Thioplast G™

Liquid Polysulfide Polymers with reactive thiol-end groups

Technical product information

January 2014

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Liquid Polysulphide Polymers

Synthesis and chemical structure

Thioplasts are produced in aqueous dispersion by polycondensation of bis-(2-chloro-ethyl)-formal with alkali polysulphide. By introducing a tri-functional co-monomer (1,2,3-trichloropropane) as cross-linking agent a macromolecular network is formed during synthesis. The network chains consist of organic segments which are linked by disulphide groups. The macromolecules are then reduced to the required chain length by reductive splitting with sodium dithionite and sodium sulfite. At the same time the split disulphide groups are converted into reactive thiol terminal groups and residual high rank polysulphidic groups (–RSx-) are transformed into disulphides.

The chain length, respectively the molecular weight and the level of branching, expressed as the mole percent of 1,2,3-trichloropropane, are varied in order to offer suitable polymer types for particular applications.

Today, nine different grades of Thioplast are manufactured (see table below) differing only in molecular weight and degree of branching. The product range will meet most application requirements, but Thioplasts can be tailor-made to meet specific customer needs.

The chemical composition of Thioplasts can be described as a blend of di- and tri-functional molecules. The formula illustrates the ideal structure:

di-functional unit

$HS\text{-}(R\text{-}SS)_n\text{-}R\text{-}SH$

tri-functional unit

$$HS\text{-}(R\text{-}SS)_a\text{-}CH_2\text{-}\underset{\underset{(SS\text{-}R)_c\text{-}SH}{|}}{CH}\text{-}CH_2\text{-}(SS\text{-}R)_b\text{-}SH$$

$R = \text{-}(CH_2)_2\text{-}O\text{-}CH_2\text{-}O\text{-}(CH_2)_2\text{-}$; $a + b + c = n$

The value for n may vary between 7 and 38 depending on the amount of the splitting agent used.

Thioplast type	Unit	G 10	G 112	G 131	G 1	G 12	G 21	G 22	G 44	G 4
n		26 - 27	23 - 25	30 - 38	20 - 21	24 - 27	13 - 16	14 - 18	< 7	< 7
Av. molecular weight	g/mol	4400 - 4700	3900 - 4400	5200 - 6500	3400 - 3600	4100 - 4600	2100 - 2700	2400 - 3100	< 1100	< 1100
SH–content	%	1.4 – 1.5	1.5 – 1.7	1.0 – 1.3	1.8 – 2.0	1.5 – 1.7	2.5 – 3.1	2.1 – 2.7	> 5.9	> 5.9
Cross-linking agent	mol-% TCP	0	0.5	0.5	2.0	0.2	2.0	0.5	0.5	2.0

Typical properties

All Thioplast types are medium to high viscous liquids of light brown colour. The average molecular weight (calculated from the thiol terminal group content) as a measure of chain length and the degree of branching determines the viscosity. Consequently, the viscosity is the most important characteristic feature of a Thioplast type.

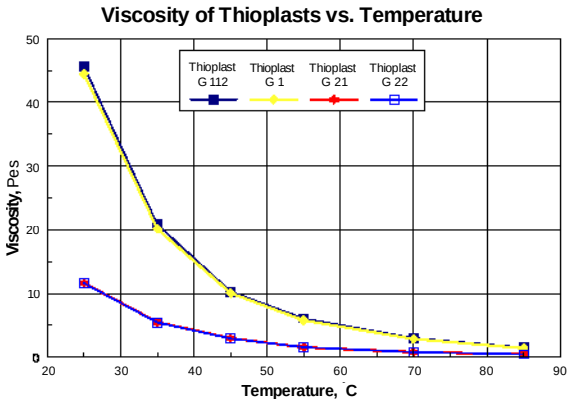
All Thioplasts are completely soluble in benzene, toluene, di-chloroethane, chloroform and similar solvents and in plasticisers such as phthalates and chlorinated paraffins. Thioplasts are partially soluble in aliphatic esters and ketones. They do not mix with water, aliphatic hydrocarbons and alcohols. Depending on the relative humidity, up to 0.3 % water is soluble in Thioplast. Finely dispersed elemental sulphur is soluble.

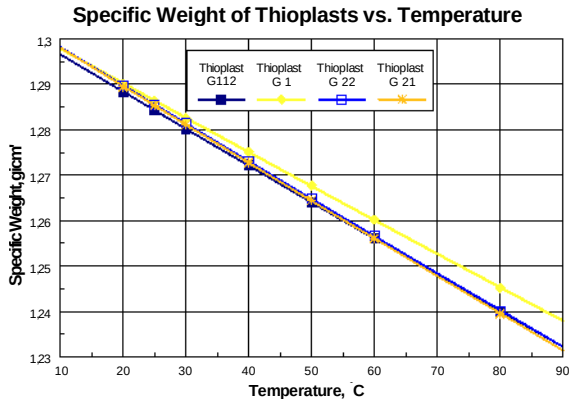
All Thioplast products are subject to extensive quality control testing to ensure consistency and reliability.

Characteristic features of the Thioplast types:

Thioplasttype	Unit	G 10	G 112	G 131	G 1	G 12	G 21	G 22	G 44	G 4
Viscosity@25 °C	Pa*s	42 – 48	38 – 50	80 – 145	41 - 52	38 - 50	10 - 20	10 - 20	max. 1.3	max. 1.3
Specific weight	g/cm^3	1.283	1.285	1.310	1.286	1.285	1.285	1.285	1.257	1.259
Volatile ingredients	%	max. 0.3	max. 0.3	max. 0.3	max. 0.3	max. 0.3	max. 0.5	max. 0.5	max. 1.0	max. 1.0
Water content	%	max. 0.3								
Sulphur content	%	37 – 38								
Free sulphur	%	max. 0.1								
Glass point	°C	ca. –60								
Flash point	°C	> 230								
Specific heat	kJ/kg*K	1.26								
Heat of combustion	kJ/kg	24,075								
Storage stability		min. 3 years in closed original packaging at a temperature < 30 °C								

The viscosity and density of Thioplasts vary considerably with temperature:





Reactions of Thioplasts

The reactive thiol terminal groups of liquid Thioplasts enable numerous chemical reactions to take place, some of which are of special importance for their application and characterisation.

OXIDATION Reactions with oxidising agents produce disulphide linkages and thus longer chains:

$$2\ {\sim}R{-}SH + [O] \rightarrow {\sim}R{-}SS{-}R{\sim} + H_2O$$

The reaction with Iodine is basic to an end group assay of liquid Thioplasts:

$$2\ {\sim}R\text{-}SH + J_2 \rightarrow {\sim}R\text{-}SS\text{-}R{\sim} + 2\ HJ$$

Strong oxidising agents such as nitric acid completely destroy Thioplasts releasing water, CO_2, SO_2 and NO_x.

ADDITION

The reactive terminal groups of epoxy resins react with liquid Thioplasts and become attached so that copolymers are formed:

$$\sim RSH + \underset{\diagdown\ \diagup \atop O}{CH_2\text{-}CH}\text{-}R' \rightarrow {\sim}R\text{-}S\text{-}CH_2\text{-}\underset{OH}{CH}\text{-}R'$$

Similar reactions are also possible with isocyanates:

$$+\ OC{=}N\text{-}R' \rightarrow {\sim}R\text{-}S\text{-}\underset{O}{C}\text{-}NH\text{-}R'$$

HYDROLYSIS

Thioplasts react with alkalis to form salts, while mineral acids break up formal groups in the organic chain.

$$\text{-}CH_2\text{-}CH_2\text{-}O\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH_2\text{-}SS\text{-} + H_2O \xrightarrow{H^+}$$
$$HCHO + \text{-}CH_2\text{-}CH_2\text{-}OH + HO\text{-}CH_2\text{-}CH_2\text{-}SS\text{-}$$

This explains the instability of cured Thioplasts towards strong mineral acids.

Curing of Thioplasts

When Thioplasts react with oxidising agents, the polymer's thiol terminal groups become linked to form disulphide linkages, the chain length increases, viscosity rises and solidification sets in - Thioplasts are cured to high molecular weight elastomers. The special advantage of this curing mechanism is the fact that it is relatively insensitive to the amount of the added curing agent.

Oxidative curing is possible with inorganic oxides and peroxides, metal oxide salts or organic hydroperoxides. Manganese(IV)-oxide of specific activity is the most often used curing agent. Because of its toxicity lead dioxide has lost its practical importance. Cumene hydroperoxide, a liquid organic oxidising agent, which is useful for obtaining pourable compositions that have compression set resistance. Calcium peroxide and sodium perborates are commonly used to prepare one component systems but also two component systems if white or pastel coloured products are requested.

Curing via addition reactions has been barely commercially used.

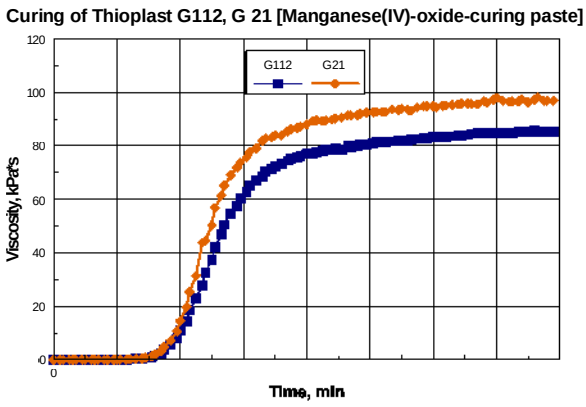
The ease of the oxidation of the thiol terminal groups is the reason for the dominant importance of the oxidative curing route. The curing agent should be added in excess relative to the stoichiometric conversion of existing SH-groups. In the

Thioplast	Manganese(VI)-oxide (*) g/100 g
G 112	5.5 – 6.1
G 1	5.4 – 5.8
G 12	5.7 – 6.3
G 21	7.5 – 9.4
G 22	7.7 – 9.8

(*) pure curing agent substance; the concentration of technical products has to be

To bring metal oxides into close contact with Thioplast, paste-like curing agents are made by thoroughly mixing of metal oxide, plasticiser, suitable retarders or accelerators, and milling on a triple-roll mill.

The curing reaction can be monitored by viscosity measurements:



Curing takes place at room temperature but can be accelerated at higher temperatures. Traces of water have a catalytic effect on the curing rate which increases during the reaction as water is released during the oxidation of the thiol groups leading to an autocatalytic reaction. This is especially evident when manganese(IV)-oxide is the curing agent. Amines and other bases also accelerate the reaction whereas acids retard it.

Properties of cured Thioplasts

The ability of Thioplasts to cure is a major aspect of their application and therefore, together with the mechanical evaluation, a major factor in quality testing.
Testing of Thioplasts generally takes place in an unmodified state, i.e. only the curing paste is added to the polymer without any fillers, plasticisers or modifying agents. Only this approach can fully bring out the properties of a particular Thioplast type.

Typical results achieved with a manganese(IV)-oxide curing paste are shown in the table below:

		G 112	G 1	G 21	G 22
Pot life	min	45	45	35	35
Elongation @ break	%	170	90	100	190
Shore-A-Hardness		35	41	40	33

The curing paste is made as described by blending manganese (IV)-oxide, accelerator and deaerator with a phthalate plasticiser. The testing formulation is given in the table:

	Parts by weight
Manganese(IV)-oxide, type FA	100
Santicizer 278	100
Perkacit DPG	6
AIREX 900	7,4

Compounding

Thioplasts are base polymers for elastic, chemical and weather resistant sealants. Using various fillers, plasticisers and special modifying additives it is possible to adjust the physical properties of Thioplast polymers to meet specific application requirements and to reduce material cost.
The choice of the Thioplast type depends on the desired processing and application properties of the compound. Higher branched types 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 types enable the formulation of pourable highly reactive compounds. High viscosity Thioplast types are mainly used for gun grade compounds.

Fillers - The effects on processing, storage and curing characteristics are to be considered in the choice of fillers. The specific surface, particle size, and the varying texture of the fillers are especially important for obtaining uniform compounds.
The main fillers are carbon black, titanium dioxide, calcium carbonate, which have the following effects on the Thioplast based composition:
Carbon black - good reinforcing effect, stabilises 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 thixotropes in addition to being extenders.

Plasticisers - control viscosity and mechanical properties of the compound. Additionally they influence adhesion, weather and chemical resistance and the curing process. Phthalates and chlorinated paraffines are especially suited for Thioplast compounds. Type and amount of plasticiser 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 a 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 behaviour 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.

Processing

Thioplast compounds are commonly formulated as one or two component systems. The A part contains the Thioplast polymer, the B part the curing agent. An one component system consists of a complete package containing all ingredients. They are mixed under low humidity conditions prior to packaging in air tight, moisture resistant containers and will cure when exposed to environmental moisture.
Preparing the compounds requires the use of planetary mixers or high speed dispersers. A triple-roll mill should be additionally used to produce a maximum of uniformity of the curing paste and reduction of occluded air.

Application of Thioplasts

Thioplasts are widely used as the base polymer for sealants applied to buildings, canals, highways, insulating glass units. Other industrial applications include aircraft sealants, moulding compounds, electrical potting compounds, concrete coatings. The use of Thioplasts as epoxy and rubber modifiers is a further important application area. Leather impregnations and binder for grinding wheels are examples of special usages of Thioplasts.
The applications listed below in the table, typify the general uses for Thioplast range of liquid polysulphide polymers.

	Thioplast								
	G 10	G 112	G 131	G 1	G 12	G 21	G 22	G 44	G 4
Insulating glass		+		+		+ +			
Construction		+ +			+ +	+	+		
Industrial applications	+ +	+ +		+		+			
Specialities	+ +	+ +	+	+ +					
Coatings								+ +	+ +
Epoxy modifiers								+ +	+ +

Safety advises

Thioplasts with molecular weight ≥ 1800 are not hazardous products (Gefahrstoffverordnung v. 26.10.1993). The Thioplast types G 4 and G 44 (molecular weight < 1800) are environmentally harzardous substances and labelled with N.
The acute oral toxicity of all Thioplasts has been measured in rats as >5 g/kg body weight. Together with a low level of resorption, the hazards for human health can therefore be regarded as minimal.

Skin irritation studies indicate that some individuals developed allergic reactions upon repeated applications to the same area of skin. It is therefore advised that longer periods of skin contact or repeated contacts should be avoided. Protective gloves should be worn as a precaution.
More information about national and international standards are available upon request.

Status of this information: January 2014

For actual changes and news please refer to www.thioplast.com

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