

# Thioplast<sup>TM</sup> EPS

Liquid Polysulfide Polymers with Reactive Epoxy-End Groups



### Thioplast™ EPS Resins

### **Epoxy-Terminated Liquid Polysulfides**

#### Introduction

Nouryon Functional Chemicals GmbH in Greiz, Germany, is the leading manufacturer of liquid polysulfide polymers with the trade name Thioplast<sup>TM</sup> G.

Thioplast™ EPS resins are epoxy-terminated, low-viscosity liquid polysulfide polymers derived from the SH-terminated polysulfide polymer Thioplast™ G. Thioplast™ EPS resins are telechelic polymers with outstanding properties which combine the flexibility of conventional Thioplast™ G liquid polysulfide polymers with the toughness of standard Bisphenol A/F-Epoxy based resins.

Thioplast™ EPS resins can be used in formulations together with other epoxy resins to increase flexibility, adhesion, aging and weathering and to improve chemical resistance.

Thioplast™ EPS resins have been specifically developed for use in high performance coatings, sealants and adhesives formulations for both interior and exterior use.

Nouryon offers two types of epoxy-functionalized liquid polysulfide polymers: aromatic and aliphatic Thioplast™ EPS resins that exhibit different physicochemical properties and behavior. Both types are particularly well suited for heavy-duty surface applications on metal and concrete.

The major advantage of Thioplast™ EPS resins compared to other polymer types is their remarkable flexibility and superior chemical resistance. Plus, formulators enjoy these

performance characteristics from polysulfide polymers without having to deal with any annoying thiol odor. Furthermore Thioplast<sup>TM</sup> EPS resins are cured with common epoxy amine hardeners. There is no need to use curing agents containing heavy metals.

Permeability to water vapor is lower than found with pure aromatic epoxy resins. That makes Thioplast<sup>TM</sup> EPS resins particularly suited for coating applications on steel and concrete. Moreover, Thioplast<sup>TM</sup> EPS resins show unique self-repair and crack-bridging behavior. Aliphatic Thioplast<sup>TM</sup> EPS resins are also excellent reactive diluents which can act as a high potential flexibilizer in classical Bisphenol A/F Epoxyformulations.

#### **Properties**

The combination of a primary polysulfide structure in the polymer backbone and epoxy termination leads to a unique class of polymers which can be employed either as a single component or in combination with commercial aromatic glycidyl ether resins and other epoxies.

Thioplast<sup>TM</sup> EPS resins exhibit a number of remarkable properties:

- rapid curing at ambient temperature
- good adhesion on many materials
- adjustable flexibility
- high impact resistance
- chemical resistance to a number of diluted acids, alkalis and organic solvents
- efficient self-healing characteristic

The combination of liquid polysulfide and epoxy resins yields telechelic polymers showing

superior properties. In addition to excellent chemical resistance and good adhesion these hybrids can be cured with a wide range of curing agents.

The following table displays which Thioplast™ EPS type is best for which application

Table 1: Applicability of ThioplastTM EPS grades.

| Туре    | Coatings | Paints | Adhesives | Sealants |
|---------|----------|--------|-----------|----------|
| EPS 25  | +++      | ++     | +         | ++       |
| EPS 35  | +++      | ++     | ++        | ++       |
| EPS 70  | +++      | ++     | ++        | +++      |
| EPS 80* | +++      | ++     | ++        | +++      |

US market only, because of TSCA-regulation

#### **Chemical Structure**

The polymer's structure is dominated by the polysulfide backbone with SS- and formal groups and highly reactive epoxy-end groups.

R= -CH2- or DGEBA/F

#### Synthesis

There are basically two routes of generating epoxy functionalized polysulfide: Via the reaction of a polysulfide with epichlorohydrin, or by the reaction with di-glycidyl ethers.

#### Aliphatic Type (Thioplast™ EPS 25, EPS 35)

n<

The synthesis route starts with the direct interaction of a low viscosity Thioplast<sup>TM</sup> G polymer and epichlorohydrin at high pH, NaOH-based environment. The resulting polymer is strictly aliphatic and depending on the Thioplast<sup>TM</sup> G polymer used already pre-branched.

#### Aromatic type (Thioplast™ EPS 70, EPS 80)

$$\begin{array}{c} & & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & \\ & & & \\ & &$$

n<7

The synthesis of the aromatic Thioplast™ EPS 70, Thioplast™ EPS 80 takes place by interaction of a low viscosity Thioplast™ G polymer and Bisphenol-A/F-Diglycidylether (DGEBA/F) forming a DGEBA/F functionalized polysulfide-based polymer.

#### Curing of Thioplast™ EPS Resins

As a rule, epoxidized polysulfides are formulated as two component systems and are cured at ambient temperature in the presence of a catalyst.

For example, component A could contain either a blend of Thioplast™ EPS with an epoxy resin, or solely Thioplast™ EPS polymers, while component B could contain a compound with active hydrogen and a catalyst.

Preferred catalysts for curing Thioplast™ EPS resins are amines:

- aliphatic amines
- cycloaliphatic amines
- amidoamines
- aromatic amines
- polyamides

Curing occurs via the mechanism of a stoichiometric polyaddition reaction following the opening of the oxirane ring.

$$\begin{array}{c} O \\ \downarrow \\ R \end{array} \begin{array}{c} + \\ \downarrow \\ \downarrow \\ R \end{array} \begin{array}{c} + \\ \downarrow \\ \downarrow \\ R \end{array} \begin{array}{c} + \\ \\ \\ R \end{array} \begin{array}{c} + \\ \\$$

Compounds with active hydrogen are:

- polysulfides, polythiols
- primary or secondary amines (no additional catalysts necessary)
- polyols

#### Different Thioplast™ EPS Types

The possibility to use the whole range of Thioplast<sup>TM</sup> G liquid polysulfides as a polymer backbone allows a great variability in viscosity and degree of branching of the resulting Thioplast<sup>TM</sup> EPS resins.

Thioplast™ EPS 25 and EPS 35 purely aliphatic epoxy resins are based on Thioplast™ G polysulfides.

Chemical reaction with aromatic glycidyl ether derivatives with Thioplast™ G leads to formation of Thioplast™ EPS 70, EPS 80 types with higher viscosity.

| Type / Characteristic          | EPS 25      | EPS 35    | EPS 70               | EPS 80* |  |
|--------------------------------|-------------|-----------|----------------------|---------|--|
| Viscosity @ 20°C (Pas)         | 2-3         | 3-4       | 5-10                 | 5-10    |  |
| Degree of branching (mol%)     | 2           | 2         | 0                    | 0       |  |
| Polymer structure              | Aliphatic   | Aliphatic | Aromatic / Aliphatic |         |  |
| Density (g/ml @ 20°C)          | 1.27        | 1.23      | 1.20                 | 1.20    |  |
| Oxygen content (weight-%)      | 2.1-2.9     | 2.3-2.6   | 4.6-5.6              | 4.6-5.6 |  |
| Epoxy-equivalent weight (g/Eq) | 550-760     | 400-500   | 280-350              | 280-350 |  |
| Appearance                     | Clear amber |           |                      |         |  |

<sup>\*</sup> US market only, because of TSCA-regulation

The most important application areas for Thioplast™ EPS resins result from their four basic properties:

- Excellent adhesion properties, particularly on concrete, metal, etc.
- Low vapour transmission properties
- Flexibility and impact resistance
- Chemical resistance

Relevant fields of application of Thioplast™ EPS resins are:

- Flexible coatings for concrete, steel and wood
- Coating systems for surfaces exposed to fuels and aggressive chemicals
- Reactive diluents for epoxy resins used in paints and adhesives
- Thioplast™ EPS may also act as a versatile flexibilizer for solvent-free and solvent-containing coating systems resulting in high chemical resistance even in thin layers.
- Suited for facilities used to store and handle substances which present high risk for contaminating water. Thioplast<sup>TM</sup> EPS resins can be formulated to satisfy the German law for such facilities ('LAU-regulation')

The following table provides an outline of possible applications of the most popular Thioplast<sup>TM</sup> EPS resins. Needless to say that the applications of Thioplast<sup>TM</sup> EPS are not restricted to those presented in this table.

Table 2: Examplary application areas for EPS products.

| Application                 |   | EPS 25 | EPS 35 | EPS 70 | EPS 80* |
|-----------------------------|---|--------|--------|--------|---------|
|                             | Anti-Corrosive Coating or Lining for Concrete | •      | •      | •      | •       |
|                             | Elastic, Chemical Resistant Flooring          | •      | •      | •      | •       |
| Buildings Civil Engineering | Adhesives for Wet Surfaces of Concrete        |        |        |        |         |
| Adhesives                   | Adhesives for Building Panels                 | •      | •      |        |         |
|                             | Adhesives for Metals                          | •      | •      |        |         |
|                             | Adhesives for Automobile Parts                | •      | •      |        |         |
|                             | Anti-Corrosive Coating for Metals             |        | •      | •      | •       |
| Coating Lining              | Chemical Resistant Coating                    |        | •      |        |         |
|                             | Impact Resistant Coating                      |        | •      | •      | •       |
|                             | Potting, Casting                              | •      | •      |        |         |
| Electrical                  | Electrical Insulator                          | •      | •      |        |         |
|                             | Electrical Components                         | •      | •      |        |         |

 $<sup>\</sup>ensuremath{^{\star}}\xspace$  US market only, because of TSCA-regulation

#### General Thioplast™ EPS Properties

Thioplast<sup>TM</sup> EPS resin is a versatile flexibilizer in solvent free coatings and shows superb chemical resistance even when applied in thin layers. Thioplast<sup>TM</sup> EPS polymers add flexibility to epoxy resins and at the same time it improves the chemical resistance of the resulting coating or adhesive. Depending on the choice of the co-reactant, specific properties of the cured product can be fine-tuned (see **tables 3a and 3b**).

**Table 3a:** Co-reactant or hardeners of Thioplast™ EPS and their effect on coating performance and characteristics. Features (Co-reactants and hardeners rated top to bottom from best to least suited)

| Fil                     | lm                      | Chemical Resistance     |                         |                        |  |  |
|-------------------------|-------------------------|-------------------------|-------------------------|------------------------|--|--|
| Flexibility             | Adhesion                | Acids                   | Solvents                | Water                  |  |  |
| Best                    | Best                    | Best                    | Best                    | Best                   |  |  |
| Polyamide               | Polyamide               | Aromatic amine          | Aliphatic amine         | Polyamide              |  |  |
| Amidoamine              | Phenalkamine            | Cycloaliphatic amine    | Aliphatic amine adducts | Phenalkamine           |  |  |
| Phenalkamine            | Amidoamine              | Aliphatic amine         | Cycloaliphatic amine    | Amidoamine             |  |  |
| Cycloaliphatic amine    | Cycloaliphatic amine    | Aliphatic amine adducts | Aromatic amine          | Cycloaliphatic amine   |  |  |
| Aromatic amine          | Aliphatic amine         | Amidoamine              | Polyamide               | Aromatic amine         |  |  |
| Aliphatic amine adducts | Aliphatic amine adducts | Phenalkamine            | Phenalkamine            | Aliphatic amine        |  |  |
| Aliphatic amine         | Aromatic amine          | Polyamide               | Amidoamine              | Aliphatic amine adduct |  |  |

**Table 3b:** Co-reactant or hardeners of Thioplast<sup>TM</sup> EPS and their effect on coating performance and characteristics. Features (Co-reactants and hardeners rated top to bottom from best to least suited)

| <b>Blush Resistance</b> | <b>Color Stability</b>  | Low Temp. Application   | <b>Corrosion Restistance</b> | Viscosity               |
|-------------------------|-------------------------|-------------------------|------------------------------|-------------------------|
| Best                    | Best                    | Best                    | Best                         | Best                    |
| Polyamide               | Polyamide               | Phenalkamine            | Polyamide                    | Cycloaliphatic amine    |
| Phenalkamine            | Amidoamine              | Aliphatic amine         | Amidoamine                   | Aliphatic amine         |
| Amidoamine              | Cycloaliphatic amine    | Aliphatic amine adducts | Phenalkamine                 | Amidoamine              |
| Cycloaliphatic amine    | Aliphatic amine adducts | Cycloaliphatic amine    | Cycloaliphatic amine         | Aromatic amine          |
| Aromatic amine          | Aliphatic amine         | Polyamide               | Aliphatic amine adducts      | Aliphatic amine adducts |
| Aliphatic amine adducts | Phenalkamine            | Amidoamine              | Aromatic amine               | Phenalkamine            |
| Aliphatic amine         | Aromatic amine          | Aromatic amine          | Aliphatic amine              | Polyamide               |

Standard characteristics of regular, non Thioplast™ EPS modified, epoxy-systems are listed in table 4.

Table 4: Standard Epoxy-coating comparison chart

|                                  | Amine Epoxies   | Polyamide Epoxies  | <b>Amidoamine Epoxies</b>  | <b>Epoxy Phenolics / Novolacs</b>  |
|----------------------------------|---|--|--|--|
| Description                      | Form very hard, adherent films with excellent chemical and corrosion resistance. Amine cured epoxies are often used as protective coatings and linings in highly corrosive environ-ments. Amine epoxies require care in handling since the amines can be moderately irritating to the skin, and may cause allergic reactions. | weathering resistance and a<br>longer pot life than amine cured<br>epoxies. Polyamide epoxies<br>generally have less solvent and   | Amidoamine are reaction products of a polyamine and a fatty acid. Their properties generally fall between those of amines and polyamides. They have good water and corrosion resistance like amines and good toughness like polyamides. They have relatively low molecular weights and low viscosities making them very good surface wetters | These coatings allow a wide range formulating latitude. Novolac epoxy resins increase the chemical resistance and solvent resistance. Increasing the level of phenolic increases the chemical and solvent resistance, but the coating loses flexibility. |
| Advantages                       | Excellent alkali and water resistance     Very good acid resistance     Excellent solvent resistance     Hard, abrasion resistant film     Excellent corrosion resistance     Excellent wetting of substrate  | Very good alkali and water resistance     Good acid resistance     Longer pot life than amines     Easy to apply     Cures more quickly than amines     Good weathering characteristics     Good film flexibility     Excellent adhesion | Excellent surface wetting     Excellent adhesion     Excellent water resistance     Low viscosity     Longer pot life than amines     Good gloss retention   | High heat resistance     Excellent chemical resistance     Excellent solvent resistance     Excellent corrosion resistance     Hard, abrasion resistant film     Disadvantages and Limitations   |
| Disadvantages<br>and Limitations | Amines can be irritating/toxic     Relatively short recoat time     Relatively short pot life     Slower dry than normal polyamides     Chalks/may discolor   | Faster drying than amines     Chalks     High viscosity     Temperature dependent     Slow cure  | Slow cure     Fair color retention     Temperature dependent   | Some may require heat cure     Relatively slow air cure     Chalks/may discolor     Relatively brittle   |

#### Self-repair capability

Intramolecular exchange of the S-S-bonds, as represented in **figure 1**, leads to a continuous rearrangement of these chemical bonds. This is the explanation for the excellent self-repair capabilities observed for cured Thioplast™ EPS resins.

To measure that self-repair capability, tensile testing experiments were performed to quantify the recovery of strength. Representative stress - strain curves for the original material are plotted in **figure 2a**, showing that the elongation at break is approx.  $65 \pm 5\%$ .

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 fully restored in just 1 hour (figure 2b).

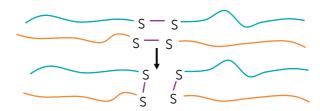
As expected, longer healing times lead to better healing, but even when the contact time between the two broken sections is as short as 15 min, a repaired sample shows an elongation at break close to 40%. Surprisingly, for all healing times, the stress - strain curves superimpose

and show only different elongations at break, indicating that the healed samples have similar elastic properties as the original material.

This material can be healed efficiently multiple times, and the mechanical properties after the second and third healing process are, within experimental error, fully restored, i.e., elongation at break of  $\sim 63 \pm 5\%$ , and no systematic decrease for consecutive breaking—healing cycles (figure 2c).

Figure 3 shows the influence of the disulfide concentration on the self-healing properties of Thioplast™ EPS / Bisphenol A/F resin blends using different ratios of epoxy resins, one free of disulfide groups (DER732) and another containing disulfide groups in its structure (Thioplast™ EPS 25).

**Figure 1:** Intramolecular exchange of the S-S-bonds in Thioplast<sup>TM</sup> EPS resins as reason for the excellent self-repair capabilities



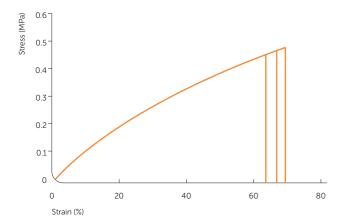
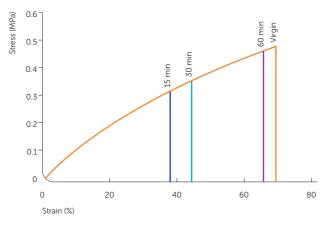


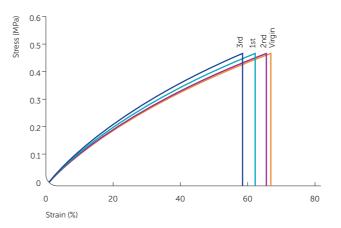
Figure 2a: Stress-strain curves of three different virgin samples to quantify the intramolecular exchange of the S-S- bonds in Thioplast™ EPS resins. Reference: Macromolecules 2011, 44, 2536-2541



 $\textbf{Figure 2b:} \ \text{Stress-strain curves of self-healed samples after different healing times.}$ 

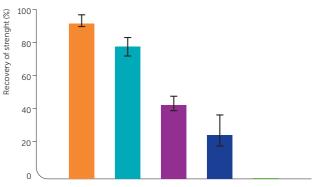






**Figure 2c:** Stress-strain curves of the virgin sample and of a self-healed sample after three breaking and healing cycles.





**Figure 3:** Recovery of strength (%) of healed samples with different concentrations of disulfide groups. Thioplast<sup>TM</sup> EPS 25 / Bishenol A/F resin blends with different content of disulfide



#### Chemical resistance

Cured Thioplast<sup>TM</sup> EPS resin systems show outstanding resistance towards various chemical and corrosive attacks. They withstand a wide range of chemical substances: water, diluted acids, alkalis, esters, ketones, mineral oils and other hydrocarbons.

**Table 5:** Chemical resistance of Thioplast™ FPS

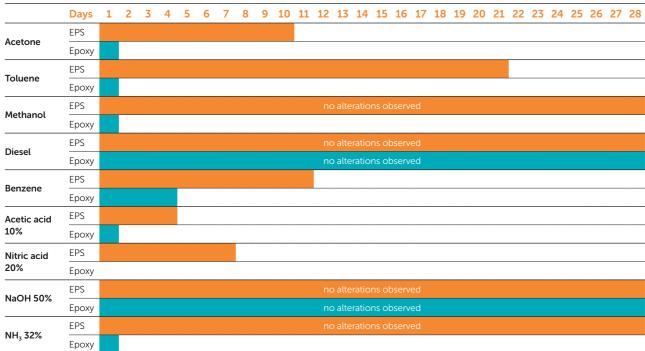
| Substance                 | Resistance | Substance                              | Resistance |
|---------------------------|------------|--|------------|
| Acetone                   | +          | Fuel oil                               | ++         |
| Formic acid conc.         | -          | Isopropanol                            | ++         |
| Formic acid 10%           | +/D        | Potassium hydroxide saturated solution | ++         |
| Ammonium hydroxide 32 %   | ++         | Methanol                               | ++         |
| Gasoline                  | ++         | Sodium hydroxide saturated solution    | ++         |
| Benzene                   | +          | Phosphoric acid conc.                  | +/ D       |
| Diesel 'Bio'-fuel         | ++         | Nitric acid half conc.                 | ++         |
| Calciumhydroxide sat.sol. | ++         | Nitric acid conc.                      | -          |
| Diesel fuel               | ++         | Nitric acid 10%                        | +/ D       |
| Diethyl ether             | ++         | Hydrochloric acid conc.                | +/ D       |
| Dichloro methane          | 0          | Hydrochloric acid 10%                  | +/ D       |
| Acetic acid conc.         | -          | Sulfuric acid conc.                    | -          |
| Acetic acid half conc.    | +          | Sulfuric acid half conc.               | +/ D       |
| Acetic acid 10%           | ++         | De-icing salt                          | ++         |
| Ethanol                   | ++         | Toluene                                | ++         |
| Formaldehyde              | ++         | Xylene                                 | ++         |

- ++ resistant for 14 d
- + resistant for 72 h
  0 resistant for 8 h
- not resistant
- D discolouring

Specimens have been cured with a hardener based on a cyclo-aliphatic amine.

The resistance of Thioplast™ EPS to organic solvents and organic acids is better than that of epoxy resins.

 Table 6: Chemical resistance of EPS compared to unmodified epoxy resin (EP)



#### Viscosity and miscibility

Thioplast™ EPS resins are compatible with commercial epoxy resins. Viscosity can easily be adjusted by altering the ratio of the resin components in the mixture.

#### Odor

Due to the presence of mercaptan end groups unmodified polysulfide like Thioplast<sup>TM</sup> G have a characteristic odor. Since mercaptan end groups are absent in Thioplast<sup>TM</sup> EPS resins they lack this unpleasant odor.

#### Reactive behaviour

Epoxidized polysulfides can be cured using aliphatic, cycloaliphatic and aromatic amines, phenalkamine adducts and Mannich base type hardeners.

#### Adhesion

Adhesion of Thioplast™ EPS resins to concrete, glass and steel is better than of unmodified polysulfides.

#### Thermal shock resistance

Thioplast™ EPS resins tolerate thermal stress between - 55° C and 120 °C very well.

#### Aromatic Thioplast™ EPS

The chemical structure of the aromatic Thioplast™ EPS grades is dominated by the polysulfide polymer chain and highly reactive epoxy end groups. The following scheme shows the chemical structure of aromatic Thioplast™ EPS 70/80 resins. DGEB A/F is an abbreviation of Di-Glycidyl Ether of Bisphenol A/F resins.

$$R = DGEB A/F Epoxy Resin or DGEB F Epoxy Resin$$

The addition of aromatic Thioplast<sup>TM</sup> EPS 70/80 has only minimal effect on the reactivity of epoxy resins. The desired properties of the system can easily be adjusted by choosing the appropriate hardener system.

**Tables 7a and 7b** show examples of hardeners. Potting times were determined using Thioplast™ EPS 70 (or Thioplast™ EPS 80) and hardener at 23°C. With all hardeners, the resin was tack-free after 12-16 h. After seven days Shore D hardness was between 20 and 25. Adhesion on concrete was excellent and no difference between the various systems was noted. Concrete breakage occurred in all adhesion tests while the Thioplast™ EPS layer remained intact.

**Table 7a:** Examples of Hardeners to cure Thioplast™ EPS 70 / Thioplast™ EPS 80

| Item                | Chemical characteristics of Amine   | H-Equivalent<br>[g/Eq] | Potting time |
|---------------------|-------------------------------------|------------------------|--------------|
| Polypox H 445       | Modified cycloaliphatic Polyamine   | 105                    | 45 min       |
| Polypox H 354       | Mod. cycloaliphatic Polyamine       | 93                     | 35 min       |
| Polypox H 015       | Mannich base, phenol free           | 75                     | 20 min       |
| Aradur 2964         | Aliphatic and cycloaliph. polyamine | 92                     | 40 min       |
| Aradur 450 S        | Mod. polyamidoamine                 | 115                    | 45 min       |
| Epilox 10 - 30      | Mod. cycloaliphatic amino adduct    | 93                     | 35 min       |
| Epilox 10 - 32      | Mod. cycloaliphatic polyamine       | 85                     | 60 min       |
| Epilox 10 - 38      | Activated polyamine                 | 95                     | 30 min       |
| Epilox 10 - 69      | Amino adduct                        | 46                     | 30 min       |
| Cardolite NC 566X80 | Phenalkamin adduct                  | 135                    | 50 min       |

**Table 7b:** Examples of Hardeners to cure Thioplast™ EPS 70 / Thioplast™ EPS 80

| Hardener            | Chemical type of hardener   | Curing<br>@ 60°C<br>(min) | Curing<br>@ 23°C/<br>50% rH<br>(min) | ShoreA<br>7d@23°C/<br>50% rH<br>5s value | ShoreA<br>14d@23°C/<br>50% rH<br>5s value | Tensile<br>strength<br>(N/mm²) | Elongation<br>@ break<br>(%) | Water<br>absorption<br>@ 23 °C<br>After 14d (%) |
|---------------------|-----------------------------|---------------------------|--------------------------------------|--|---|--------------------------------|------------------------------|---|
|                     |                             |                           |                                      |  |   |                                | C/50% rH.<br>H 60 °C         |   |
| Epikure 3223        | Aliphatic Amine             | 20                        | 100                                  | 96                                       | 92  | 16.58                          | 38                           | 2.23  |
| Aradur 2973 CH      | Aliphatic<br>Polyamine      | 60, gelled                | 110, gelled                          | 59.5                                     | 75  | 8.26                           | 38                           | 1.69  |
| Aradur 2992 CH      | Aliphatic<br>Polyamine      | 10, gelled                | 20                                   | 50.9                                     | 78  | 9.66                           | 83                           | 2.34  |
| Epikure 3601        | Anhydride                   | 150                       | 240, gelled                          | 59.9                                     | 95  | 34.19                          | 3                            | 1.27  |
| Aradur 850 CH       | Aromatic Amine<br>Adduct    | 60, gelled                | 180, gelled                          | 56.1                                     | 92  | 14.78                          | 46                           | 1.28  |
| Aradur 863 XW 80 CA | Aromatic Amine<br>Adduct    | 240, gelled               | 240, gelled                          | 39.5                                     | 95  | 20.08                          | 21                           | 1.49  |
| Polypox 060H        | Cycloaliphatic<br>Polyamine | 60, gelled                | 90, gelled                           | 60.9                                     | 88  | 10.59                          | 48                           | 1.67  |
| Epicure 3370        | Cycloaliphatic<br>Polyamine | 25                        | 180                                  | 78                                       | 73  | 6.33                           | 89                           | 3.03  |
| Epicure 3383        | Cycloaliphatic<br>Polyamine | 50                        | 240                                  | 70                                       | 70  | 6.49                           | 63                           | 1.83  |
| Epikure 3115        | Polyamides                  | 50                        | 240, gelled                          | 92                                       | 91  | 11.17                          | 41                           | 2.8   |
| Epikure 3140        | Polyamides                  | 35                        | 240, gelled                          | 91.5                                     | 89  | 15.73                          | 48                           | 2.37  |
| Aradur 891 BD       | Polyamidoamine              | 60 gelled                 | 180, gelled                          | 51.3                                     | 93  | 9.94                           | 54                           | 2.43  |
| Epikure 3015        | Polyamidoamine              | 35                        | 240, gelled                          | 72.5                                     | 75  | 3.88                           | 62                           | 2.74  |
| Epikure 3046        | Polyamidoamine              | 50                        | 240, gelled                          | 83.5                                     | 88  | 7.62                           | 57                           | 2.4   |
| Aradur 460 J 90 BD  | Polyamidoamine/<br>Ethanol  | 60, gelled                | 180, gelled                          | 50.9                                     | 92  | 6.12                           | 34                           | 2.49  |
| Aradur 46S          | Polyamine Adduct            | 40, gelled                | 50, gelled                           | 53.1                                     | 72  | 6.51                           | 68                           | 1.3   |
| Jeffamine D 230     | Polyetheramines             | 90, gelled                | 24h, gelled                          | 46.5                                     | 48  | 3.27                           | 78                           | 2.69  |
| Jeffamine D 400     | Polyetheramines             | 240, gelled               | 24h, gelled                          | 39.9                                     | 53  | 1.15                           | 36                           | 3.08  |

The properties reported in **table 8** refer to mixtures of Thioplast™ EPS 70 and a Bisphenol A/F-resin Epilox T 19-27. A cycloaliphatic hardener, Aradur 2964, was used for curing.

**Table 8:** Properties of Thioplast™ EPS 70 / EPS blends and a Bisphenol A/F-resin (Hardener: Aradur 2964)

| Epilox 19-27 (wt %)            | 0        | 20       | 40       | 60       | 80       | 100    |
|--------------------------------|----------|----------|----------|----------|----------|--------|
| EPS 70 / EPS 80 (wt %)         | 100      | 80       | 60       | 40       | 20       | 0      |
| Viscosity (Pa*s)               | 8.7      | 8.2      | 7.8      | 7.5      | 7.3      | 7.2    |
| Mixing ratio Resin : hardener  | 100:29.7 | 100:33.9 | 100:38.2 | 100:42.5 | 100:46.7 | 100:51 |
| Potting time (min)             | 40       | 40       | 40       | 37       | 35       | 30     |
| Shore D                        | 22       | 35       | 55       | 63       | 70       | 75     |
| Max. elongation after 28 d (%) | 100      | 65       | 40       | 6        | 2        | None   |



#### Weathering stability

Cured resin systems show very good resistance to weathering. Weathering resistance was determined by irradiating with Xenon arc light over a period of 500 h. With increasing Thioplast™ EPS resin content, the degree of yellowing and surface degradation is reduced. Pure Thioplast™ EPS 70 / EPS 80 gives the best results and pure Bisphenol A/F resin the worst. Shore D hardness is hardly affected.

#### Flexibility

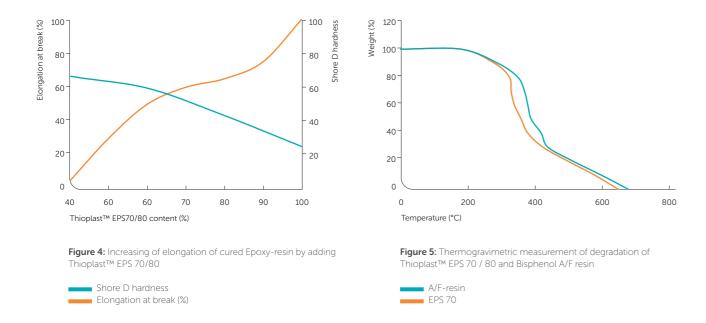
Elasticity and flexibility of cured Thioplast™ EPS resin is more than six times higher than that of pure aromatic epoxies based on Bisphenol A/F resin (figure 4). Addition of Thioplast™ EPS resin to Bisphenol-A/F-resins increases impact resistance. Starting from very hard, non-flexible epoxies one can produce coatings with low or high flexibility by varying the proportions of Thioplast™ EPS resins.

#### Impact resistance

It is possible to formulate very flexible epoxy coatings with simultaneous high hardness by using 55% Thioplast™ EPS 70/80 resin. Impact strength increases to levels several times higher than before. Chemicals and mechanical properties meet the highest demands.

#### Good heat stability

The thermal degradation behaviour of Thioplast<sup>TM</sup> EPS 70/80 resins and their formulations is very similar to that of conventional epoxy resins (**figure 5**).



#### Aliphatic Thioplast™ EPS

The aliphatic Thioplast™ EPS 25 and EPS 35 resins have been developed for exterior use. The low viscosity allows for the use as reactive and flexibilizing diluents for epoxy resins and for the aromatic epoxidized polysulfides Thioplast™ EPS 70, EPS 80.

The chemical structure is dominated by the polysulfide polymer chain with aliphatic epoxy end groups based on epichlorohydrin. The following scheme shows the chemical structure of aliphatic Thioplast<sup>TM</sup> EPS resins.

n = 5-10

#### Viscosity reduction

The low viscosity of Thioplast™ EPS 25 and EPS 35 allows for easy handling at low temperatures. Thioplast™ EPS 25 and EPS 35 resins work as reactive thinner of Thioplast™ EPS 70 / EPS 80 resins as well as in with other epoxybased resins. **Figure 6** illustrates the dependence of resin viscosity on the Thioplast™ EPS 25 content at 25°C.

#### Flexibility

The addition of Thioplast™ EPS 25 or EPS 35 to regular Bisphenol A/F and Novolac resins results in highly flexible epoxies used in

- high-quality sealants and
- adhesives
- highly elastic, chemically resistant coating

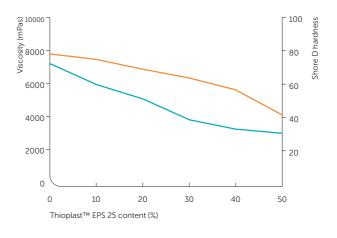


Figure 6: Relationship between viscosity and Thioplast™ EPS 25 content in Bisphenol A/F resins and Thioplast™ EPS 70 / EPS 80 at 25°C

Viscosity (mPas)
Shore D hardness

Figures 7 and 8 show the exeptional increase in flexibility of a standard Bisphenol A/F epoxy-based resin by the addition of EPS 25 and EPS 35. Even at concentrations as low as 10 %, an elongation of break of higher than 20 % is achieveable with EPS 35.

Formulations with high Thioplast™ EPS content are easy to process. Mixtures consisting of aromatic and aliphatic Thioplast™ EPS result in extremely flexible, soft products.

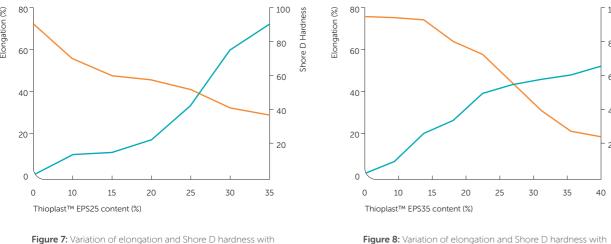


Figure 7: Variation of elongation and Shore D hardness with Thioplast™ EPS 25 content in standard formulations





┌ 100

80

60

40



**Table 9** shows the unformulated stiochiometric curing of Thioplast™ EPS 25 with some industry-standard amine curatives.

**Table 9:** Examples of hardeners to cure Thioplast™ EPS 25

| Hardener            | ner Chemical type of hardener |                      | Tensile strength     | Elongation@<br>break | Wa   | ater absorpt<br>@ 23 °C (%) |      |
|---------------------|-------------------------------|----------------------|----------------------|----------------------|------|-----------------------------|------|
|                     |                               | 7d @ 23°C/<br>50% rH | 1d 23°C<br>rH. + 14c |                      |      |                             |      |
|                     |                               | 5s value             | (N/mm²)              | (%)                  | 7d   | 14d                         | 21d  |
| Epikure 3223        | Aliphatic Amine               | 25                   | 0.32                 | 18.75                | 1.26 | 1.34                        | 1.46 |
| Aradur 2973 CH      | Aliphatic Polyamine           | 22                   | 0.19                 | 19.34                | 1.37 | 1.5                         | 1.63 |
| Aradur 2992 CH      | Aliphatic Polyamine           | 10                   | 0.31                 | 21.92                | 1.48 | 1.58                        | 1.68 |
| Epikure 3601        | Anhydride                     | 13                   |                      |                      |      |                             |      |
| Aradur 850 CH       | Aromatic Amine Adduct         | gel, sticky          |                      |                      |      |                             |      |
| Aradur 863 XW 80 CA | Aromatic Amine Adduct         | gel, sticky          |                      |                      |      |                             |      |
| Polypox 060H        | Cycloaliphatic Polyamine      | gel, sticky          |                      |                      |      |                             |      |
| Epikure 3115        | Polyamides                    | gel, sticky          |                      |                      |      |                             |      |
| Epikure 3140        | Polyamides                    | gel, sticky          |                      |                      |      |                             |      |
| Aradur 891 BD       | Polyamidoamine                | 12                   | 0.29                 | 20.28                | 1.15 | 1.27                        | 1.53 |
| Epikure 3015        | Polyamidoamine                | gel, sticky          |                      |                      |      |                             |      |
| Epikure 3046        | Polyamidoamine                | 20                   | 0.22                 | 15                   | 1.05 | 1.08                        | 1.12 |
| Aradur 460 J 90 BD  | Polyamidoamine/ Ethanol       | gel, sticky          |                      |                      |      |                             |      |
| Aradur 46S          | Polyamine Adduct              | 19                   | 0.40                 | 24.4                 | 1.53 | 1.52                        | 1.64 |
| Jeffamine D 230     | Polyetheramines               | gel, sticky          | 0.24                 | 25.75                | 1.77 | 1.81                        | 2.04 |
| Jeffamine D 400     | Polyetheramines               | gel, sticky          | 0.28                 | 23.53                | 2.08 | 2.16                        | 2.21 |

The same stoichiometric curing with exemplary industrial standard amine curatives has also been performed with the new Thioplast<sup>TM</sup> EPS 35 (table 10). Compared to Thioplast™ EPS 25, the reactivity is greatly increased.

**Table 10:** Examples of hardeners to cure Thioplast™ EPS 35.

| Hardener*       | Chemical type of hardener | ShoreA 7d<br>@ 23°C/50% rH 5s<br>value | Tensile strength Elongation@break 1d 23°C/50% rH. + 14d 60 ° |      |
|-----------------|---------------------------|--|--|------|
|                 |                           |  | [N/mm <sup>2</sup> ]   | [%]  |
| Epikure 3140    | Polyamide                 | 13.4                                   | 0.24   | 26.1 |
| Aradur 891 BD   | Polyamidoamine            | 32.9                                   | 0.39   | 34.6 |
| Aradur 2973 CH  | Aliphatic Polyamine       | 42.7                                   | 0.35   | 20.8 |
| Aradur 450-1 S  | Polyaminoamine            | 28.3                                   | 0.31   | 40.7 |
| Aradur 15-1     | Polyamine                 | 6.6                                    | 0.10   | 60.0 |
| Aradur 2965     | Cycloaliphatic polyamine  | 38                                     | 0.41   | 34.8 |
| Jeffamine D 400 | Polyetheramines           | 13.2                                   | 0.2  | 60.9 |

<sup>\*</sup> Thioplast™ EPS 35 cured in a stoichiometric ratio

#### Starting Formulations For Thioplast™ EPS 25, EPS35 and EPS 70/80

#### Standard Formulations using Thioplast™ EPS 70 / EPS 80

Thioplast™ EPS 70 works as a versatile flexibilizer for solvent-free coatings showing superb chemical resistance even when applied in thin layers. Thioplast™ EPS adds flexibility to epoxy resins and at the same time improves the chemical resistance of the resulting product.

Varying the ratio of Thioplast™ EPS to epoxy resin (by weight) allows for adjustment of properties according to specific needs of a particular application.

**Table 11:** Standard formulations for Thioplast™ EPS 70 or Thioplast™ EPS 80

|                           | Formulation 1 green sample | Formulation 2 blue sample | Formulation 3 yellow sample |
|---------------------------|----------------------------|---------------------------|-----------------------------|
| Component A               |                            |                           |                             |
| Thioplast™ EPS 70 / 80    | 35                         | 55                        | 75                          |
| Bisphenol A/F resin*      | 40                         | 20                        | -                           |
| Novarez LA 300**          | 5                          | 5                         | 5                           |
| Filler***                 | 15                         | 15                        | 15                          |
| Pigment                   | 5                          | 5                         | 5                           |
| Total component A         | 100                        | 100                       | 100                         |
| Component B               |                            |                           |                             |
| Component B Aradur 2964   | 31                         | 27                        | 22                          |
| Potting time @23 °C (min) | 30                         | 32                        | 35                          |
| Max. elongation (%)       | 4                          | 10                        | 70                          |
| Shore D @ 21d             | 60                         | 39                        | 22                          |
| Strength @ break (N/mm²)  | 34                         | 11.8                      | 5.5                         |

<sup>\*</sup> A/F resin: Epoxy equivalent approx.180g/equiv.; Viscosity: 6000 - 8000 mPas. Also pure Bisphenol A-resins may be used.

\*\* Instead of Novares LA 300 reactive diluents, benzyl-alcohol or other diluents suited for Epoxy resins may be used. When using such diluents check for adhesion decrease.

The elongation of the resulting polymer increases rapidly at a Thioplast™ EPS 70 / EPS 80 content between 55 and 80%. Shore D hardness declines almost linearly in the same interval.

#### Adhesion testing

Adhesion on concrete surfaces was tested according to DIN.ISO 4624 and DIN EN 1348 using an adhesion testing device (HZP12D1). The result was cohesive breakage of concrete in all cases (**picture 1**)

#### Crack bridging

Values for crack bridging have been determined according to DIN 28052-6. The widening of crack occurred at a speed of 0.02 mm/min. For all three formulations crack bridging of at least 0.3 mm could be demonstrated (21°C, 1 mm layer). At 0°C crack bridging is 0.2 mm for the green and 0.3 mm for the yellow and the blue formulation. At -20°C we measured 0.2 mm for all samples. With thicker layers and different layer architecture higher values for crack bridging may be reached.



Picture 1: Adhesion on concrete surfaces

#### Standard formulations using Thioplast™ EPS 25 / EPS 35

**Table 12** shows formulation examples for the aliphatic Thioplast™ EPS 25 grade.

**Table 12:** Standard formulations for Thioplast<sup>TM</sup> EPS 25

|                           | Formulation 4 green sample | Formulation 5 grey sample | Formulation 6 blue sample | Formulation 7 yellow sample |
|---------------------------|----------------------------|---------------------------|---------------------------|-----------------------------|
| Component A               |                            |                           |                           |                             |
| Thioplast™ EPS 25         | 10                         | 20                        | 30                        | 40                          |
| Bisphenol A/F resin       | 65                         | 55                        | 45                        | 35                          |
| Filler                    | 20                         | 20                        | 20                        | 20                          |
| Pigment                   | 5                          | 5                         | 5                         | 5                           |
| Total Component A         | 100                        | 100                       | 100                       | 100                         |
| Component B               |                            |                           |                           |                             |
| Aradur 2964               | 34.7                       | 31.1                      | 27.5                      | 24                          |
| Potting time @ 25 °C (h)  | 33                         | 35                        | 37                        | 42                          |
| Max. elongation (%)       | 13                         | 17                        | 63                        | 78                          |
| Shore D after 21 d @ r.t. | 67                         | 60                        | 52                        | 26                          |
| Strength @ break (N/mm²)  | 22                         | 16                        | 8                         | 5                           |

The elongation and Shore D hardness are very similar to those found with Thioplast™ EPS 70. Testing for adhesion and crack bridging gave analogous results.

<sup>\*\*\*</sup> Chalk, talc, quartz powder, kaolin, barite or titanium dioxide may be used as fillers. Note that hardness and elongation may change depending on the filler used. For the standard formulations shown here a mixture of talc AT1 and quartz powder W 8 was used. Talc, barite and kaolin are recommended for producing coatings with high chemical resistance.

**Table 13** shows standard formulations with Thioplast™ EPS 35. The reactivity is significantly increased compared to EPS 25. Also the flexibility of the cured EPS 35-based material is higher at lower concentrations.

**Table 13:** Standard formulations for Thioplast™ EPS 35

|                          | Formulation 4<br>EPS35 | Formulation 5<br>EPS35 | Formulation 6<br>EPS35 | Formulation 7<br>EPS35 |
|--------------------------|------------------------|------------------------|------------------------|------------------------|
| Component A              |                        |                        |                        |                        |
| Thioplast™ EPS 35        | 10                     | 20                     | 30                     | 40                     |
| Bisphenol A resin        | 65                     | 55                     | 45                     | 35                     |
| Filler                   | 20                     | 20                     | 20                     | 20                     |
| Pigment                  | 5                      | 5                      | 5                      | 5                      |
| Total Component A        | 100                    | 100                    | 100                    | 100                    |
| Component B              |                        |                        |                        |                        |
| Aradur 2964              | 31.4                   | 26.7                   | 23.3                   | 20.6                   |
| Potting time @ 25°C [h]  | >2                     | >2                     | >3                     | >3                     |
| Max. elongation [%]      | 27                     | 50                     | 59                     | 66                     |
| Shore D after 21d @ r.t. | 74                     | 58                     | 32                     | 20                     |
| Strength @ break [N/mm2] | 27                     | 16                     | 9                      | 6                      |

#### Applicability of EPS Formulations 1 - 7

#### Formulations 1, 4 and 5

This formulation is only slightly flexibilized. It is recommended for floor coating in facilities with heavy traffic (trucks and fork-lift trucks - meet the German LAU regulations).

#### Formulations 2 and 6

A low content of Thioplast<sup>TM</sup> EPS 70 yields a formulation with low elasticity which is particularly suited for coatings that need to have crack bridging capability. It can be used for storage and handling areas (LAU) for substances that are water hazardous and in sewage plants involving light traffic.

Since this formulation provides excellent barrier properties to water vapor it may be used as a coating material for steel, titanium and PP parts (pipe coating). It is also well suited for heavy duty coatings to be used in industrial areas like slaughterhouses, large-scale catering facilities and laundries where frequent use of hot vapor and aggressive cleaners can be expected.

#### Formulation 3 and 7

Due to the high content of Thioplast™ EPS this formulation is highly elastic and is, therefore, particularly suited for the coating of containment basins in tank farms for fuels and chemicals, especially when high tolerance of large temperature differences and extensive motion is expected.

#### References

This choice of reference projects shall illustrate the versatility of Thioplast™ EPS resins in different applications.

#### Coating of shop floors

Coating of the floor in a wholesale slaughter-house with Thioplast<sup>TM</sup> EPS was applied when conventional EP based coatings failed due to the extreme technical demands. This floor is subjected to wheel traffic and is cleaned frequently with steam cleaning devices and aggressive cleaners. This application requires very good adhesion and tightness, especially at the interface to build-in tables, supports and rails (picture 2).

#### Containment basin for oil and chemicals

The restoration of containment basins for oil tanks requires crack-bridging, chemically resistant coatings, which in addition are insensitive against humidity diffusing from the underground. This coating can be completed by using polysulfide based joint sealants (picture 3).

Extreme conditions can be found in truck-wash stations and in chemical plants. The floor coating has to withstand organic solvents, diluted alkali and acids and changes in temperatures. It also needs to have to have anti-slip properties and to tolerate the mechanical stress caused by traffic of heavy trucks (**picture 4**).



**Picture 2:** Thioplast™ EPS coating of the floor in a slaughterhouse



**Picture 3:** Polysulfide based joint sealant as a crack-bridging, chemically resistant coating



Picture 4: Floor coating of a truck-wash station in a chemical plant

#### Heavy duty corrosion protection

Good gas tightness, very good resistance to marine climate and excellent adhesion to steel make EPS products ideal candidates for heavyduty corrosion protection. One example may be the restoration of industrial shipping areas and naval ports (**picture 5**).

#### Coatings for sewage plants and sewer

The combination of anti-fouling properties, high chemical resistance and low gas diffusion rates suggest the use of Thioplast<sup>TM</sup> EPS for coatings of sewage plants and sewers (**picture 6**).

#### Marine protective coatings

Thioplast™ EPS resins are used as components for marine and protective coatings applications. The material fulfils many specific demands of these applications due to the outstanding properties of Thioplast™ EPS resins, e.g. very good adhesion on different surfaces, anti-fouling (formulation dependent) properties and high chemical resistance (picture 7).



Picture 5: Heavy-duty corrosion protection of industrial shipping



**Picture 6:** Thioplast™ EPS coatings of sewage plant



Picture 7: Marine and protective coatings applications



#### **Reference Formulations**

Basic reference formulations are available upon request. Please contact your Nouryon regional representative or technical manager for additional information by an extra technical info brochure.

#### Status of this information: July 2019

- For actual changes and news please refer to https://sulfurderivatives.nouryon.com/ thioplast/
- Technical Customer Service: Dr. Volker Burkhardt (volker.burkhardt@nouryon.com)
- Business Development: Dr. Christian Probst (christian.probst@nouryon.com)
- Nouryon Funtional Chemicals GmbH, 07973 Greiz, Germany

#### Legal disclaimer

All information, recommendations and suggestions appearing in this literature concerning the

use of the products are based upon tests and data believed to be reliable, however, it is the user's responsibility to determine the suitability for his own use of the products described here. Since the actual use by others is beyond the control of Nouryon Functional Chemicals GmbH no guarantee expressed or implied is made by Nouryon Functional Chemicals GmbH as to the effect of such use or the results to be obtained, nor does Nouryon Functional Chemicals GmbH assume any liability arising out of the use by others of the products referred to herein. Nor is the information herein to be construed as absolutely complying with existing applicable laws or government regulations. Nothing herein contained is to be construed as permission or as a recommendation to infringe any patent. All orders accepted shall be subjected to the standard conditions of sale of the manufacturing company, Nouryon Functional Chemicals GmbH

## Nouryon

Nouryon Liebigstraße 7 07973 Greiz - Germany T 03661-78-0 F 03661-78-202/-219 sulfurderivatives.nouryon.com

We are a global specialty chemicals leader. Industries worldwide rely on our essential chemistry in the manufacture of everyday products such as paper, plastics, building materials, food, pharmaceuticals, and personal care items. Building on our nearly 400-year history, the dedication of our 10,000 employees, and our shared commitment to business growth, strong financia performance, safety, sustainability, and innovation, we have established a world-class business and built strong partnerships with our customers. We operate in over 80 countries around the world and our portfolio of industry-leading brands includes Eka. Dissolvine. Trigonox, and Berol.