistant to hydrolysis. For this reason, Thioplast® G polysulfides and sealants based on Thioplast® G polysulfides exhibit excellent durability in application involving long term water immersion (e.g. water reservoirs, sewage treatment plants etc.).

Resistance to water in e.g. contaminated fuels is also a serious consideration in the sealing of aircraft fuel tanks.

Another requirement for durability in water is the resistance to bacterial attack and other biodeterioration processes. There is resistance of pure Thioplast® G polysulfides to a wide range of bacteria, including those having sulfur in their food cycle (e.g. Thiobacillus).

Poorly formulated sealant compounds with too low Thioplast® G content, get deteriorated rapidly though polymer reversion, exhibiting softening of the sealant surface up to a depth of 2-4 mm.

The mechanistic route is postulated as the bacterial attack of the plasticizer, producing acidic by-products capable of cleaving the Thioplast® G polysulfides backbone.

The optimum sealant formulation for sewage and water environment had a Thioplast® G content of higher 40wt%, manganese dioxide as curative and a chlorinated paraffin as plasticizer.

Major markets and application

Thioplast® G polysulfide applications include high quality sealants for e.g. insulating glass units, building and road construction, water canals, sewage plants, gasoline stations, runway constructions at airports, concrete coatings, intumescent coatings and sealants in fresh water tank applications, boat hulls and decks and printing rolls.

In aerospace applications, sealants based on Thioplast® G polysulfides are used e.g. for aircraft integral fuel tanks, all sealing in the fuselage and windows and used as electrical potting compounds.

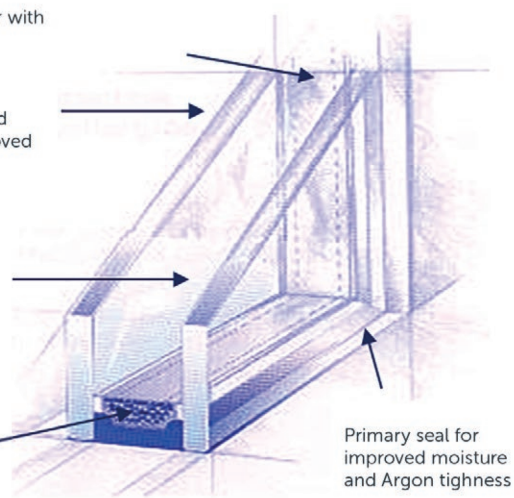
Insulating glass sealants

Dual seal windows contain a primary seal along the edge of the spacer usually made from polyisobutylene (PIB). PIB has the lowest permeability to moisture vapor transmission and extends the lifetime of the insulating glass (IG) unit.

The outer edge of the IG-unit is closed off with the secondary seal of a Thioplast® G polysulfides based IG sealant.

A secondary sealant has many important functions in the insulating glass unit. The most important function is to hold the unit together. A secondary sealant must be strong enough to maintain the cavity between the glass panes, but also it should remain elastic enough to compress and stretch as environmental changes dimensionally stress the unit. Thioplast® G polysulfides provide both the strength and elasticity required. These properties can be tailored to any specific environment, be it the Alaskan tundra or the Gobi desert.

The intermediate air space is nowadays filled with a nobel gas such as argon or krypton to improve the insulation effect. Thioplast® G polysulfides have the lowest permeability for moisture vapor and inert gases compared to any other polymer used in secondary IG-sealants.



Other sealants such as silicones have a three times higher gas permeability and can be used in dual-seal IG-units only. That relies mandatory on the integrity of the primary PIB seal.

One of the signs that an insulating glass unit has failed is clearly the moisture condensation inside the panes of the inner cavity. Therefore, it stands to reason that the seals should act as a barrier to moisture incursion. Thioplast® G polysulfides based sealants form a very tight chemical lattice that is smaller than the diameter of a water molecule. Water is obstructed from passing through and long-term moisture protection is achieved.

Thioplast® G polysulfides based IG- sealants can be used either in dual-seal (with PIB) or single-seal (without PIB) IG-units. If there are small leaks in the primary seal of dual-seal IG-units, the Thioplast® G polysulfides based IG-sealant provides a perfect safety backup for the lifetime of the IG-unit.

Besides water vapor and gas diffusion, other requirements for good edge sealants are water- and UV resistance, heat and cold resistance (–50 to 90° C), adhesion to glass and metal, and easy application. Thioplast® G polysulfides based IG- sealants show here as well the best performances.

With Thioplast® G polysulfides based sealants a great curing characteristic could be achieved. Thioplast® G polysulfides are cured with readily available catalysts, can be formulated to give the optimal pot life, and completely cure over a wider mixing ratio range than other two component sealants. Another criterion is compatibility with other adhesives and sealants used in the manufacturing and glazing processes.

Thioplast® G polysulfides are more chemically resistant to other typical components than silicones or polyurethanes, so a secondary seal won’t be compromised by what a glazer might be using in installation.

Aerospace Sealants

Today all civilian and military aircraft use Thioplast® G polysulfides based aerospace sealants, adhesives and coatings, not only to seal fuel tanks, but throughout the fuselage.

Many applications call for Thioplast® G polysulfides based aerospace sealants according to a specification such as a Mil Spec, ASTM, SAE, ISO or an internal company specification, such as an Airbus or Boeing specification.

Thioplast® G polysulfides based aerospace sealants have exceptional good resistance to kerosene, gasoline, diesel and jet fuel and has made them the standard polymer for aerospace sealants, adhesives and coatings.

Beside their outstanding resistance to fuels, Thioplast® G polysulfides based aerospace sealants show excellent adhesion to many different materials such as various metal alloys, titanium and protective coatings used in aircraft construction.

The sealants must also perform well in extremely variable weather conditions.

Additionally, they have very good low temperature properties.

There are stringent requirements for these sealants:

- Resistance to swell, leaking and attack in jet fuel, water and antifreeze agents
- Resistance to hydraulic oils
- Adhesion to aluminium, titanium, other metals and composites
- Strength and resilience under dynamic conditions
- Low temperature flexibility to -55°C
- No polymer crystallisation below -55°C
- Intermittent heat resistance to 150°C
- Low permeation to fuel vapor, water vapor and air
- Resistance to UV

Construction Sealants

Thioplast® G polysulfides-based construction sealants have reputation for high performance worldwide.

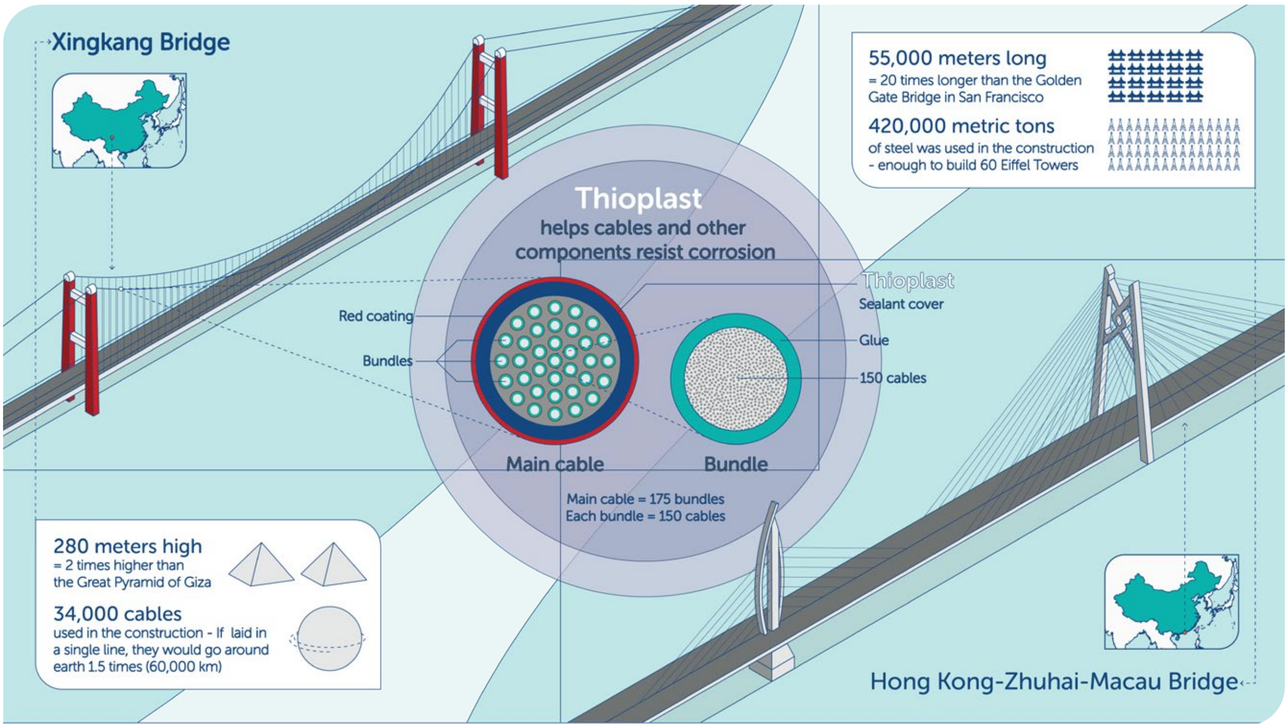
Thioplast® G polysulfides-based construction sealants are used to seal glass in aluminium frames, concrete moving joints, steel/stone joints and in many other applications.

Immersion in water for long periods or continuous exposure to high humidity are especially difficult conditions for organic-based materials to withstand.

Sealants for use in water purification or wastewater treatment plants have special demands for physical, chemical, and microbiological properties. Thioplast® G polysulfides-based sealants have proven themselves useful in this area.

Thioplast® G liquid polysulfide polymers makes them useful as sealants and coatings for secondary containment areas, where they prevent chemicals, solvents, fuels etc. from seeping into the ground in the event of spillage or a storage tank leak.

Thioplast® G liquid polymers
protect some of the world's most complex structures



Thioplast® G polysulfides-based coatings and sealants are also used for bridges, air fields, and road construction. At Nouryon, many of our products help protect and improve the durability of bridges and other structures.

For example, we work with partners in China to protect some of the most technologically complex bridges in the world. Two such bridges are the Xingkang bridge and the Hong Kong-Zhuhai-Macau bridge, or HZMB

The 1400-meter-long Xingkang bridge is an engineering marvel located in the Sichuan province. At 280 meters, the bridge is one of the highest in world, and it's also one of the longest suspension bridges ever built, with a main span of 1100 meters.

Meanwhile, the HZMB connects Hong Kong, Zhuhai, and Macau. The bridge is a 55-kilometer-long system consisting of a series of three bridges, and four artificial islands to connect the various sections. It is both the world's longest sea bridge and the longest fixed link on earth - 20 times longer than the Golden Gate bridge in San Francisco.

For these bridges, durability is crucial, and Nouryon's Thioplast® G polysulfides play a key role in ensuring that durability.

Thioplast® G liquid polysulfide polymers are used in sealants applied to cables and other bridge components to resist corrosion.
As they cure, these polymers become rubber-like and show excellent resistance to weathering by water and UV light. As a result, Thioplast® G polysulfides help extend the service life of a cable from 60 to up to 100 years, increasing safety and reducing the need for maintenance.

Thioplast® G polysulfides' superior performance has helped make it the leading product used in polysulfide based sealants and Nouryon the global market leader in liquid polysulfide polymers. Nouryon is the only company in China with the product performance and expertise necessary to meet the requirements of these bridges.

Through Nouryon's focus on developing the essential chemistry behind Thioplast® G polysulfides, we help our customers achieve what was once thought impossible and help communities safely explore once inaccessible places, stay connected, and make the most of their time.

Epoxy flexibilizers

Thioplast® G liquid polysulfide polymers are used as flexibilizer in epoxy based sealants, adhesives or coating formulations.

Compounders can target the desired properties for a specific application through the selection and balance of the epoxy resin, the Thioplast® G polysulfides – epoxy ratio, curing agent and filler.

Most of the compounds are two-component: One component contains the epoxy resin, the second contains the Thioplast® G polysulfides and the curing agent, mostly amine based.

Thioplast® G polysulfides – epoxy formulations are used for a variety of applications including adhesives, protective coatings, barrier coatings, electrical potting compounds, fire protection (intumescent) coatings, resilient plastic tooling materials, aggregate epoxy - Thioplast® G polysulfide mortars and surface sealers.

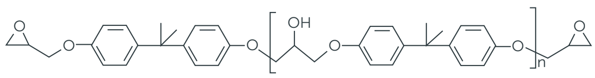
Thioplast® G polysulfides has been promoted as a flexibilizer for epoxy resins and used up to levels of 50 wt%. This level of incorporation affects the physical strength of an epoxy system and lowers the heat deflection temperature (ASTM D648).

The use of the low viscos G4 and G44 polymers in fire resistant building sealants is a further important application area. Intumescent polysulfide sealants form a strong carboniferous foam on burning. The foam acts as barrier to heat and to the spread of fire.

Thioplast® G polysulfides based intumescent sealants have all properties of a standard polysulfide based building sealant like

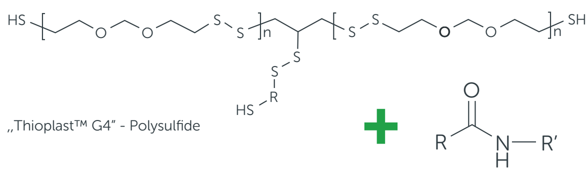
- Flexibility over a wide temperature range
- Resistance to weathering
- Resistance to chemicals, solvents and water
- Adhesion to a wide range of substrates
- Ease of application
- Non-staining to adjacent surfaces

A component



„EPON 828" - BisphenolAexpoxy derivative

B component



„Thioplast™ G4" - Polysulfide

„Ancamide 702B75" - Polyamide

Properly designed Thioplast® G polysulfide-epoxy blends have the following characteristics:

- Improved adhesion to a variety of substrates, including aluminium, rusty and oily steel and wet concrete
- Improved durability, especially in high humidity or corrosive environments
- Improved chemical resistance, particularly to fuels and oils
- Improved impact resistance and flexibility down to -30°C (depending on the epoxy-resin used)

Thioplast® G polysulfide-epoxy systems applications:

- Underwater adhesion
- Adhesion of construction elements in wet locations such as tunnels
- Coating for use in highly corrosive environments found on ships, offshore oil platforms, chemical plants, pipelines and storage tanks
- Repair of porous and leaking fuel storage tanks
- Durable intumescent coatings for steel
- Coatings for swimming pools and water parks
- Crack repair of epoxy floor coatings

Summary of major markets and applications for different grades

Product and property	Application area
Sealant: Oil, fuel and solvent resistance	• Aircraft sealants • Airport pavements • Petrol stations, to prevent the contamination of groundwater • Areas where spillage of aircraft fuel or hydraulic directive fuel is common • Areas where solvent spillage is common • Chemical plants and refineries • Chemical warehouses • Paving associated with motorways and bridge decks.
Sealant/coating: Water and sewage resistance	Potable water tanks, waste water tanks, irrigation canals, sewage storage and treatment tanks
Sealant: High-temperature resistance	In building structures to reduce the risk of fire (e.g., expansion and compression joints, construction gaps, fire protection panels, fire doors, pipe outlets in buildings (intumescent coating)
Sealant: Ultraviolet radiation and ozone resistance, low-temperature resistance.	• Expansion and compression joints • Building and civil engineering application
Coating: Oil and solvent resistance	To prevent the spillage of secondary containments above or below ground level in fuel storage tanks
Sealant: Gas and moisture vapor transmission	• Insulating glass sealants • Protective coating

Curing

Curing of Thioplast® G polysulfides to high-molecular-weight elastomers is most widely done by oxidizing the terminal thiol groups to disulfides.

The most commonly used curing agents are oxygen donors such as manganese (IV) oxide, Inorganic peroxides and organic hydroperoxides, lead peroxide, permanganates or dichromates.

Theoretically, the Thioplast® G polysulfides converts from 2RSH to R-SS-R regardless of the dioxide used. In practice, each dioxide takes the polymer to different levels of cure.

In consequence of this chemical reaction, a polymer network based on disulfide structures gets formed. This occurs at ambient temperature within minutes to a few hours depending on the selected curative.

Inorganic oxides and peroxides are insoluble in liquid Thioplast® G polysulfides and hence the cure can be classed as heterogeneous.

Curatives with a stronger oxidation characteristic, such as permanganates or dichromates, yield a very high modulus sealant with improved thermal resistance.

Organic hydroperoxides tend to yield high-modulus elastomeric polymers.

The curing mechanism of inorganic peroxides and organic hydroperoxides like calcium peroxide, zinc peroxide, barium peroxide, sodium perborates or organic hydroperoxides like t-butyl hydroperoxide or cumene hydroperoxide is based on the chemical reaction with water or moisture that forms hydroperoxide (H2O2).

Due to the fact, that organic hydroperoxides are highly reactive and additionally soluble in Thioplast® G polysulfides, curing reaction must be strictly controlled to avoid chain scission and reversion. Organic hydroperoxides which yield acidic by-products by decomposition should be avoided since these can lead to polymer degradation.

By far, the most widely used inorganic peroxide to cure Thioplast® G polysulfides are specifically activated manganese (IV) oxides.

Recommended suppliers of activated manganese (IV) oxide are Shepherd in the US (Grade: Type II NG) or Honeywell in Germany (Grades: FA, L-Prime, FA-N).

Cumene hydroperoxide is useful for obtaining white and pourable sealant formulations having high compression set resistance.
T-butyl hydroperoxide will cure Thioplast® G polysulfides by forming a polymeric network with good resistance against UV.

Calcium peroxide and sodium perborates are commonly used to prepare one component systems but also two component systems if white or colored sealants are requested.

Dichromate cured polysulfide sealants have superior resistance to swelling in hot water than those cured with manganese (IV) oxide.

Commonly used curatives

Manganese (IV) dioxide

- Improved heat resistance and lower toxicity.
- Good UV resistance and adhesion even during weathering.
- Standard acceleration gives about 30 minutes of work life and curing within approximately 8 hrs at 23/50 NC.

Calcium peroxide

- requires moisture for activation.
- Provide light coloured one-part moisture-curing systems.
- BaO used as a dehydrating agent for system shelf-life stability.

Cumene hydroperoxide

- Provides good compression set resistance.
- Used more in casting systems than in adhesives or sealants.

Sodium perborate

- Provides light coloured, non-staining one- or two-part sealants.
- Provides low modulus, high elasticity, good water, UV, and mold resistance.

Inorganic chromates

- Used in older aircraft sealants to improve corrosion- and heat resistance.
- HSE suspicion. Replacement ongoing.

Other influential additives include acids and bases. All reactions involving -RSH can be catalyzed by the addition of a base; conversely, can be retarded by the addition of acid.

In practice, amines and similar compounds are used as catalysts, while weak acids such as stearic or oleic acids are used as retarders. It has been found that organic (mono) mercaptans, used as chain stoppers to reduce the amount of crosslinking, can have a severe retardation effect on curing even at a very low content.

Activated MnO2 is relatively insensitive to the mixing ratio as special additional advantage.

Traces of water have a strong catalytic effect on the curing speed.

Curing speed increases as water is additionally released during the oxidation curing of the thiol groups by activated MnO2 as a kind of autocatalytic reaction.

The easiness of the oxidation of the thiol terminal groups is the reason for the dominant importance of the oxidative curing route.

The curing agent should be added in a significant excess relative to the stoichiometric conversion of existing SH-groups.

Curing takes place at room temperature but can be significantly accelerated at higher temperatures.

Oxidizing agents used to cure

Curative	Accelerator (Retarder)	Technology where applied
Lead Peroxide	Sulfur (Stearic acid, Lead stearate)	Building sealants
Manganese Dioxide	TMTD, TMG, Water	Building sealants, civil engineering, insulating glass, aircraft sealants, coatings, tapes
Na- Perborate	TMG, BaO, NaOH	Building sealants
Na- Dichromate	Water, Base	Aircraft sealants
K- Permanganate	Water, Base	Building sealants
Zinc Oxide	TMTD	Hydroxyl terminated millable rubber
Zinc Peroxide	Ca(OH)2 , TMTD	Building sealants
Calcium Peroxide	BaO	Building sealants
Cumene hydroperoxide	Bases, TMG	Building sealants

Water has an essential catalytic effect on the cure reaction of Thioplast® G polysulfides. Most reactions can be permanently or severely retarded by the removal of trace water. Zeolites and BaO have been found as water scavengers and are used in the design of water-activated single-component sealant formulations.

Content of curative to cure

Curative	Amount in g/100 g Thioplast® G polysulfide
Manganese (IV) dioxide	3.9 x SH [%]
Calcium peroxide / BaO	4.3 x SH [%]
Sodium perborate monohydrate	2.1 x SH [%])
Cumene hydroperoxide / t-Butyl hydroperoxide	4.6 x SH [%]
Lead dioxide	4.7 x SH [%]

In two-component sealants, a level of 0.1 - 0.3 wt% water is mandatory in the MnO2-based curative part to initiate the curing.

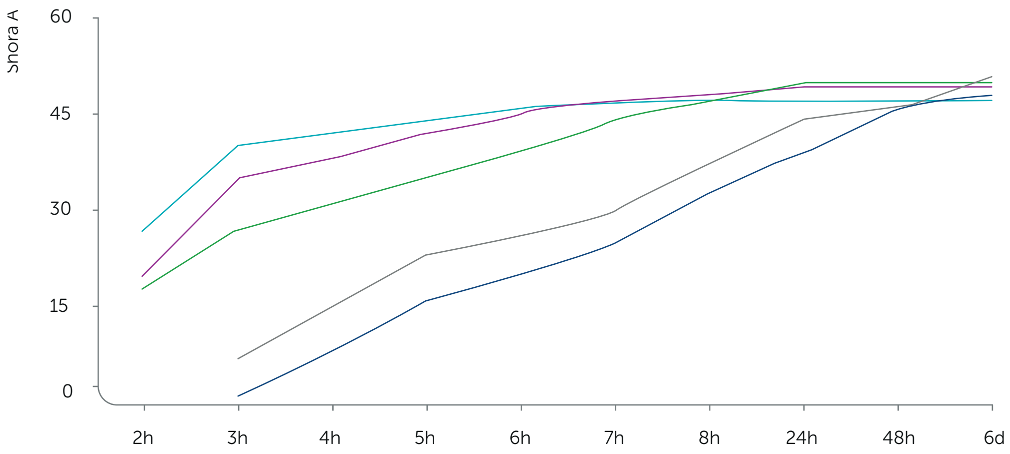
It is interesting that BaO, which is used as water scavengers to remove water to retard curing during the preparation of single-pack systems, also acts as a catalyst. In this case, BaO attracts water and creates a basic environment by forming Ba(OH)2 to catalyze the cure once sufficient water is present.

Oxidizing agents to cure Thioplast® G polysulfides are formulated as curing pastes using fillers, plasticizers and curing rate modifiers, like acids (e.g. stearic- or isostearic acids) with retarding- or amines with acceleration effect.

Physical characteristic of cured Thioplast® G polysulfides (pure polymer, MnO2 paste cured)

		Thioplast® G12	Thioplast® G10	Thioplast® G21	Thioplast® G2
Pot Life	min	45	45	30	30
Elongation@break	%	290	350	120	210
Shore A Hardness		32	30	39	33

Curing characteristic at different mixing ratios



Effect of cross-linking on the physical properties of liquid polysulfide polymers (MnO2 paste cured)

	Thioplast® G1	Thioplast® G112	Thioplast® G12
Polymer [phr]	100	100	100
Branching [mol% TCP]	2.0	0.5	0.2
SRF Carbon Black [phr]	30	30	30
Stearic Acid [phr]	1	1	1
TMTD Catalyst	6	6	6
Tensile Strength [N/mm2]	3.44	3.96	3.38
Tensile strength @300% [N/mm2]	2.58	1.72	1.38
Elongation [%]	210	450	520
Shore A Hardness	53	45	40

Stoichiometric controlled chemical reactions of Thioplast® G polysulfides with dienes, epoxies, thiirans, vinyl-and allylethers, and phenolic resins are additionally possible and of commercially use.

Additionally, the thiol end grWoups of Thioplast® G polysulfides are highly reactive to di-isocyanates, such as 1,3-toluene di-isocyanate (m-TDI), diphenylmethane-4,4´-di-isocyanate (MDI) or multifunctional liquid isocyanates.

Using Thioplast® G polysulfides instead of common hydroxy-terminated polymers brings the physical advantages of Thioplast® G polysulfides to the cured product. Thus, good chemical and solvent resistance, weatherability, adhesion etc. can be attained.

In addition, isocyanate-cured Thioplast® G polysulfides based sealant systems have advantages over oxidative-cured systems, such as improved adhesion to plastic substrates paired with high elongation and consequently high tensile strength.

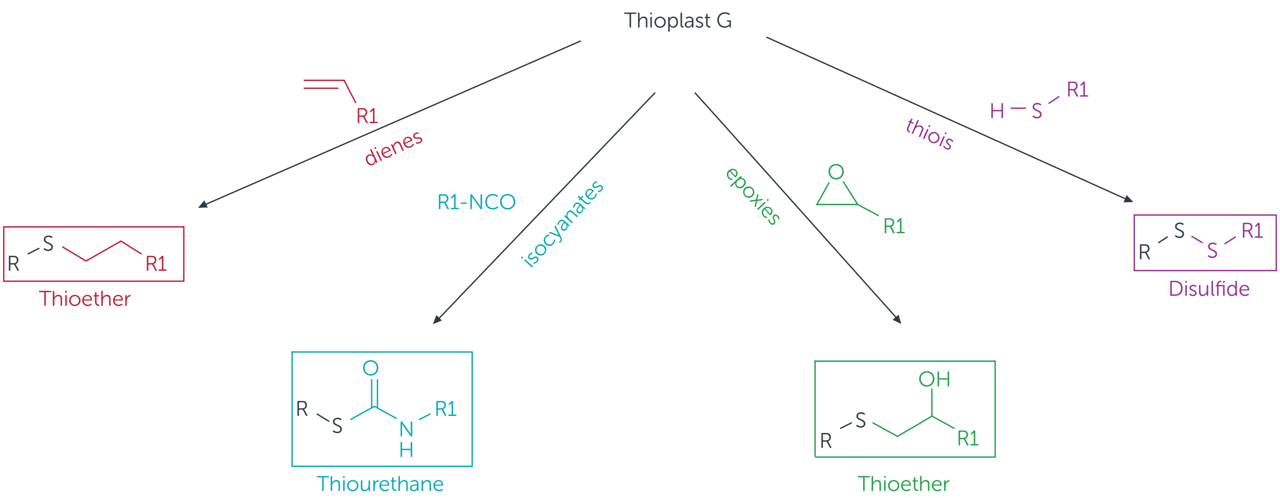
Most commercially used is the stoichiometric addition reactions of Thioplast® G polysulfides with novolac- or bisphenol A/F epoxy resins at ambient temperature.

Formulation with tertiary amine like e.g. 1,4-diazabicyclo[2.2.2]octan (dabco 33LV) or 2.4.6-tri-(dimethylaminomethyl)-phenol (ancamine K54) with a small amount of ethanol (lewis acid) greatly accelerates the cure and will lead to high tensile strength and high elongation.

In formulations, developed for adhesives or sealants, the epoxy resin is the major component and the Thioplast® G polysulfides is used in different ratios to adjust the level of flexibilization.

By adding up to 50 wt% of G4 or better G44 to A/F-epoxy resins, an increased flexibility, tensile strength, greater impact resistance, less brittleness and elongation could be achieved.

Stoichiometric controlled curing



At elevated temperatures, phenolic resins get cured with stoichiometric added Thioplast® G polysulfides through a polycondensation reaction by releasing water. The product may be considered as a block copolymer of the rigid phenolic resin and the flexible Thioplast® G polysulfides.

This results in adhesives with high flexibility, high impact strength, excellent chemical resistance and good adhesion to many substrates.
A 2-component sealant recipe is supplied with the Thioplast® G polysulfides formulated with pigments, fillers (silica, natural $CaCO_3$ and precipitated $CaCO_3$) and plasticizer along with other additives such as adhesion promoters and antioxidants. The curing agent is formulated as a thoroughly mixed or milled paste based on plasticizers, fillers and catalysts.

In 1-component Thioplast® G polysulfides based sealant recipes, Ca- or Ba-peroxide is commonly used for curing. The formulation does not cure as long as the system is moisture free. When exposed to the air, moisture will penetrate the compound and forms H2O2 that finally initiates the curing.

Manganese (IV) dioxide as curative

The major hardener used for curing Thioplast® G polysulfides is an activated manganese (IV) dioxide with the function of an oxidizing agent to cure the SH-end groups generating disulfide linkages.

$$2\ \text{-R-SH} + [0] \longrightarrow \text{-R-SS-R-} + \text{H20}$$

The oxidation of Thioplast® G polysulfides by manganese (IV) dioxide strongly depends on the surface and size of the manganese (IV) dioxide particle, activation and on the soluble alkali on it.

Activated manganese (IV) dioxide is available in several grades and varies from grade to grade in water content, total alkalinity, pH and particle size.

The two-stage oxidation of liquid polysulfides by activated manganese (IV) dioxide

Comparing the "stick work life" of manganese (IV) dioxide cured Thioplast® G polysulfides with the total rate of curing, the time for the start of the cross-linking (stick work life) should be at about 80 % of the chemical conversion (oxidation) of the thiol end groups.

The next 20% of the conversion, or essentially the complete cure (hardening), should occur in an additional period of twice the stick work life.

In practice, a far longer period for the cure is observed. Conclusion is, that activated manganese (IV) dioxide cures Thioplast® G polysulfides at a relatively rapid rate, but once the molecules are immobilized, the availability of the oxidizing manganese (IV) dioxide surface declines strongly.

Highly flexible Thioplast® G44 – epoxy blend

Effect of accelerator "ageing" on the characteristics of the system

The decline in alkalinity of the system will gradually increase the stick work life and the ultimate cure rate of Thioplast® G polysulfides based sealants.

Nevertheless, a given amount of oxidation and availability of acid and bases will have wildly different effects on the stick work life.

For activated manganese (IV) dioxide, the higher alkalinity will generate a much greater oxidation rate.

This rate is proportional to the alkali concentration in the MnO2 particle and surface. In fact, the oxidation ability of manganese (IV) dioxide is nil at a pH of 7.

Extra added water increases the cure rate of the Thioplast® G polysulfides as a contradictory effect from the loss of alkalinity. The manganese (IV) dioxide particle basically is already quite wet and water is present in the sealant base as a result of the water content out of the fillers.

Such water will increase the initial cure rate (stick work life) but have an unfavourable effect on the second cure rate (hardening) of Thioplast® G polysulfides. It does this by literally extracting the alkali from the surface of the manganese (IV) dioxide particle during ageing of the curative by putting it into solution or dispersion and shorten the gel time.

As a result, the manganese (IV) dioxide surface get inactivated for the final hardening step because of the missing alkali.

The effect on the slope of the work life cure curve can become disastrous under such conditions and needs to take in account proper formulated Thioplast® G polysulfides based sealant recipes.

In an interesting series of experiments, an activated manganese (IV) dioxide, containing approx. 0.9 % sodium hydroxide and approx. 3 % water, was dehydrated, in one case to zero water content and in the other case 2 % additional water was added to the system.

In both cases, where the system was dehydrated and where additional water was added, the product failed to cure completely. The resulting Thioplast® G polysulfides based sealants had a Shore A of only 25 (versus 50 as a control) and were surface tacky.

Effect of variables on the cure of Thioplast® G polysulfides with manganese (IV) dioxide

Polar solvents and plasticizers

Like water, polar solvents and plasticizers, whether in the base or the accelerator, extract water and some alkalinity from the manganese (IV) dioxide particle, thereby shortening the stick work life, but interfering with final cure.

Thus, methyl-ethyl-ketone will lower the ultimate hardness of Thioplast® G polysulfides based sealants by inactivating the manganese (IV) dioxide surface.

Heat

The effect of heat is not unlike to that of polar solvents.

At higher temperatures, the Thioplast® G polysulfides themselves plus any other polar ingredients are better solvents for the hydrated manganese (IV) dioxide surface and thereby will inactivate it.

Thus, we have the strange result of many manganese (IV) dioxide cured Thioplast® G polysulfides based sealant formulations: Quick-set times at elevated temperature, but hardening rates are appreciably lower than at room temperature.

If toluene is used as solvent, higher ageing temperature will drive the toluene out of the sealant surface and will increase the polarity of the sealant.

The surface desiccates, causing a transfer of alkaline from the surface of the manganese (IV) dioxide particles into the Thioplast® G polysulfides based sealant matrix, with the consequence of a tacky and uncured sealant layer due to missing alkali on the activated manganese (IV) dioxide surface.

Stearic acid is relatively ineffective since its high molecular weight requires large amounts for significant neutralization of the alkali on the manganese (IV) dioxide surface.

At the same time, the neutralization reaction produces free water which greatly shortens the stick work life but lengthens the cure rate.

Effect of acids on cure rate and cure slope

Acids, such as stearic acid or isostearic acid, show relatively small influence on cure rate but unfavourably disturb the cure slope.

This is conveniently defined as the ratio of time to reach Shore A 20 divided by the stick work life time. Stearic acid seriously affects the adhesion ability of Silane adhesion promoters as well.

Effect of active manganese (IV) dioxide concentration

The cure time and the cure slope of Thioplast® G polysulfides change with the concentration of active manganese (IV) dioxide. The effect is dramatic near the equivalence point but declines as the excess manganese dioxide increases.

Effect of other additives - Inhibitors

Phenolic resins, as well as epoxies, greatly retard and even stop manganese (IV) dioxide cures of Thioplast® G polysulfides, even at very low contents. They increase the cure time and lower the slope of the cure curve.

Effect of other additives - activators

TMTD

Tetramethyl-thiuram-disulfide (TMTD) has been found to be a very useful activator ("catalyst") for the manganese (IV) dioxide related oxidation of Thioplast® G polysulfides.

TMTD is the most applied activator in the curative of Thioplast® G polysulfides based sealants and get used as a primary or secondary accelerator in multiple blend accelerator systems together with Di-phenyl-guanidine (DPG) or carbamates like zinc dimethyl-dithio-carbamate (ZDMC).

As major reason for the very good activation performance of TMTD in Thioplast® G polysulfides based sealants, it is believed, that TMTD is sufficiently soluble to be able to cross the phase barrier between the manganese (IV) dioxide particle and the increasingly immobile thiol in a cured or partly cured sealant matrix.

DPG

Di-phenyl-guanidine (DPG) is used as primary accelerator in Thioplast® G polysulfides based sealants and leads to sealants with high tensile strength performance.

As a rough guidance, content of DPG in Thioplast® G polysulfidesbased sealants need to be in the range of 20 to 25% of the TMTD content used in the curative.

ZDMC

Zinc di- methyl-dithio-carbamate (ZDMC) is a very fast primary or secondary (ultra) accelerator in the curative of sealants based on Thioplast® G polysulfides. Compared to DPG or TMTD, ZDMC gives faster cures and leads to higher tensile strength in cured sealants.

Problems with TMTD

Because of its di-sulfid structure, TMTD takes part in the cross-linking reaction during the cure, giving products of higher hardness than would be obtained by the given TCP cross-link density. In this respect TMTD is not unlike well dispersed sulfur.

It has further been noted, that TMTD might cause adhesion difficulties, again like sulfur, in a certain excess.

Therefore, the amount of TMTD should be mandatory limited to the requirements of the end use. It is recommended to limit the TMTD content in the curative to approx. 1.7 wt% to avoid cross-reactions with the Thioplast® G polysulfide.

TMTD chemically reacts with Thioplast® G polysulfides rather rapidly when added to the sealant base. In consequence, oxygen of the air will oxidize the SH in Thioplast® G polysulfides generating skinning on the sealant base surface.

If TMTD is added to the curative, the oxidation potential of the manganese (IV) dioxide towards organic substances is increased. But fairly-stable plasticizers readily will get oxidized, even at room temperature. The effect is even dramatic if an organic amine such as DPG or TMG is additionally used in the curative as co-activator.

Properties of cured liquid Thioplast® G polysulfides

General aspect

The use of Bis-(2-chloroethyl) formal as the predominant monomer in the manufacture of Thioplast® G polysulfides results in the formation of polymers with very good low temperature properties. The glass-transition temperature of these polysulfide polymers is at approx. -55°C. In addition, Thioplast® G polysulfides do not have any tendency to crystalize above the glass-transition temperature.

Sulfur is the obvious distinguishing feature of a Thioplast® G polysulfides, accounting of around 37% by weight. This determines the solubility parameter of the polymer and imparts resistance to swell in hydrocarbon fuels and solvents and significant chemical resistance.

The resistance to ageing, to hydrocarbon fuels and solvents and low temperature flexibility will be proportional to the level of Thioplast® G polysulfides used in the sealant formulation.

Swelling in solvents is directly related to the degree of crosslinking in the final cured Thioplast® G polysulfides.

Exceptional good swelling resistance of Thioplast® G polysulfides is noticed in hydrocarbons, gasoline, jet fuel, diesel, esters, ethers and ketones.

In addition, Thioplast® G polysulfides show excellent oxygen and ozone resistance, gas- and moisture impermeability and crack resistance.

The formal group, as part of the polymer backbone, is responsible for this low-temperature flexibility.

The absence of carbon-carbon double bonds or aromatic structures in the polymer backbone significantly reduce the sensibility against oxygen, ozone, and UV. Thus, systems based on Thioplast® G polysulfides are generally resistant to weathering.

The polymer backbone of Thioplast® G polysulfides consists of hydrocarbon chains containing ether (acetal) linkages, joined by disulfide bridges. Consequently, all Thioplast® G grades are slightly polar polymers and give excellent resistance to gas permeation and have good low water vapour transmission rates. These two characteristics, excellent gas permeation and low water vapor transmission rate, are the most important feature parameter for insulating glass sealants and protective coatings.

Formulations used in aerospace applications tend to have polymer contents of around 60% by weight or even higher.

For construction sealants the range is 20 to 35% by weight.

In contrast, sealants used for manufacturing of insulating glass sealants have polymer contents in the range of 20 to 25% by weight.

The lifetime of the cured sealants will depend on how much the sealant is exposed to UV, to chemicals and to water.

Poor adhesion, fungal growth and staining of adjacent surfaces are related more to the use of high levels of inappropriate plasticizers.

Thioplast® G polysulfides are unique in their ability to internally relieve stress even in the cure state by interchange reactions between thiol terminal groups and disulfide linkages.

The rate of stress relaxation depends on temperature, UV light or catalysts, especially basic inorganic salts such as NaSH, NaOH and primary or secondary amines. The process is energized by the strain energy in the vicinity of two polymer disulfide groups.

The energy of activation for this interchange process is at approximately 100 kJ/mol for polymers with S2, S3 or S4 structures in the polymer backbone.

The observed stress relaxation may mainly result from trace quantities of S3 or S4 structures in the polymer backbone.

Solvent Resistance

A very important property of Thioplast® G polysulfides is their outstanding resistance to solvents, aliphatic hydrocarbons, aviation fuels and mineral oil.

The solvent resistance of Thioplast® G polysulfides depends quite closely on the sulfur content of the polymer and can be improved by addition of dispersed sulfur in the range of 0.1 wt% that generates in consequence S3 or S4 structures in the polymer backbone.

Thioplast® G polysulfides in the uncured state are completely miscible with solvents like benzene, toluene, dichloroethane, chloroform and similar solvents and in plasticizers such as phthalates, benzoates and chlorinated paraffin's. There is no chemical compatibility to water or aliphatic hydrocarbons. In the cured state, this kind of solubility will disappear and a relatively low-level swelling characteristic will remain.

Fuel resistance of cured Thioplast® G polysulfides vs. other polymers (7 days immersion at 20°C)

The swelling characteristic is strongly related to the degree and quality of the cross-linking in the final cured Thioplast® G polysulfides. Swelling of Thioplast® G polysulfides depends therefore on the curing performance caused by the selected manganese (IV) dioxide or any other peroxides used.

Additionally, the TCP-branching of the selected Thioplast® G polysulfides is highly important. In fact, G1 with branching of 2 mol% TCP shows lower swelling tendency in solvents compare to G112 with four times lower TCP branching.

Very good resistance to swell is noticed in aromatic hydrocarbons, alcohols, esters, ethers and ketones.

Liquid Thioplast® G polysulfides show certain swelling tendency in most halogenated hydrocarbons and are in consequence weak in the swollen state. But, Thioplast® G polysulfides are resistant to swell in Chloro-Fluro-carbons (CFC´s).

	Thioplast® G1	Thioplast® G112	Thioplast® G12
Polymer [phr]	100	100	100
Branching [mol% TCP]	2.0	0.5	0.2
SRF Carbon Black [phr]	30	30	30
Stearic Acid [phr]	1	1	1
TMTD Catalyst	6	6	6
Tensile Strength [N/mm2]	3.44	3.96	3.38
Tensile strength @300% [N/mm2]	2.58	1.72	1.38
Elongation [%]	210	450	520
Shore A Hardness	53	45	40

Chemical resistance

Thioplast® G polysulfides are sensitive against strong aqueous solutions of oxidizing acids, e.g. 50% sulfuric acid or 10% nitric acid, but very stable in even strong bases.

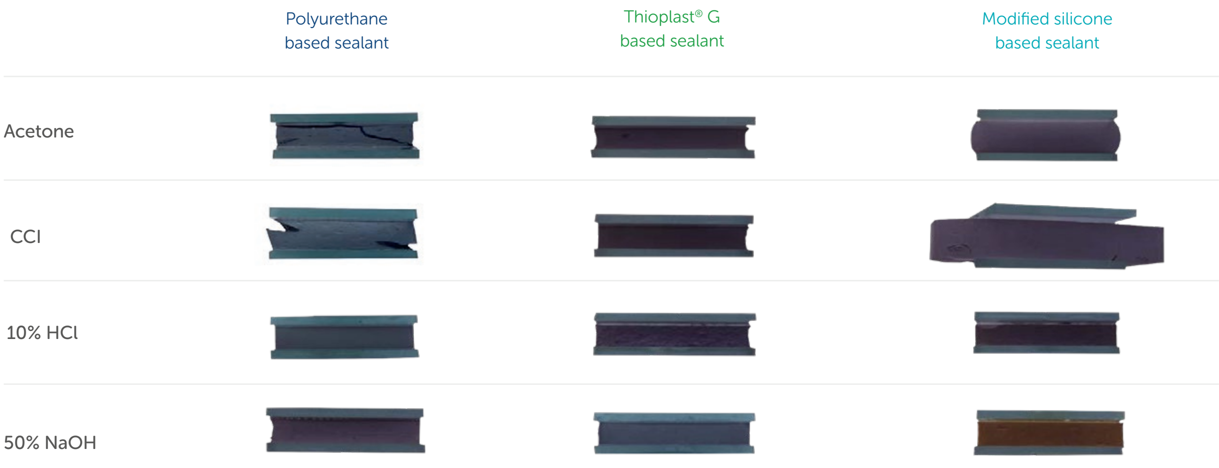
In an acid-catalysed hydrolytic attack, formal-dehyde gets released. In a first step, the released formaldehyde will reduce the disulfide bond of the Thioplast® G polysulfides backbone to mercaptan and will get oxidized in parallel to formic acid which in itself will further attack other formal groups. Calcium oxide can neutralize formic acid and absorb water and is therefore an effective stabilizer.

The terminal mercaptan group can react with an available hydroxyl group to give a mono-sulfide structure. The degradation results in weight loss and loss of flexibility due to a monosulfide structure formation.

Thioplast® G polysulfides get de-polymerized by organic mono-mercaptanes in solvents because of the attack on the sulfur-sulfur bond in the polymer backbone. That characteristic is very useful to remove cured polysulfide sealants from substrates.

Diluted acids and aqueous solutions of alkali metal hydroxides, chlorides or sulfates will not degrade liquid Thioplast® G polysulfides.

Resistance of cured Thioplast® G polymsulfides vs. other polymers (7 days immersion at 20ºC)



Water resistance

Cured Thioplast® G polysulfides are widely resistant to serious swelling in water and show very good durability in applications involving long term water immersion. Application examples are water reservoirs, sewage reservoirs etc. Thioplast® G polysulfides meet the very stringent requirements for the use of organic materials in potable water according the UK-norm BS 1620.

Optimal sealant formulations have a Thioplast® G content of higher than 50% by weight, manganese (IV) oxide as curative and a chlor-paraffin (min 52% chlorine) as plasticizer. Good resistance to fungal attack will be achieved as well by using sodium-perborate as curative.

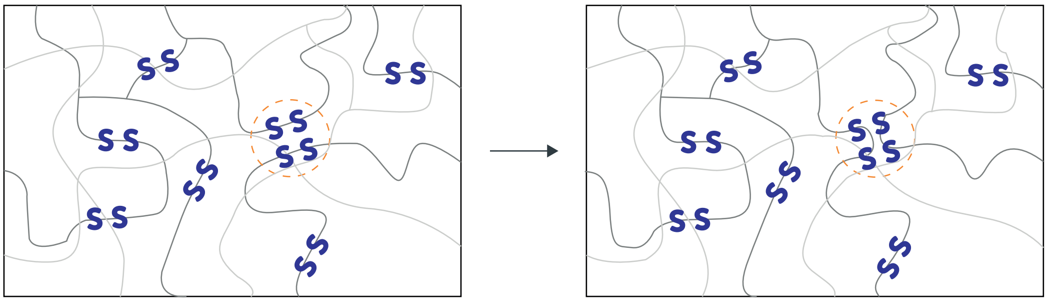
Stress Relaxation and self-repair capability

The timescale, in which intrinsic self-healing processes occur is closely related to the glass transition temperature (Tg) of the polymer. Below this temperature, the movement of the polymer is completely frozen and the material becomes brittle.

When it comes to self-healing, a low Tg is favorable. In DSC measurements, Thioplast® G polysulfides show a Tg at around -55°C, which ensures good self-healing abilities even at very low temperatures.

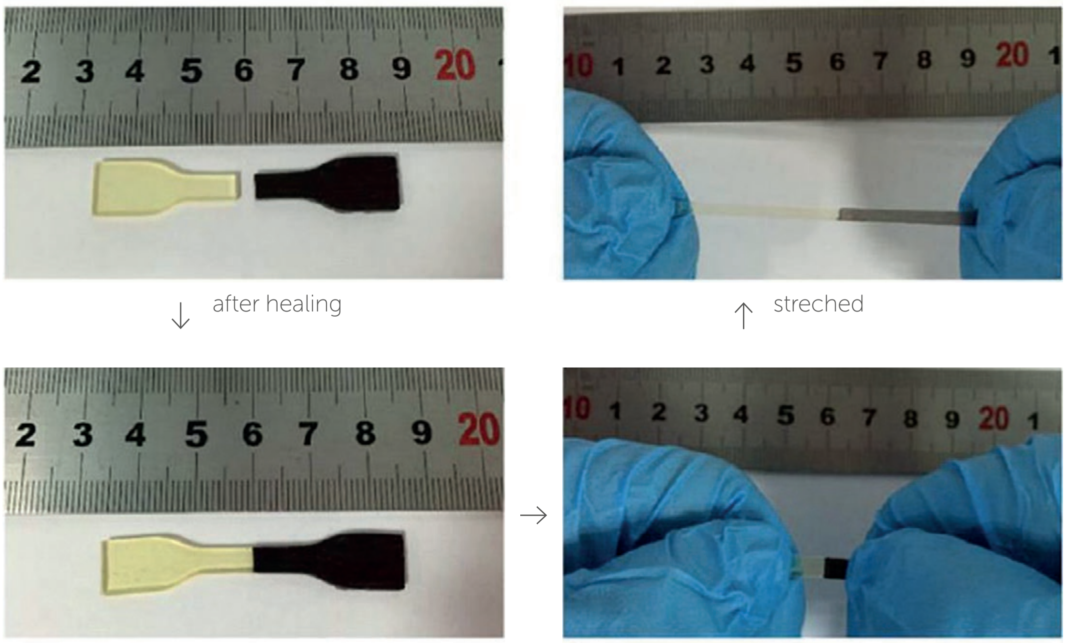
Thioplast® G polysulfides are capable of intermolecular sulfur exchange reactions between thiol terminal groups and disulfide linkages to internally relieve stress in the cure state

The rate of stress relaxation depends on temperature, UV light or catalysts, especially basic inorganic salts such as Na2S, NaSH, NaOH, Fe3+ and amines.



When a sample breaks during the tensile test and the fractures are immediately put into as close as possible contact and heated at 60 °C, the mechanical properties are almost fully restored in a few hours.

Tensile test specimen before and after cutting and in the un-stretched – stretched state



Wentong Gao, M.B. (2017), ACS Applied materials and Interfaces,15798-15808

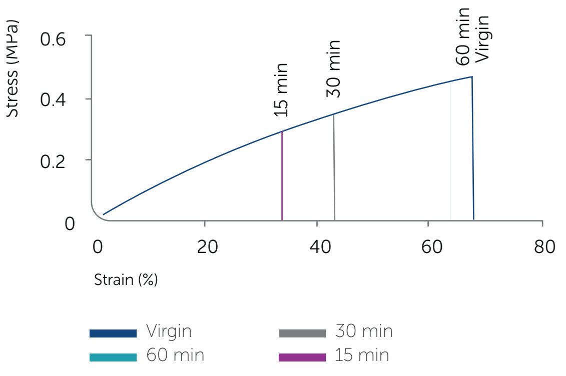
This phenomenon appears to result from the random interaction of trace residual thiol groups with the polymer disulfide groups forming an interchange between disulfide groups of neighbouring chains.

The process is energized by the strain energy in the vicinity of two polymer disulfide groups. The activation energy of this interchange process is at approx. 100 kJ/mol for disulfide and tetrasulfide polymers.

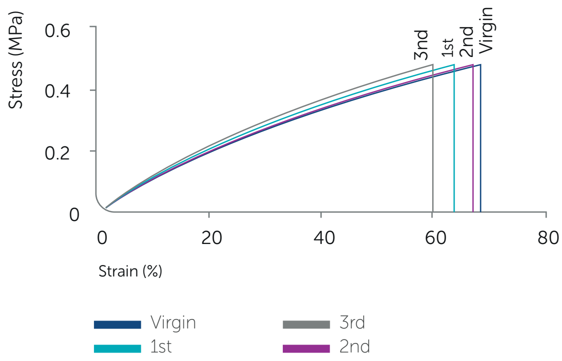
The observed stress relaxation may result from trace quantities of trisulfide and tetrasulfide structures remaining in the cured Thioplast® G polysulfides.

Because the sulfur-sulfur bond in a Thioplast® G polysulfides freely interchange with themselves and with the mercaptan end groups, it is possible, by blending two different Thioplast® G polysulfides, to obtain a polymer with intermediate molecular weight.

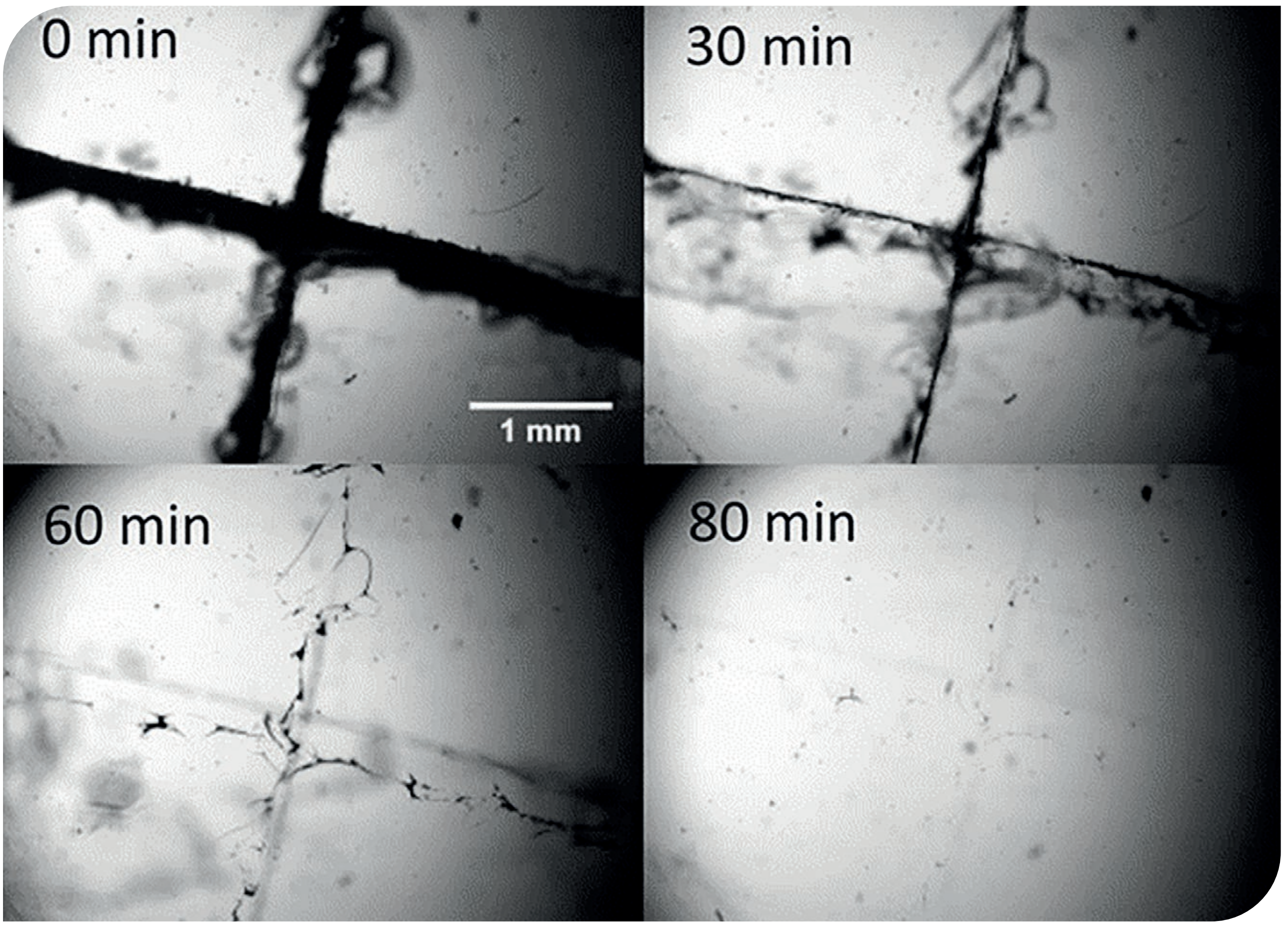
The same principle applies to branching. It is possible to generate a polymer with an intermediate level of branching.



Stress-strain curves as a function of the healing time. Broken samples during the tensile test experiments are put into contact at 60°C and allowed to heal for different times
Judit Canadell, Han Goossens, and Bert Klumperman; Macromolecules 2001 44 (8), 2536-2531



Stress-strain curves after repetitive healing experiments
Judit Canadell, Han Goossens, and Bert Klumperman; Macromolecules 2001 44 (8), 2536-2531



Optical microscopy images of a Thioplast® -film before (top left) and after (bottom right) the selfhealing process
U. Lafont, H. van Zeijl, and S. van der Zwaag; ACS Applied Materials & Interfaces 2012 4 (11), 6280-6288

Sealant formulation

Thioplast® G polysulfides are formulated with a variety of plasticizers, reinforcing agents like silica and calcium carbonate and polymer extenders.

Processing the Thioplast® G polysulfides in sealants and adhesives requires the use of high-shear mixing equipment like high speed disc- or butterfly dissolver. Recommended are single shaft dissolver with large dissolver disc and sword scraper.

Polysulfide adhesives and sealants are formulated using Thioplast® G polysulfides, curing agents, reinforcing fillers, plasticizers, and adhesion additives.

Thioplast® G polysulfides based sealants and adhesives are available in various structural viscosity ranges, from low viscos self-leveling to high viscos non-sagging, thixotropic sealants.

In epoxy-adhesives, Thioplast® G polysulfides are used to provide flexibility, high impact strength, and chemical and solvent resistance while maintaining the good adhesive properties of the epoxy.

In these systems, the viscosity is sufficiently low. The use of solvents is not required even for conventional or airless spray. If solvents are necessary, ketones, esters, alcohols, and aromatic hydrocarbons are suitable.

Thioplast® G polysulfides based adhesives and sealants are formulated using base polymer, curing agents, reinforcing fillers, plasticizers, and adhesion additives.

Compounded products are significantly different in their requested application properties and performances because of the use of different Thioplast® G grades at different contents and various curing systems.

Thioplast® G polysulfides are base polymers for elastic, chemical and weather resistant sealants.

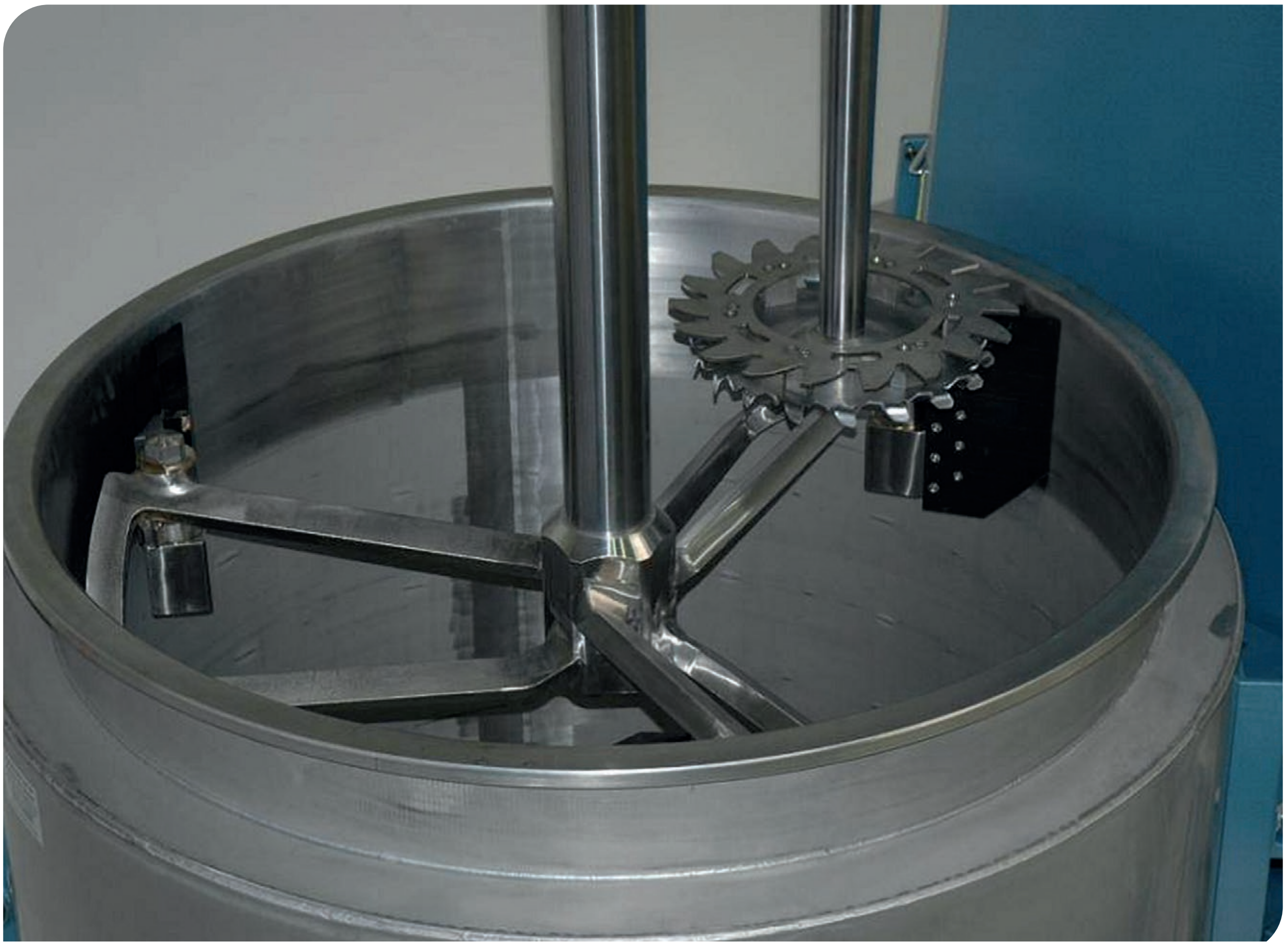
By using various fillers, plasticizers and special modifying additives, it is possible to adjust the physical properties of the resulting sealants to meet specific application requirements.

The choice of the Thioplast® G grade depends on the desired processing and application properties of the compound.

Higher branched Thioplast® G grades provide high elastic hard products after curing whereas lower branched types lead to weak elastic products that have excellent resistance to chemicals and weathering.

Low viscosity Thioplast® G grades enable the formulation of pourable highly reactive compounds. High viscosity Thioplast® G grades are mainly used for gun grade compounds.

Processing, storage and curing characteristics of the compound are to be considered in the right choice of fillers. The specific surface, particle size, and the varying texture of the fillers are especially important for obtaining uniform compounds with the expected right performances.



High performance dispersion via single shaft Butterfly dispenser and additional highspeed double sucking disc
Picture by WILHELM NIEMANN GmbH & Co., www.niemann.de

Thioplast® G polysulfide based sealant formulations for different applications

	Sealants				
Components	One part	Building	Insulating glass	Aircraft	General Purpose
Thioplast® G	20	35	25	65	35
Fillers	50	40	57,5	25	35
Plasticizer	25	20	14		27
Adhesion promotor	2	2	0,5	5	
Curative	3	3	3	5	3

The main fillers are carbon black, titanium dioxide, calcium carbonate, silica which have the following effects on Thioplast® G polysulfides based sealant compositions:

- Carbon black - good reinforcing effect, stabilization against UV
- Titanium dioxide - pigmenting and medium reinforcing effect
- Calcium carbonate – ground calcium carbonates serve as an extender and have only a low reinforcing effect.
- Precipitated calcium carbonates are functional fillers. They function as thixotropic fillers in addition to being extenders.
- Plasticizers - control viscosity and mechanical properties of the compound. Additionally, they influence adhesion, weather and chemical resistance and the curing process. Benzoates and chlorinated paraffines are especially suited for Thioplast® G compounds. Type and amount of plasticizer depend on the desired properties of the final product.
- Adhesion promoters - improve adhesion to various substrates. Epoxy-resins, modified phenolic and hydrocarbon resins, silanes can be used. However, in some cases, such as masonry substrates, ceramic tiles, metals, enhanced adhesion may be difficult to obtain. The use of an external primer is usually required in these cases.
- Retarders and accelerators - control application time (pot life) and curing process. Stearates, stearic acid retard, amines accelerate the curing rate.
- Rheological additives – control the flow behavior of the compound. Thixotropy can be achieved through the addition of fine particle size fillers (e.g. precipitated calcium carbonates, non-acidic clays, fumed silicas), organic agents (e.g. modified castor oils), or combinations of both. For pourable compounds surface control additives and/or deaerators (modified polysiloxanes, polar acidic esters) can be used in order to improve flow.

Thioplast® G polysulfide based sealant formulations for different applications

	Thioplast® G									
	G10	G112	G131	G1	G12	G21	G21F	G22	G44	G4
Insulating Glass	-	+	-	+	-	+++	+++	++	+	+
Construction	+	+++	-	+	++	-	++	+++	+	+
Industrial application	++	+++	+++	+	++	+	+	+	+	+
Aerospace	+++	+++	+++	++	+++	+	+	+++	+++	+++
Coatings	-	-	-	-	-	-	-	+	+++	+++
Epoxy Modifierers	-	-	-	-	-	-	-	+	+++	+++

To provide higher physical properties, fillers improve shrinkage after curing, reduce the cost of the sealant recipe, affect colour change and extend pot life.

All Thioplast® G polysulfides based sealants require adhesion promoters. In two-part sealants, silanes and phenolic resins are used to enhance adhesion. Phenolic resins are mainly used in aircraft sealants, where durable adhesion to aluminium is important.

Pasticizers

Phthalates, phosphates, and benzoates have for years replaced the more toxic chlorinated di-phenyls or hydrogenated terphenyls as plasticizers in Thioplast® G polysulfides based sealants.

Fogging- or volatility effects of plasticizers are especially important in applications such as insulating glass sealants.

Plasticizers are used to reduce the elastic modulus in Thioplast® G polysulfides based sealants.

A general approach is to use Thioplast® G polysulfides which gives high modulus and high compression set. A suited plasticizer will reduce the modulus slightly but will increase the flexibility of the cured compound.

The best results in insulating glass sealants are achieved by using relatively non-volatile plasticizers like dipropylene glycol dibenzoate. Phthalates are not recommended anymore as plasticizer due to their health risks to human beings.

In Thioplast® G polysulfides based construction sealants, chlorinated plasticizers with a chlorine content of 52% or 56% are used and still recommended.

The use of chlorinated plasticizers with less than 52% will lead to plasticizer separation due to chemical incompatibility to Thioplast® G polysulfides. They are strongly not recommended.

High performance dispersion via single shaft high speed dispenser and large double sucking disc
Picture by WILHELM NIEMANN GmbH & Co., www.niemann.de

Health, safety and environment

Sulfur-containing polymers, such as Thioplast® G polysulfides, have a characteristic odor. Toxicity tests conducted on representative Thioplast® G grades indicate that they are not eye or skin irritants, do not cause allergic skin reactions and have no oral toxicity (LD50 > 5 g/kg). Tests on the lower-molecular-weight Thioplast® G products show similar findings. Liquid Thioplast® G polysulfides are classified as non-hazardous under the criteria set forth in the Hazard Communication Standard (29 CFR 1910.1200) by the U.S. Occupational Safety and Health Administration (OSHA).

Reference Formulations

Reference formulations for different applications are available upon request. Please contact your Nouryon regional representative or technical manager for additional information.

To find out more about our polysulfides, visit our website:
nouryon.com/products/thioplast-polysulfides

or contact us at:
E: thioplast@nouryon.com

08-02-2023

Nouryon

Nouryon is a global, specialty chemicals leader. Markets and consumers worldwide rely on our essential solutions to manufacture everyday products, such as personal care, cleaning goods, paints and coatings, agriculture and food, pharmaceuticals, and building products. Furthermore, the dedication of around 7,800 employees with a shared commitment to our customers, business growth, safety, sustainability and innovation has resulted in a consistently strong financial performance. We operate in over 80 countries around the world with a portfolio of industry-leading brands. Visit our website and follow us @ Nouryon and on LinkedIn.

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