

Heat de- and rebondable, in-situ polymerized resin composition**Technical Field**

[01] The invention relates to a heat de- and rebondable polymer formed by the *in-situ* reaction between a difunctional mercaptan hardener and a difunctional thiol-reactive resin, said polymer has a softening point above about 70°C.

Background of the Invention

[02] Mercaptans cure epoxies through an active hydrogen on a sulfur group (S-H). Commercially available mercaptan hardeners typically have multiple S-H groups available for curing. Mercaptan hardeners are especially popular as they provide polymers with excellent properties; for example, good bonding to wood, metal and plastic, fast curing times, and low toxicity.

[03] However, the polymers formed with polymer mercaptans known in the prior art do not exhibit at the same time, good adhesion, high thermomechanical properties, and thermal reversible bonding abilities.

[04] Thermoset polymers formed by the reaction of mercaptans and thiol-reactive resins in general show good adhesion and high thermomechanical properties. However, they do not have a softening point and hence do not facilitate thermal reversible bonding properties. In contrast, thermoplastic-like materials formed by known resin compositions based on difunctional mercaptans show poor adhesion and low thermomechanical properties.

[05] WO2012140194A2, the contents of which are incorporated herein by reference, describes the process of producing a thermoplastic polymer containing sulphur atoms having a melting point above 40°C and below the degradation temperature of the material. However, the thermoplastic is exclusively produced by thiol-ene click reactions and not all resins are considered. For example, epoxy-based resins are not discussed.

Object of the Invention

[06] Therefore, the object underlying the present invention is to provide resin compositions based on mercaptans that exhibit similar properties to thermoset polymers but have a reversible bonding ability. To fulfil this need, we have shown that selected difunctional mercaptan hardeners, when

reacted with difunctional thiol-reactive resins, result in materials that have a high softening point in the desired range of the applications.

Disclosure of the Invention

[07] The present invention will be described with respect to particular aspects and embodiments.

[08] It is to be noticed that the term "comprising", used in the claims, should not be interpreted as being restricted to the means listed thereafter; it does not exclude other elements or steps. It is thus to be interpreted as specifying the presence of the stated features, steps or components as referred to, but does not preclude the presence or addition of one or more other features, steps or components, or groups thereof. Thus, the scope of the expression "a compound comprising components X and Y" should not be limited to compounds consisting only of components X and Y. It means that with respect to the present invention, the only relevant components of the compound are X and Y.

[09] Throughout this specification, reference to "one embodiment" or "an embodiment" are made. Such references indicate that a particular feature, described in relation to the embodiment is included in at least one embodiment of the present invention. Thus, appearances of the phrases "in one embodiment" or "in an embodiment" in various places throughout this specification are not necessarily all referring to the same embodiment, though they could. Furthermore, the particular features or characteristics may be combined in any suitable manner in one or more embodiments, as would be apparent to one of ordinary skill in the art.

[010] It is to be understood that although preferred embodiments and/or materials have been discussed for providing embodiments according to the present invention, various modifications or changes may be made without departing from the scope and spirit of this invention.

[011] The terms "preferred" and "preferably" refer to embodiments that may afford certain benefits, under certain circumstances. However, other embodiments may also be preferred, under the same or other circumstances. Furthermore, the recitation of one or more preferred embodiments does not imply that other embodiments are not useful and is not intended to exclude other embodiments from the scope of the present disclosure.

[012] Where substituent groups are specified by their conventional chemical formula, written from left to right, they equally encompass the chemically identical substituents that would result from writing the structure from right to left, for example, $-\text{CH}_2\text{O}-$ is equivalent to $-\text{OCH}_2-$.

[013] The term “optional” or “optionally” means that the subsequently described event or circumstance may or may not occur, and that the description includes instances where said event or circumstance occurs and instances where it does not.

[014] Throughout this disclosure, the term “about” is used to indicate that a value includes the inherent variation of error for the quantifying device, mechanism, or method, or the inherent variation that exists among the subject(s) to be measured. For example, but not by way of limitation, when the term “about” is used, the designated value to which it refers may vary by plus or minus ten percent, or nine percent, or eight percent, or seven percent, or six percent, or five percent, or four percent, or three percent, or two percent, or one percent, or one or more fractions therebetween.

[015] The phrases “or combinations thereof” and “and combinations thereof” as used herein refers to all permutations and combinations of the listed items preceding the term. For example, “A, B, C, or combinations thereof” is intended to include at least one of: A, B, C, AB, AC, BC, or ABC and, if order is important in a particular context, also BA, CA, CB, CBA, BCA, ACB, BAC, or CAB. Continuing with this example, expressly included are combinations that contain repeats of one or more items or terms such as BB, AAA, CC, AABB, AACC, ABCCCC, CBBAAA, CABBB, and so forth. The skilled artisan will understand that typically there is no limit on the number of items or terms in any combination, unless otherwise apparent from the context. In the same light, the terms “or combinations thereof” and “and combinations thereof” when used with the phrases “selected from” or “selected from the group consisting of” refers to all permutations and combinations of the listed items preceding the phrase.

[016] The object of the invention is solved by a de- and re- bondable polymer prepared from the reaction between a difunctional mercaptan hardener and a difunctional thiol-reactive resin; wherein said polymer has a softening point greater than about 70 °C, preferably between about 90 and about 150 °C.

[017] The polymers of the invention exhibit similar thermomechanical and bonding properties to thermoset polymers but can be de- and re-bonded at elevated temperature. Resin compositions comprising the polymers of the invention can therefore be used as recyclable adhesive and recyclable

resin for composite applications, can easily be debonded/ rebonded/ reshaped and, therefore, are particularly useful as a sustainable product.

[018] Used herein, a difunctional mercaptan hardener is any compound comprising approximately two mercaptan (-SH) groups. The term sulfhydryl can also be used to describe a mercaptan group.

[019] A difunctional thiol reactive resin is any resin containing approximately two functional groups that are capable of reacting with thiols to form a covalent bond.

[020] The softening point is the temperature at which a material softens beyond some arbitrary softness. It can be determined, for example, by the Vicat method (ASTM-D1525 or ISO 306), Heat Deflection Test (ASTM-D648) or a ring and ball method (ISO 4625 or ASTM E28-67/E28-99 or ASTM D36 or ASTM D6493 - 11 or JIS K 6863). A ring and ball apparatus can also be used for the determination of softening point of bituminous materials. In some embodiments, the softening point is measured using a Mettler, DIN 51920 softening point determination device.

[021] In a further embodiment of the first aspect of the invention, the de- and re- bondable polymer has a G' onset of greater than 40 °C, preferably greater than 45 °C.

[022] G' onset, sometimes referred to as the glass transition (T_g) temperature, is the temperature at which molecular mobility begins to take place, below which molecular mobility is frozen and the elastomer becomes rigid and glassy. G' onset can be measured according to any method known by the skilled person. For example, the procedure described in ISO6721. That is, by performing dynamic mechanical analysis using an ARES-G2 rheometer with a temperature ramp rate of 2K/min, a frequency of 1 Hz and a strain of 0.15%.

[023] In a further embodiment of the first aspect of the invention, the de- and rebondable polymer has a lap shear strength above about 1MPa at 60°C, preferably above about 1MPa at 80°C.

[024] Lap shear strength is a measure of the ability of a material to withstand stresses set in a plane, where the exerted shear force is moving the two substrates in opposite directions. It is one of the most common stresses that a bonded joint can face during service, especially in structural bonding applications. Lap shear strength can be measured using any method known to the skilled person. For example, that set out in the ISO 4587 test procedure. This procedure is typically performed for an aluminium to aluminium bond joint but also other substrates like metallic, glass or polymeric substrates can be used. The substrates are usually roughened, cleaned, and dried prior to the

application of the adhesive. The parts with the adhesive between them are clamped or fixtured during the curing process. Once the adhesive is fully cured, the substrates would be pulled in opposite directions (in shear) until the substrates separate. The force needed to pull the substrates apart is then used to determine the lap shear strength.

[025] In a further embodiment of the first aspect of the invention, the difunctional mercaptan hardener and difunctional thiol-reactive resin have a preferred average functionality between about 1.8 and about 2.2.

[026] Providing a mercaptan hardener and difunctional thio-reactive resin with an average functionality between about 1.8 and about 2.2, enables the preparation of linear polymers with preferred thermoplastic properties. If the functionality is below about 1.8, the polymer length could be relatively short and therefore the polymer properties could be negatively affected. If the functionality is above about 2.2, there is a risk that the resultant polymer will thermoset and not be able to be softened.

[027] In a further embodiment, the molar ratio of the mercaptan hardener to the thiol-reactive resin ranges from about 0.5 to about 2.0, preferably from about 0.9 to about 1.1.

[028] By preparing a polymer wherein the specific molar ratio between the mercaptan hardener and thiol-reactive resin is from about 0.5 to about 2.0 enables the preparation of thermoplastic polymers with preferred properties. The polymers of the invention are formed by step growth polymerization. The stoichiometric ratio of both monomers therefore influences the molecular weight of the resulting polymer. If there is too much thiol-reactive resin, the thiol reactive resin groups may homopolymerize resulting in the formation of a crosslinked polymer without the desired softening and melting points. If the amount of thiol reactive polymer is too low, the polymer chains may be too short.

[029] In certain embodiments, the difunctional thiol-reactive resin is selected from difunctional epoxy resins, diene resins (e.g., difunctional (meth)acrylates), difunctional isocyanates and combinations thereof. Preferably, the thiol-reactive resin is an epoxy resin.

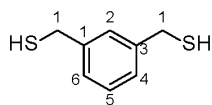
[030] Examples of difunctional epoxy resins include those selected from glycidyl ethers based on difunctional aromatic alcohols, such as bisphenol F, bisphenol A (optionally brominated), bisphenol S, resorcinol, and dihydroxy-naphthalene's, (ii) glycidyl ethers of difunctional saturated or unsaturated,

branched or unbranched, cyclic or open-chain aliphatic alcohols, such as ethylene glycol, butanediol, hexanediol, cyclohexanedimethanol, and neopentylglycol; (iii) glycidyl esters of dicarboxylic acids such as phthalic acid, tetrahydrophthalic acid, and hexahydrophthalic acid and dimeric fatty acid (iv) and combinations thereof.

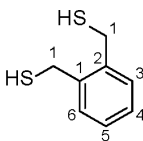
[031] Suitable examples of difunctional isocyanate resins include those selected from aliphatic diisocyanates such as hexamethylene-1,6-diisocyanate, 2,2,4- or 2,4,4-trimethylhexamethylene-1,6-diisocyanate; alicyclic diisocyanates such as cyclohexane-1,4-diisocyanate, dicyclohexylmethane-4,4'-diisocyanate; aromatic diisocyanates such as p-phenylene diisocyanate, tolylene-2,4- or -2,6-diisocyanate, diphenylmethane-2,4- or -4,4'-diisocyanate, naphthylene-1,5-diisocyanate, xylylene-1,3- or -1,4-diisocyanate, and combinations thereof.

[032] It is also possible to use diphenylmethane diisocyanates containing a carbodiimide group or uretonimide group or modified difunctional isocyanates containing an allophanate group, urethane group, biuret group and/or urethidione group.

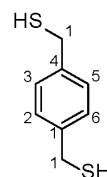
[033] In certain embodiments, the difunctional mercaptan is selected from the group consisting of 1,1'-[isopropylidenebis(p-phenyleneoxy)]bis[3-mercaptopropan-2-ol], 1,3-phenylenedimethanethiol, 1,2-phenylenedimethanethiol, 1,4-phenylenedimethanethiol, 3,3'-(1,3-phenylenebis(oxy))bis(1-mercaptopropan-2-ol), 3,3'-((propane-2,2-diylbis(4,1-phenylene))bis(oxy))bis(propane-1-thiol), octahydro-1H-4,7-methanoindene-1,5-dithiol, 3,3'-((methylenebis(4,1-phenylene))bis(oxy))bis(1-mercaptopropan-2-ol), 5-(1-mercaptopropan-2-yl)-2-methylcyclohexane-1-thiol and combinations thereof. The structures of these difunctional mercaptans are shown below:



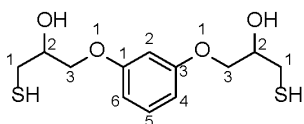
1,3-phenylenedimethanethiol



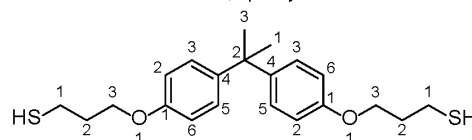
1,2-phenylenedimethanethiol



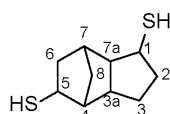
1,4-phenylenedimethanethiol



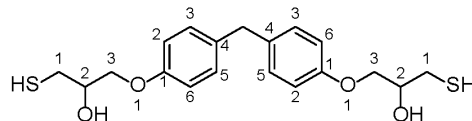
3,3'-(1,3-phenylenebis(oxy))bis(1-mercaptopropan-2-ol)



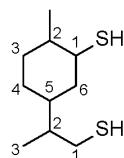
3,3'-((propane-2,2-diylbis(4,1-phenylene))bis(oxy))bis(propene-1-thiol)



octahydro-1H-4,7-methanoindene-1,5-dithiol

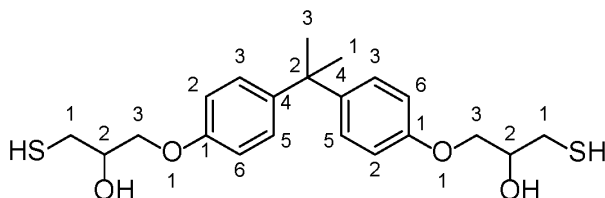


3,3'-((methylenebis(4,1-phenylene))bis(oxy))bis(1-mercaptopropan-2-ol)



5-(1-mercaptopropan-2-yl)-2-methylcyclohexane-1-thiol

Most preferably, the difunctional mercaptan is 1,1'-[isopropylidenebis(p-phenyleneoxy)]bis[3-mercaptopropan-2-ol].



[034] The inventors have surprisingly found that 1,1'-[isopropylidenebis(p-phenyleneoxy)]bis[3-mercaptopropan-2-ol] when cured with Araldite® GY 240 (diglycidyl ether of bisphenol A) forms a resin with a softening point above about 70 °C with high structural adhesion properties up to about 80 °C.

[035] In certain embodiments, the polymer is combined with further components selected from fillers (e.g., calcium carbonate, silica, aluminium trihydroxide, alumina, hollow spheres, carbon black, boron nitride), fibers (carbon fiber, glass fiber, natural fibers, polymer based fiber), adhesion promoter

(siloxane based, phosphate based), flexibilizers, dyes, pigments, toughening agents (e.g., core shell rubber), UV stabilizer, Antioxidants, flame retardants and the like, as well as mixtures of any two or more thereof.

[036] In certain embodiments, the polymer is cured at a temperature range of about 25°C – about 80°C.

[037] In certain embodiments, curing takes place in the presence of a catalyst/accelerator. Preferably, the catalyst is selected from amine based catalysts (such as, JEFFCAT® ZR-70) or phosphorus based catalysts (such as, trioctyl phosphine).

[038] The presence of a catalyst/accelerator may speed up the rate of curing or reduce the temperature at which curing occurs. In some embodiments, the presence of a catalyst/accelerator improves the properties of the resultant resin.

[039] A further aspect of the present invention is a process for preparing the polymer of any one of the preceding claims, said process comprising:

- i) mixing the difunctional mercaptan hardener and the difunctional thiol-reactive resin to produce a mixture;
- ii) curing the mixture at a temperature between about 25°C – about 80°C.

[040] In a further aspect of the invention is provided a composition comprising a difunctional mercaptan hardener; and a difunctional thiol-reactive resin.

The difunctional mercaptan hardener and the difunctional thiol-reactive resin are the same as those described above.

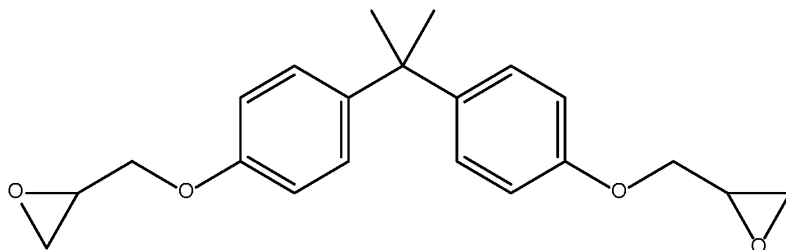
In some embodiments, the composition may comprise further additional components. For example, including but not limited to fillers (e.g., calcium carbonate, silica, aluminium trihydroxide, alumina, hollow spheres, carbon black, boron nitride), fibers (carbon fiber, glass fiber, natural fibers, polymer based fiber), adhesion promoter (siloxane based, phosphate based), flexibilizers, dyes, pigments, toughening agents (e.g., core shell rubber), UV stabilizer, Antioxidants, flame retardants and the like, as well as mixtures of any two or more thereof.

Examples

[041] More details and advantages will become obvious from the following examples. 1,8-Dimercapto-3,6-dioxaoctane, methanesulfonic acid, triethylamine, thioacetic acid were supplied by *Sigma-Aldrich/ Merck*. The components used have the following compositions.

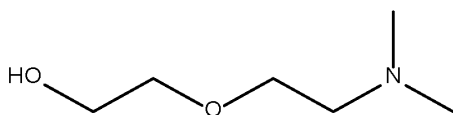
Araldite® GY 240 – Diglycidyl ether of Bisphenol-A

1,1'-[isopropylidenebis(p-phenyleneoxy)]bis[3-mercaptopropan-2-ol]

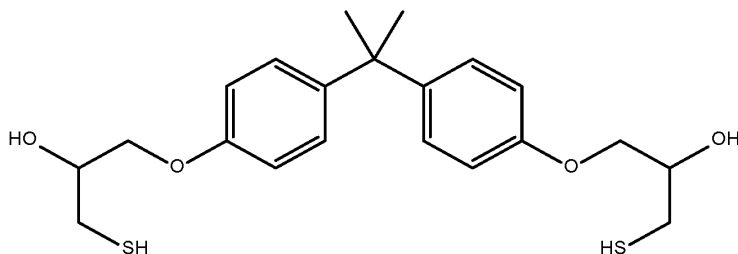


JEFFCAT® ZR-70 – amine based catalyst.

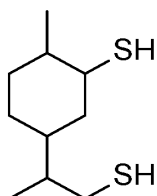
2-(2-dimethylaminoethoxy)ethanol



1,1'-[isopropylidenebis(p-phenyleneoxy)]bis[3-mercaptopropan-2-ol]



5-(1-mercaptopropan-2-yl)-2-methylcyclohexane-1-thiol



Synthesis procedure of 1,1'-[isopropylidenebis(p-phenyleneoxy)]bis[3-mercaptopropan-2-ol]:

Thioacetic acid (43.8 mL, 0.62 mol) was charged in a 250 mL three-neck round bottom flask. The flask was purged with nitrogen, then triethylamine (0.6 g, 6.0 mmol) was slowly added to the mixture over 10 min. Araldite® GY 240 (100 g, 0.56 mol of epoxy functional group) was dissolved in ethanol (30.0 g) and the resulting solution was added dropwise to the previous described mixture under nitrogen, keeping the internal temperature between 20-60°C. After complete addition, the mixture was stirred for a further 3 h.

The resultant mixture was heated to 65°C and a solution of methanesulfonic acid (9.6 g, 0.11 mol) in ethanol (12.0 g) was added over 10 min. After a reaction time of 5 h at 65°C, the mixture was cooled down to room temperature and ethyl acetate (10.0 g) was added. Then, water (50.0 g) was added and the mixture was adjusted to pH=3 using a 25 wt% aqueous solution of NaOH. The organic layer was separated, washed twice with brine (2 x 50 ml), filtered and concentrated under reduced pressure to obtain the desired product as a yellow high viscous oil.

The obtained product was identified from its ¹H-NMR spectrum.

Example 1

[042] 135 pbw of 1,1'-[isopropylidenebis(p-phenyleneoxy)]bis[3-mercaptopropan-2-ol] (*synthesized as described above*), 100 pbw of Araldite® GY 240 (*Huntsman*) and 1 pbw of JEFFCAT® ZR-70 (*Huntsman*) were mixed and cured at 80°C for 1 h to yield a plate with about 2 mm thickness.

Comparative Example 1

[043] 54 pbw of 1,8-Dimercapto-3,6-dioxaoctane (*Sigma-Aldrich/ Merck*), 100 pbw of Araldite® GY 240 (*Huntsman*) and 1 pbw of JEFFCAT® ZR-70 (*Huntsman*) were mixed and cured at 80°C for 1 h to yield a plate with about 2 mm thickness.

[044] The following tests were performed on the resultant formulations. The results are shown in Table 1 below.

G' onset (T_g, glass transition temperature) determination

G' onset was tested using the protocol set out in ISO6721. Dynamic mechanical analysis was performed using an ARES-G2 rheometer with a temperature ramp rate of 2K/min, a frequency of 1 Hz and a strain of 0.15%. That is, the specimen is subjected to a sinusoidal torque or angular displacement at a frequency significantly below the fundamental torsion resonance frequency, usually 1 Hz. The

amplitudes of the torque and displacement cycles applied to the specimen and the phase angle between these cycles are measured. The storage (G') and loss (G'') components of the shear complex modulus and the loss factor ($\tan \delta$) are calculated. Initial and final temperatures were adapted according to the thermomechanical properties of materials.

Softening point determination (Mettler, DIN 51920)

The resultant formulations were mixed and cured at 1 h in the crucible of a Mettler, DIN 51920 softening point determination device.

Lap Shear Strength testing (according to ISO 4587):

The resulting formulations were applied on Alu L165 plates previously sandblasted and degreased. Specimens were bonded by contact pressure and cured at 80°C for 1 h. Lap shear strength tests were performed at 25°C, 40°C, 60°C and 80°C.

Component		Ex.1 (pbw)	Comp. Ex.1 (pbw)
	1,1'-[isopropylidenebis(p-phenyleneoxy)]bis[3-mercaptopropan-2-ol]	135	-
	1,8-Dimercapto-3,6-dioxaoctane	-	54
	JEFFCAT® ZR-70	1	1
	Araldite® GY 240	100	100
Property	G' onset (°C)	53	2
	Softening point (°C)	141	66
	Lap Shear Strength at 25°C on Alu L165 (MPa)	9.2 ± 1.6	8.5 ± 0.5
	Lap Shear Strength at 40°C on Alu L165 (MPa)	12.0 ± 0	0.2 ± 0.2
	Lap Shear Strength at 60°C on Alu L165 (MPa)	12.9 ± 1.2	0.3 ± 0.2
	Lap Shear Strength at 80°C on Alu L165 (MPa)	1.6 ± 0.5	0.2 ± 0.1

Table 1: The effect of softening point on thermomechanical and adhesion properties of the resins of example 1 and comparative example 1.

[045] It was found that the material of Example 1 having a softening point above 70°C maintained high adhesion properties up to 80°C. In contrast, the material of Comparative Example 1 having a softening point below 70°C (Comp. Ex. 1) exhibited no adhesion strength at and above 40°C.

Example 2

[046] Thermal reversible bonding capabilities of the inventive resin composition, formed by *in situ* reaction between 1,1'-[isopropylidenebis(p-phenyleneoxy)]bis[3-mercaptopropan-2-ol] and Araldite® GY240, was compared with a commercial polymericaptan-based adhesive (Araldite®2012). Thermal reversible bonding properties were evaluated by lap shear strength test on aluminium at 25°C (initial bonding), 130°C (debonding step) and after the rebonding step again tested at 25°C.

[047] 135 pbw of 1,1'-[isopropylidenebis(p-phenyleneoxy)]bis[3-mercaptopropan-2-ol] (*synthesized as described above*), 100 pbw of Araldite® GY 240 (*Huntsman*) and 2 pbw of JEFFCAT® ZR-70 (*Huntsman*) were mixed and cured at 80°C for 1 h to yield a plate with about 2 mm thickness.

Example 3

[048] Thermal reversible bonding capabilities of the inventive resin composition, formed by *in situ* reaction between 5-(1-mercaptopropan-2-yl)-2-methylcyclohexane-1-thiol and Araldite® GY240, was compared with a commercial polymericaptan-based adhesive (Araldite®2012). Thermal reversible bonding properties were evaluated by lap shear strength test on aluminium at 25°C (initial bonding), 130°C (debonding step) and after the rebonding step again tested at 25°C.

[049] 57 pbw of 5-(1-mercaptopropan-2-yl)-2-methylcyclohexane-1-thiol, 100 pbw of Araldite® GY 240 (*Huntsman*) and 2 pbw of JEFFCAT® ZR-70 (*Huntsman*) were mixed and cured at 80°C for 1 h to yield a plate with about 2 mm thickness.

Comparative Example 2

[050] 100 pbw of Araldite®2012/A (*Huntsman*) and 100 pbw of Araldite®2012/B (*Huntsman*), a two component epoxy adhesive based on epoxy resin and a mercaptan curing agent, were mixed and cured at 80°C for 1 h to yield a plate with about 2 mm thickness.

G' onset (T_g, glass transition temperature) determination:

G' onset tests were performed according to (ISO6721) as described above.

Softening point determination (Mettler, DIN 51920):

The resultant formulations were cured at 80°C for 1 h in the crucible of the softening point determination device.

Lap Shear Strength testing (according to ISO 4587):

The resulting formulations was applied on Alu L165 plates previously sandblasted and degreased. Specimens were bonded by contact pressure and cured at 80°C for 1 h. Lap shear strength tests were performed at 25°C, 40°C, 60°C and 80°C.

[051] The results of Example 2, Example 3 and comparative Example 2 are shown below in Table 2.

Component		Ex.2 (pbw)	Ex.3 (pbw)	Comp. Ex.2 (pbw)
	1,1'-[isopropylidenebis(p-phenyleneoxy)]bis[3-mercaptopropan-2-ol]	135		
	5-(1-mercaptopropan-2-yl)-2-methylcyclohexane-1-thiol		57	
	Araldite®2012/A			100
	Araldite®2012/B			100
	JEFFCAT® ZR-70	2	2	
	Araldite® GY 240	100	100	
Property	G' onset (°C)	59	48	38
	Softening point (°C)	141	135	no softening point
	Lap Shear Strength at 25°C on Alu L165 (MPa)	14.9 ± 0.4	12.2 ± 0.6	28.6 ± 2.8
	Lap Shear Strength at 40°C on Alu L165 (MPa)	12.0 ± 0.8	11.6 ± 2.4	19.2 ± 0.6
	Lap Shear Strength at 60°C on Alu L165 (MPa)	13.9 ± 1.9	9.7 ± 1.4	7.1 ± 2.3
	Lap Shear Strength at 80°C on Alu L165 (MPa)	5.0 ± 0.8	1.2 ± 0	4.6 ± 0.3
	Lap Shear Strength at 130°C on Alu L165 (MPa)	0.0 ± 0.0	0.0 ± 0.0	2.2 ± 0.2
	Lap Shear Strength at 25°C on Alu L165 (MPa) after 1 st rebonding	15.6 ± 1.9	17.0 ± 1.7	not rebondable
	Lap Shear Strength at 25°C on Alu L165 (MPa) after 2 nd rebonding	13.9 ± 1.3	17.3 ± 0.6	not rebondable

Table 2: Components and results of Example 2, Example 3 and comparative Example 2.

[052] It was found that the two inventive polymers formed can be easily debonded at 130°C, without applying any strength, and can be rebonded to yield a similar (or slightly improved) lap shear

strength at 25°C. In contrast, commercial Araldite®2012 cannot be debonded at 130°C without applying significant strength and once broken cannot be rebonded.

[053] The above-disclosed subject matter is to be considered illustrative, and not restrictive, and the appended claims are intended to cover all such modifications, enhancements, and other embodiments, which fall within the true scope of the present invention. Thus, to the maximum extent allowed by law, the scope of the present invention is to be determined by the broadest permissible interpretation of the following claims and their equivalents, and shall not be restricted or limited by the foregoing detailed description.

What is claimed:

1. A de- and rebondable polymer prepared from the reaction between a difunctional mercaptan hardener; and a difunctional thiol-reactive resin; wherein said polymer has a softening point, determined using a Mettler, DIN 51920 softening point determination device, greater than about 70 °C, preferably about 90 °C to about 150 °C.
2. The de-and rebondable polymer of claim 1, wherein the difunctional mercaptan hardener and difunctional thiol-reactive resin have an average functionality between about 1.8 and about 2.2.
3. The de- and rebondable polymer of claim 1 or claim 2, wherein the molar ratio between mercaptan hardener to thiol-reactive resin ranges from about 0.5 to about 2.0, preferably from about 0.9 to about 1.1.
4. The de- and rebondable polymer of any one of claims 1 to 3, wherein the difunctional thiol-reactive resin is selected from a difunctional epoxy resin, difunctional (meth)acrylate, difunctional isocyanate and combinations thereof.
5. The de- and rebondable polymer of any preceding claim, wherein the de- and re- bondable polymer has a G' onset of greater than about 40 °C, preferably greater than about 45 °C.
6. The de- and rebondable polymer of any preceding claim, wherein the difunctional thiol-reactive resin is a difunctional epoxy resin, preferably an epoxy resin selected from the group consisting of (i) glycidyl ethers based on difunctional aromatic alcohols, such as bisphenol F, bisphenol A (optionally brominated), bisphenol S, resorcinol, and dihydroxy-naphthalene's, (ii) glycidyl ethers of difunctional saturated or unsaturated, branched or unbranched, cyclic or open-chain aliphatic alcohols, such as ethylene glycol, butanediol, hexanediol, cyclohexanedimethanol, and neopentylglycol; (iii) glycidyl esters of dicarboxylic acids such as phthalic acid, tetrahydrophthalic acid, and hexahydrophthalic acid and dimeric fatty acid (iv) and combinations thereof.
7. The de- and rebondable polymer of any one of claims 1 to 5, wherein the difunctional thiol-reactive resin is a difunctional isocyanate resin, preferably an isocyanable resin selected from the group consisting of hexamethylene-1,6-diisocyanate, 2,2,4- or 2,4,4-trimethylhexamethylene-1,6-diisocyanate; alicyclic diisocyanates such as cyclohexane-1,4-diisocyanate, dicyclohexylmethane-4,4'-

diisocyanate; aromatic diisocyanates such as p-phenylene diisocyanate, tolylene-2,4- or -2,6-diisocyanate, diphenylmethane-2,4- or -4,4'-diisocyanate, naphthylene-1,5-diisocyanate, xylylene-1,3- or -1,4-diisocyanate, and combinations thereof.

8. The de- and rebondable polymer of any one of claims 1 to 5, wherein the difunctional thio-reactive resin is a diisocyanate containing a carbodiimide group or uretonimide group or modified difunctional isocyanates containing an allophanate group, urethane group, biuret group and/or urethidione group.

9. The de- and rebondable polymer of any preceding claim, wherein the de- and rebondable polymer has a lap shear strength above about 1MPa at 60°C, preferably above about 1MPa at 80°C.

10. The de- and rebondable polymer of any preceding claim, wherein the difunctional mercaptan is selected from the group consisting of 1,1'-[isopropylidenebis(p-phenyleneoxy)]bis[3-mercaptopropan-2-ol], 1,3-phenylenedimethanethiol, 1,2-phenylenedimethanethiol, 1,4-phenylenedimethanethiol, 3,3'-(1,3-phenylenebis(oxy))bis(1-mercaptopropan-2-ol), 3,3'-((propane-2,2-diylbis(4,1-phenylene))bis(oxy))bis(propane-1-thiol), octahydro-1H-4,7-methanoindene-1,5-dithiol, 3,3'-((methylenebis(4,1-phenylene))bis(oxy))bis(1-mercaptopropan-2-ol), 5-(1-mercaptopropan-2-yl)-2-methylcyclohexane-1-thiol and combinations thereof, preferably wherein the difunctional mercaptan is 1,1'-[isopropylidenebis(p-phenyleneoxy)]bis[3-mercaptopropan-2-ol] and combinations thereof.

11. The de- and rebondable polymer of any preceding claim, wherein the difunctional mercaptan is 1,1'-[isopropylidenebis(p-phenyleneoxy)]bis[3-mercaptopropan-2-ol], or 5-(1-mercaptopropan-2-yl)-2-methylcyclohexane-1-thiol and the thiol reactive resin is diglycidyl ether of bisphenol-A.

12. The de- and rebondable polymer of any preceding claim, wherein the polymer is combined with further components selected from fillers (e.g., calcium carbonate, silica, aluminium trihydroxide, alumina, hollow spheres, carbon black, boron nitride), fibers (carbon fiber, glass fiber, natural fibers, polymer based fiber), adhesion promoter (siloxane based, phosphate based), flexibilizers, dyes, pigments, toughening agents (e.g.: core shell rubber), UV stabilizer, antioxidants, flame retardants and the like, as well as mixtures of any two or more thereof.

13. The de- and rebondable polymer of any preceding claim wherein the difunctional mercaptan and the thiol-reactive resin are cured a temperature range of about 25°C to about 80°C.
14. The de- and rebondable polymer of any preceding claim, wherein the curing takes place in the presence of a catalyst/accelerator, preferably a catalyst/accelerator selected from the group consisting of amine based catalysts such as, 2-(2-dimethylaminoethoxy)ethanol (JEFFCAT® ZR-70) and phosphorus based catalysts such as, trioctyl phosphine.
15. The de- and rebondable polymer of any preceding claim, wherein the curing takes place in the absence of a catalyst/accelerator.
16. A process for preparing the polymer of any one of the preceding claims, said process comprising:
- (i) mixing the difunctional mercaptan hardener and the difunctional thiol-reactive resin to produce a mixture;
 - (ii) curing the mixture.
17. The process of claim 16, wherein the mixture is cured at a temperature of between about 25°C and about 80°C.