

Curable Epoxy Systems Comprising a Phenolic Polymer

TECHNICAL FIELD

- 5 The invention relates to an epoxy system comprising an epoxy resin and a phenolic polymer. The invention also relates to the use of the phenolic polymer as accelerator or as hardener for epoxy resins, for example in coating and adhesive systems.

BACKGROUND OF THE INVENTION

10

- Epoxy resins constitute a broad class of polymers having good adhesion and electrical properties, high glass transition temperatures, excellent resistance to corrosion and solvents and are well-known for their use in adhesives, coatings and composites. Those resins are characterized by epoxide groups which are cured via a crosslinking
- 15 reaction with a multifunctional nucleophilic curing agent, such as amines, or a reaction with itself. This curing process is in general accelerated or even induced by a Lewis acidic or basic catalyst. Commonly known accelerators for epoxy/amine systems include for example alkylated phenols, particularly bisphenol A, nonylphenol or styrenated phenols, the combination of those alkylated phenols with tertiary
- 20 amines, salicylic acid or benzyl alcohol. Examples of commercially available accelerators that are frequently applied include Novares® LS500, Sanko® MSP, or Kumnox® 3111. Despite a high efficiency and an inexpensive availability all those systems are confronted by different applicational or processing issues. For example, bisphenol-A shows allergenic as well as teratogenic properties and exhibits a high
- 25 crystallization tendency in formulated systems resulting in a performance decrease. Nonylphenol acts as an endocrine disruptor limiting its application possibilities, meanwhile styrenated phenols and salicylic acid are currently under comparable

considerations. The benzyl alcohol as volatile substance causes migration effects and declines the glass transition temperature of the cured epoxy resin, which is a critical property for many applications.

- 5 EP 0 126 625 A2 describes a phenolic product prepared by reacting a phenol compound substituted with OH, C1-8 alkyl or alkenyl or a phenyl group, a -C(CH₃)₂C₆H₅ group or a -C(CH₃)₂C₆H₄OH group with a benzene compound substituted with two independent occurrences of -C(CH₃)CH₂ or -C(CH₃)₂OH in the presence of an acidic catalyst.

10

US 9 074 041 B2 describes a curable epoxy resin composite formulation for preparing a composite shaped article comprising a reinforcing material and an epoxy resin composition comprising at least one epoxy resin having an average of more than one glycidyl ether group per molecule, at least one alkanolamine curing agent and at least one styrenated phenol.

15

US 9 464 037 describes an adduct of styrenated phenols and hydroxylamines as well as a method of its synthesis. The resin is prepared via an acid catalyzed alkylation reaction.

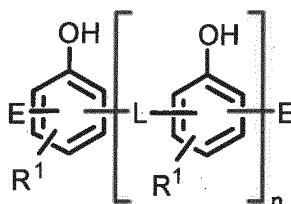
20 SUMMARY OF THE INVENTION

The object of the invention is regarded in the provision of an accelerator for epoxy resins that does not have the disadvantages shown above. In particular, a nonvolatile, non-toxic polymeric accelerator system for curing of epoxy resins with comparable or improved acceleration properties like the prior art accelerators would be desirable.

25

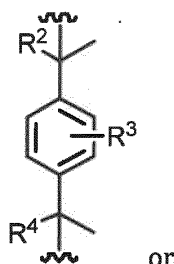
This object is solved with an epoxy system comprising an epoxy resin and

a phenolic polymer having a number average molar mass (M_n) of from 200 to 1,500 g/mol comprising a phenol compound, a linker group L and end group E, said phenolic polymer having the structure as presented in formula 1 below:

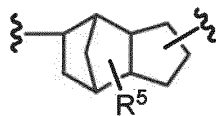


Formula 1

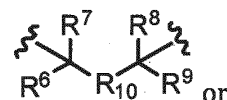
wherein the linker group L has the meaning of



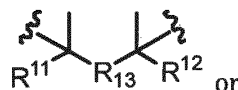
or



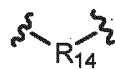
or



or



or



Formula 5

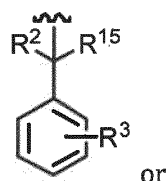
Formula 6

Formula 2

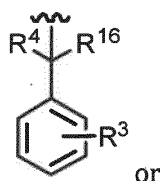
Formula 3

Formula 4

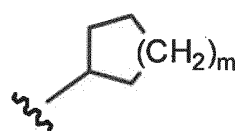
each end group E has the meaning of H or is a group of formula 2, 3, 4, 5 or 6 with only one bond to a phenol compound in formula 1 or has the meaning of



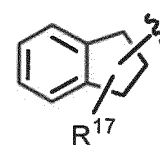
or



or



or



Formula 2c1

Formula 2c2

Formula 3c1

Formula 3c2

and wherein

R^1 is H, C₁₋₁₅ alkyl, or C₁₋₁₅ oxyalkyl, or C₆H₅(CR¹⁸R¹⁹)_o-Z-, preferably H, C₁₋₁₅ alkyl, or C₁₋₁₅ oxyalkyl,

R^2 , R^4 , R^6 , R^7 , R^8 , R^9 , R^{11} and R^{12} are independently from each other H or C₁₋₅ alkyl,

5 R^3 and R^5 are H, OH, NO₂, halogen, C₁₋₅ alkyl or C₁₋₅ oxyalkyl,

R_{10} and R_{13} are C₁₋₅ alkyl or C₅₋₆ cycloalkyl,

R_{14} is C₅₋₁₂ cycloalkyl, optionally substituted with a methyl or an ethyl group,

R^{15} , R^{16} , and R^{17} are independently from each other H or C₁₋₅ alkyl, preferably -CH₃,

R^{18} and R^{19} are independently of each other H or CH₃

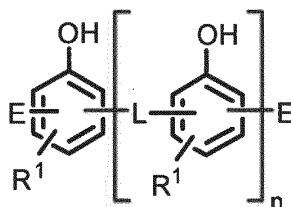
10 Z is a covalent bond or -O-,

o is 1 or 0,

m is an integer from 1 to 7 and

n is an integer of from 2 to 21.

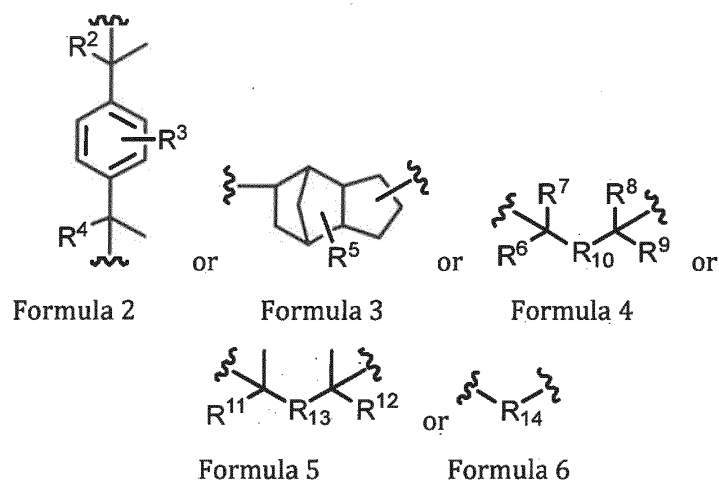
15 The invention is furthermore directed to the use of a phenolic polymer having a number average molar mass (M_n) of from 200 to 1,500 g/mol comprising a phenol compound, a linker group L and end group E, said phenolic polymer having the structure as presented in formula 1 below:



Formula 1

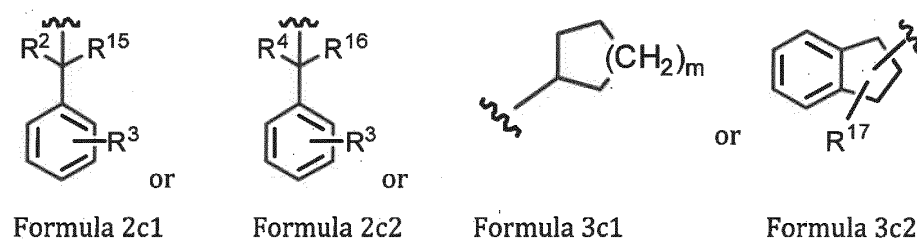
wherein the linker group L has the meaning of

- 5 -



5

each end group E has the meaning of H or is a group of formula 2, 3, 4, 5 or 6 with only one bond to a phenol compound in formula 1 or has the meaning of



10 and wherein

R¹ is H, C₁₋₁₅ alkyl, or C₁₋₁₅ oxyalkyl, or C₆H₅(CR¹⁸R¹⁹)_o-Z-, preferably H, C₁₋₁₅ alkyl, or C₁₋₁₅ oxyalkyl,

R², R⁴, R⁶, R⁷, R⁸, R⁹, R¹¹ and R¹² are independently from each other H or C₁₋₅ alkyl,

R³ and R⁵ are H, OH, NO₂, halogen, C₁₋₅ alkyl or C₁₋₅ oxyalkyl,

15 R¹⁰ and R¹³ are C₁₋₅ alkyl or C₅₋₆ cycloalkyl,

R¹⁴ is C₅₋₁₂ cycloalkyl, optionally substituted with a methyl or an ethyl group,

R¹⁵, R¹⁶, and R¹⁷ are independently from each other H or C₁₋₅ alkyl, preferably -CH₃,

R¹⁸ and R¹⁹ are independently of each other H or CH₃

20 Z is a covalent bond or -O-,

o is 1 or 0,

m is an integer from 1 to 7 and

n is an integer of from 2 to 21

as an accelerator for the curing of epoxy resins, in particular in the presence of a

5 hardener comprising amine functionalities

or

as a hardener for epoxy resins, in particular in the presence of a co-hardener comprising amine functionalities.

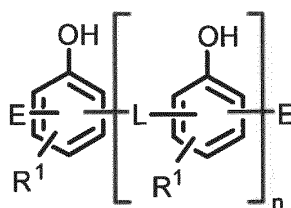
10 The invention is furthermore directed to a kit of parts comprising an epoxy resin and

a phenolic polymer having a number average molar mass (M_n) of from 200 to

1,500 g/mol comprising a phenol compound, a linker group L and end group E, said

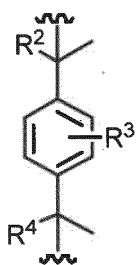
phenolic polymer having the structure as presented in formula 1 below:

15

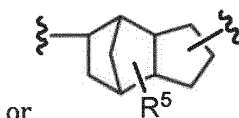


Formula 1

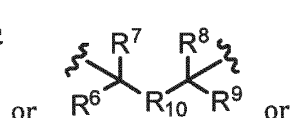
wherein the linker group L has the meaning of



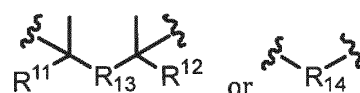
Formula 2



Formula 3



Formula 4



or R¹⁴

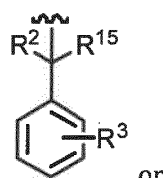
20

Formula 5

Formula 6

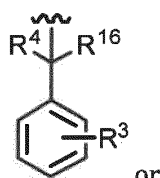
each end group E has the meaning of H or is a group of formula 2, 3, 4, 5 or 6 with only one bond to a phenol compound in formula 1 or has the meaning of

5



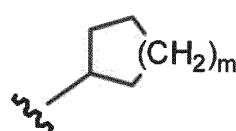
Formula 2c1

or



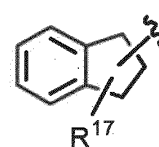
Formula 2c2

or



Formula 3c1

or



Formula 3c2

and wherein

R¹ is H, C₁₋₁₅ alkyl, or C₁₋₁₅ oxyalkyl, or C₆H₅(CR¹⁸R¹⁹)_o-Z-, preferably H, C₁₋₁₅ alkyl, or C₁₋₁₅ oxyalkyl,

R², R⁴, R⁶, R⁷, R⁸, R⁹, R¹¹ and R¹² are independently from each other H or C₁₋₅ alkyl,

10 R³ and R⁵ are H, OH, NO₂, halogen, C₁₋₅ alkyl or C₁₋₅ oxyalkyl,

R₁₀ and R₁₃ are C₁₋₅ alkyl or C₅₋₆ cycloalkyl,

R₁₄ is C₅₋₁₂ cycloalkyl, optionally substituted with a methyl or an ethyl group,

R¹⁵, R¹⁶, and R¹⁷ are independently from each other H or C₁₋₅ alkyl, preferably -CH₃,

15 R¹⁸ and R¹⁹ are independently of each other H or CH₃

Z is a covalent bond or -O-,

o is 1 or 0,

m is an integer from 1 to 7 and

n is an integer of from 2 to 21, and

20 a hardener comprising amine, anhydride, phenolic, and/or thiol, in particular amine, functionalities.

The phenolic polymer according to the invention accelerates the curing of epoxy resins, for example in adhesive systems or in coatings. The hardened epoxy resins

25 have good mechanical properties and also good chemical resistivity.

It was further found that using the phenolic polymer according to the invention in epoxy systems or kit-of-parts according to the invention or as an accelerator may provide controlled acceleration properties in epoxy resins. At the same time, the phenolic polymer according to the invention may not result in the reduction of the mechanical strength of epoxy systems. Moreover, it was found that epoxy resins or epoxy systems comprising the phenolic polymer according to the invention may have a high mechanical resistance. Further, epoxy resins or epoxy systems comprising the phenolic polymer according to the invention may have a high chemical resistance. Epoxy resins or epoxy systems, in particular cured epoxy systems, comprising the phenolic polymer according to the invention may also have a high glass transition temperature (T_g). Epoxy resins or epoxy systems, in particular cured epoxy systems, comprising the phenolic polymer according to the invention may also have a high thermal stability. Lastly, epoxy resins or epoxy systems, in particular cured epoxy systems, comprising the phenolic polymer according to the invention may have an improved adhesion to metal and mineral surfaces and/or a higher corrosion resistance.

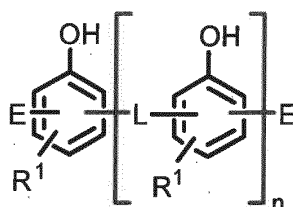
PREFERRED EMBODIMENTS OF THE INVENTION

The phenolic polymer according to the invention may also be referred to as a terpolymer.

In the following, the components in the phenolic polymer and its properties are first described further.

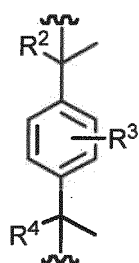
According to a preferred embodiment of the invention, R^1 is H, C_{1-10} alkyl, in particular C_{1-8} alkyl, more particularly C_{1-5} alkyl, or C_{1-10} oxyalkyl, in particular C_{1-8} oxyalkyl, more particularly C_{1-5} oxyalkyl.

According to a preferred embodiment, the phenolic polymer has the structure as presented in formula 1 below:

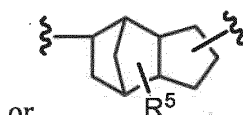


Formula 1

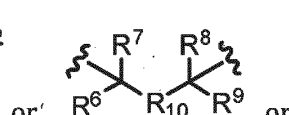
wherein the linker group L has the meaning of



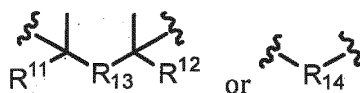
Formula 2



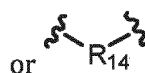
Formula 3



Formula 4



Formula 5



Formula 6

each end group E has the meaning of H or is a group of formula 2, 3, 4, 5 or 6 with only one bond to a phenol compound in formula 1, and wherein

R¹ is H, C₁₋₁₅ alkyl, or C₁₋₁₅ oxyalkyl,

R², R⁴, R⁶, R⁷, R⁸, R⁹, R¹¹ and R¹² are independently from each other H or C₁₋₅ alkyl,

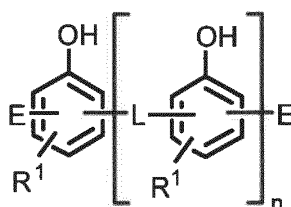
R³ and R⁵ are H, OH, NO₂, halogen, C₁₋₅ alkyl or C₁₋₅ oxyalkyl,

R₁₀ and R₁₃ are C₁₋₅ alkyl or C₅₋₆ cycloalkyl,

R₁₄ is C₅₋₁₂ cycloalkyl, optionally substituted with a methyl or an ethyl group, and

n is an integer of from 2 to 21.

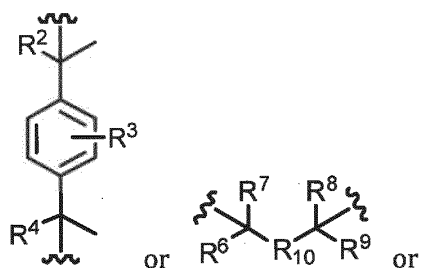
According to a preferred embodiment, the phenolic polymer has the structure as presented in formula 1 below:



5

Formula 1

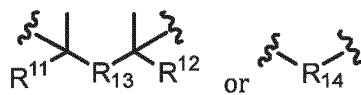
wherein the linker group L has the meaning of



Formula 2

Formula 4

10

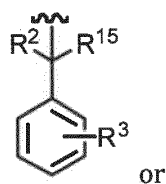


Formula 5

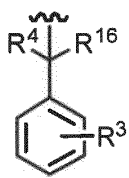
Formula 6

each end group E has the meaning of H or is a group of formula 2, 4, 5 or 6 with only one bond to a phenol compound in formula 1 or has the meaning of

15



Formula 2c1



Formula 2c2

and wherein

R^1 is H, C_{1-15} alkyl, or C_{1-15} oxyalkyl, , or $C_6H_5(CR^{18}R^{19})_o-Z-$, preferably H, C_{1-15} alkyl, or C_{1-15} oxyalkyl,

R^2 , R^4 , R^6 , R^7 , R^8 , R^9 , R^{11} and R^{12} are independently from each other H or C_{1-5} alkyl,

R^3 and R^5 are H, OH, NO_2 , halogen, C_{1-5} alkyl or C_{1-5} oxyalkyl,

5 R^{10} and R^{13} are C_{1-5} alkyl or C_{5-6} cycloalkyl,

R^{14} is C_{5-12} cycloalkyl, optionally substituted with a methyl or an ethyl group, and

R^{18} and R^{19} are independently of each other H or CH_3

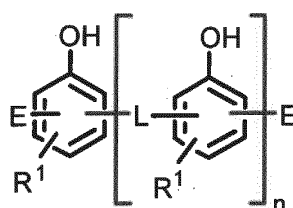
Z is a covalent bond or $-O-$,

o is 1 or 0,

10 n is an integer of from 2 to 21.

According to a preferred embodiment, the phenolic polymer has a number average molar mass (M_n) of from 200 to 1,500 g/mol comprising a phenol compound, a linker group L and end group E, said phenolic polymer having the structure as presented in

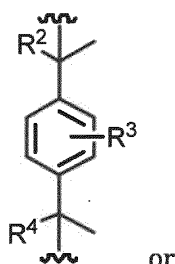
15 formula 1 below:



Formula 1

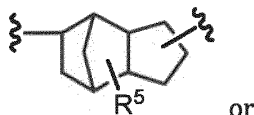
wherein the linker group L has the meaning of

20



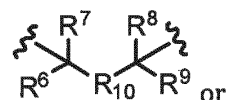
Formula 2

or

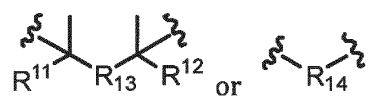


Formula 3

or



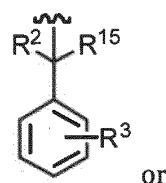
Formula 4



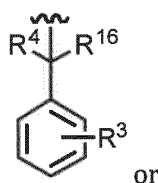
Formula 5

Formula 6

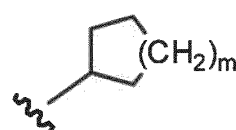
- each end group E is a group of formula 2, 3, 4, 5 or 6 with only one bond to a phenol
 5 compound in formula 1 or has the meaning of



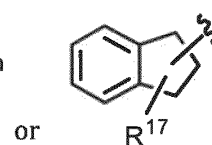
Formula 2c1



Formula 2c2



Formula 3c1

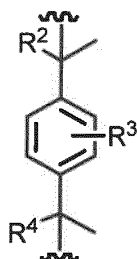


Formula 3c2

and wherein

- R^1 is H, C_{1-15} alkyl, or C_{1-15} oxyalkyl, or $C_6H_5(CR^{18}R^{19})_o-Z$, preferably H, C_{1-15} alkyl, or
 10 C_{1-15} oxyalkyl,
 R^2 , R^4 , R^6 , R^7 , R^8 , R^9 , R^{11} and R^{12} are independently from each other H or C_{1-5} alkyl,
 R^3 and R^5 are H, OH, NO_2 , halogen, C_{1-5} alkyl or C_{1-5} oxyalkyl,
 R_{10} and R_{13} are C_{1-5} alkyl or C_{5-6} cycloalkyl,
 R_{14} is C_{5-12} cycloalkyl, optionally substituted with a methyl or an ethyl group,
 15 R^{15} , R^{16} , and R^{17} are independently from each other H or C_{1-5} alkyl, preferably $-CH_3$,
 R^{18} and R^{19} are independently of each other H or CH_3
 Z is a covalent bond or $-O-$,
 o is 1 or 0,
 m is an integer from 1 to 7 and
 20 n is an integer of from 2 to 21.

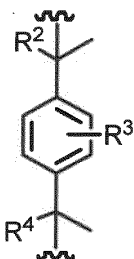
According to a preferred embodiment, the linker group L has the meaning of



Formula 2,

- wherein R^2 , R^3 , and R^4 are independently from each other H or C₁₋₅ alkyl, preferably
 5 wherein independently from each other R^3 is H, R^2 is H or CH₃, and R^4 is H or CH₃,
 more preferably wherein R^3 is H and R^2 and R^4 are H or R^3 is H and R^2 and R^4 are CH₃.

According to a preferred embodiment, the linker group L has the meaning of



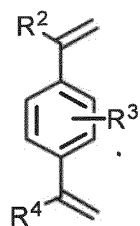
10 Formula 2,

- wherein R^2 , R^3 , and R^4 are as defined herein for formula 2, in particular are H. It was
 found that phenolic polymers, in which the linker group L has the aforementioned
 meaning, in particular when R^2 , R^3 , and R^4 are H, have good properties. In particular,
 phenolic polymers with lower softening points can be achieved. With lower softening
 15 points, the processability and/or compatibility with other compounds such as epoxide
 resins may be improved.

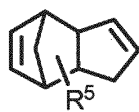
- The phenolic polymer can be prepared by polymerizing an optionally R^1 -substituted
 phenol compound, wherein R^1 is as defined herein, with one of the monomers of
 20 formulae 2a to 5a or a substituted or non-substituted C₅₋₁₂ cycloolefinic compound
 having at least two double bonds in a series of Friedel Crafts alkylation reactions.
 Alternatively to the monomers of formulae 2a to 5a, a monomer of formula 2b may be

employed. The reaction is performed according to the known synthesis method of a Friedel Crafts alkylation reaction. The structure of the monomers according to formulae 2a to 5a or C₅₋₁₂ cycloolefinic compound, which act as the linker L in the polymerization reaction, is selected as follows:

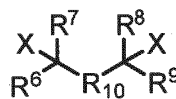
5



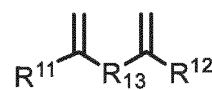
Formula 2a



Formula 3a



Formula 4a

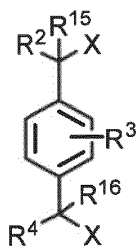


Formula 5a or

- 10 a C₅₋₁₂ cycloolefinic compound that is optionally substituted with a methyl or an ethyl group and preferably comprises two non-conjugated double bonds, wherein R² to R¹³ have the meaning as explained before with view to the residues of formulae 2, 3, 4, and 5, and
- X is a hydroxyl group or a halogen selected of chlorine, bromine and iodine.

15

The structure of formula 2b is as follows



Formula 2b,

- wherein R², R³, and R⁴ are as explained before with view to the residues of formula 2,
- 20 R¹⁵ and R¹⁶ are independently from each other H or C₁₋₅ alkyl and X is a hydroxyl group or a halogen selected of chlorine, bromine and iodine. Preferably, the residues R², R⁴, R¹⁵ and R¹⁶ have the meaning of H and/or alkyl having 1 to 2 carbon atoms. In a particular preferred embodiment, the residues R², R⁴ have the meaning of H and the

residues R¹⁵ and R¹⁶ have the meaning of -CH₃. Most preferably, the residues R¹⁵ and R¹⁶ have the meaning of -CH₃.

According to a preferred embodiment of the invention the residues R², R⁴, R⁶, R⁷, R⁸,
5 R⁹, R¹¹ and R¹² of the phenolic polymer of formula 1 and accordingly in the monomers according to formulae 2a, 3a, 4a and 5a have the meaning of H and/or alkyl having 1 to 2 carbon atoms. In a particular preferred embodiment, the residues R², R⁴, R⁶, R⁷, R⁸, R⁹, R¹¹ and R¹² have the meaning of H.

10 Formulae 2a, 2b, 3a, 4a, 5a or the optionally methyl or ethyl substituted C₅₋₁₂ cycloolefinic compound as shown above represent the starting compounds for the polymerization of the phenolic polymer whereas the groups of formulae 2, 3, 4, 5, and 6 represent the corresponding resulting units L after polymerization in the phenolic polymer.

15 The starting compounds of formulae 2a, 3a, 4a, 5a and the optionally methyl or ethyl substituted C₅₋₁₂ cycloolefinic compound can be used as purified substances, but can also be used in a way, where the specific starting compound is part of a compound mixture. In particular, this can be the case if divinylbenzene is used as a starting
20 compound in the polymerization of the phenolic polymer. In case of employing such a compound mixture the starting compound, in particular the starting monomer for the linker group L, should be present in the mixture at least in an amount of 50 wt.% to 100 wt.%, preferred 50 wt.% to 80 wt.%, based on the weight of the compounds of the mixture.

25 The phenol compound, which is subjected to polymerization with the compounds of formulae 2a to 5a and the optionally methyl or ethyl substituted C₅₋₁₂ cycloolefinic compound R¹⁴ to produce a phenolic polymer of formula 1 can be selected from phenol, benzylphenol, (alpha-methylbenzyl)phenol, (alpha,alpha-
30 dimethylbenzyl)phenol, benzyloxyphenol, (alpha-methylbenzyloxy)phenol, (alpha,alpha-dimethylbenzyloxy)phenol, phenylphenol, phenoxyphenol, C₁₋₁₅ alkyl

phenol, in particular C₁₋₁₀ alkyl phenol, more particularly C₁₋₈ alkyl phenol, even more particularly C₁₋₅ alkyl phenol, and C₁₋₁₅ oxyalkyl phenol, in particular C₁₋₁₀ oxyalkyl phenol, more particularly C₁₋₈ oxyalkyl phenol, even more particularly C₁₋₅ oxyalkyl phenol, for example, o-cresol, m-cresol, p-cresol, ethyl phenol and isopropyl phenol.

5

- The catalyst for the polymerization can be a Lewis acid or a Broensted acid. Preferably the catalyst is selected from AlCl₃, BF₃, ZnCl₂, H₂SO₄, TiCl₄ or mixtures thereof. The catalyst can be used in an amount of from 0.1 to 1 mol %. After the phenol compound is melted by heating at a temperature of 25 °C to 180 °C, preferably 35 °C to 100 °C, or
- 10 dissolved in a suitable solvent (e.g. toluene), the catalyst is added. Thereafter, a monomer compound selected of formulae 2a to 5a or the optionally methyl or ethyl substituted C₅₋₁₂ cycloolefinic compound is added dropwise to the phenol compound. Alternatively, the catalyst is added to a mixture of the phenol compound and the monomer compound of formulae 2a to 5a or the optionally methyl or ethyl substituted
- 15 C₅₋₁₂ cycloolefinic compound. The reaction mixture may be cooled, for example from -10°C to 10°C, when adding the catalyst. The time period of addition of a compound of formulae 2a, 3a, 4a, or 5a or the optionally methyl or ethyl substituted C₅₋₁₂ cycloolefinic compound can be selected to be 10 minutes to 2 hours. The reaction can be continued for 1.5 to 2.5 hours. The polymerization reaction can be performed at a
- 20 temperature of from 40 °C to 200 °C, preferably 60 °C to 150 °C, more preferably 60 °C to 100 °C. Preferably, the polymerization is performed at ambient pressure. The polymerization can be quenched by the addition of suitable additives, preferably lime. The obtained polymers can be purified by filtration and/or steam distillation.
- 25 The molar mass (M_n) of the phenolic polymer is in the range of from 200 to 1,500 g/mol, preferably in the range of from 350 or 400 to 800 g/mol.

- The phenolic polymer preferably has a mass average molecular mass (M_w) of 500 to 12,000 g/mol, more preferably from 600 to 10,000 g/mol, even more preferably from
- 30 700 to 9000 g/mol.

The phenolic polymer preferably has a z-average molecular mass (M_z) of 800 to 35,000 g/mol, more preferably from 900 to 25,000 g/mol, even more preferably from 1,000 to 20,000 g/mol.

5 The number average molecular mass (M_n), the mass average molecular mass (M_w), and the z-average molecular mass (M_z) may in particular be determined using gel permeation chromatography (GPC). In GPC, styrene-divinylbenzene copolymers may be used as column material. A 3 μm precolumn and three 3 μm 1000 Å main columns may be used. A SECcurity²-System by PSS-Polymers may be used. The substances may
10 be detected with an RI detector. Unstabilized ULC/MS-grade THF is preferably used as eluent. The measurements are preferably run isothermal at 40°C. For the calibration curve, ReadyCal-Kit Poly(styrene) low (M_p 266-66,000 Da) by PSS-Polymer may be used as external standard.

15 It was found that phenolic polymers with lower molecular weights in the aforementioned ranges exhibited improved properties, in particular improved compatibility and miscibility with epoxy resins. This resulted in accelerated curing and in some cases in improved mechanical properties and/or improved chemical resistivity.

20

The phenolic polymer advantageously has a glass transition temperature (T_g) of from -10°C to 90°C, preferably from -10°C to 70 °C, more preferably from -5°C to 50°C, and most preferably from 0°C to 40°C. It was found that phenolic polymers with a glass transition temperature in the aforementioned ranges show good processability

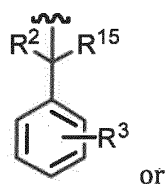
25 and/or good solubility in other compounds such as epoxy resins.

The glass transition temperature is preferably measured using differential scanning calorimetry (DSC). A DSC 2/400 with intra cooler from Mettler Toledo may be employed. For the measurement, aluminum crucibles with pin holes, in particular ME-
30 26763 AL-Crucibles, may be employed. For the evaluation of the glass transition temperature, a heating-cooling-heating-cooling sequence may be employed with a

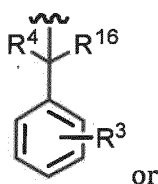
heating / cooling rate of 10 K/min within a measuring window between -40°C to 150°C. The T_g evaluation is preferably performed in accordance to DIN 53765, in particular DIN 53765:1994-03.

- 5 The phenolic polymer may comprise 50 wt. % to 70 wt. % of the phenol compound. The phenolic polymer may comprise 20 wt. % to 50 wt. % of the linker group L, in particular of difunctional monomers (linker L) selected from a divinylbenzene compound, a dicyclopentadiene compound or a compound of formula 4, 5 or 6, based on the weight (mass) of the phenolic polymer. The divinylbenzene compound is
- 10 preferably a compound of formula 2, more preferably a compound of formula 2 wherein R², R³, and R⁴ are as defined herein, most preferably wherein R², R³, and R⁴ are H. The dicyclopentadiene compound is preferably a compound of formula 3. Further, the phenolic polymer may comprise 0 wt. % to 50 wt. %, in particular 5 wt. % to 40 wt. %, more particularly 10 wt. % to 35 wt. %, monofunctional monomers (end
- 15 group E), based on the weight (mass) of the phenolic polymer. The term monofunctional monomer used before refers to a compound, which can be present in the starting mixture of compounds of formulae 2a, 4a, 5a and the optionally methyl or ethyl substituted C₅₋₁₂ cycloolefinic compound for the polymerization of the phenolic polymer, which however has only one double bond or one halogen capable to react in
- 20 the polymerization reaction to obtain the phenolic polymer. Such modified starting compound or monofunctional starting compound acts as a chain stopper in the polymerization reaction. It can form the end group E of formula 1. Further examples of end groups E are described below. According to an embodiment, the end group E is not H. According to another embodiment, the end group E is a mixture of H and at
- 25 least one further end group E as specified herein that is not H.

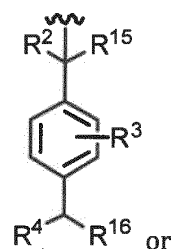
According to a preferred embodiment, the end group E may have the meaning of



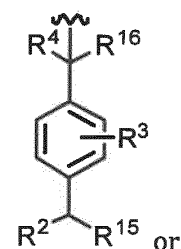
Formula 2c1



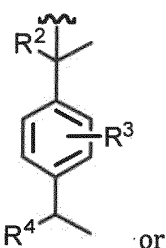
Formula 2c2



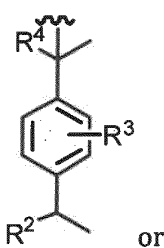
Formula 2c3



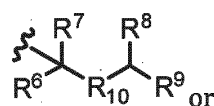
Formula 2c4



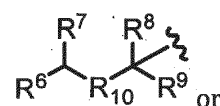
Formula 2c5



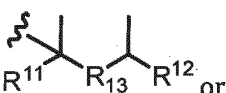
Formula 2c6



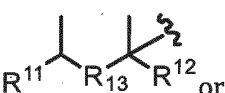
Formula 4c1



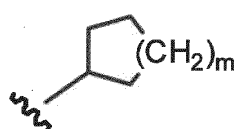
Formula 4c2



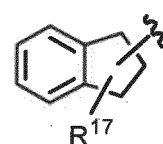
Formula 5c1



Formula 5c2



Formula 3c1



Formula 3c2

wherein R^2 to R^{13} have the meaning as explained before with view to the residues of formulae 2, 3, 4, and 5,

m is an integer from 1 to 7 and

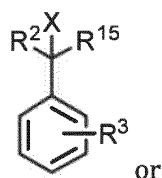
- 5 R^{15} , R^{16} , and R^{17} are independently from each other H or C_{1-5} alkyl, preferably $-CH_3$.

When using end groups E that are different from H, in particular end groups E with the meaning of the aforementioned formulas, the accelerating properties of the phenolic polymer can be adjusted. It was found that when the aforementioned end groups E were incorporated into the phenolic polymer, the acceleration could be increased. Moreover, the compatibility of the phenolic polymer with other compounds, in particular epoxy resins, could be improved.

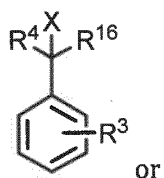
The end group E may also have the meaning of a C₅₋₁₂ cycloalkyl group optionally substituted with a methyl group or an ethyl group.

Accordingly, the end group E may advantageously be obtained from monofunctional

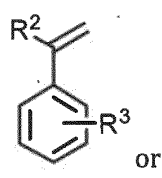
5 monomers having the meaning of



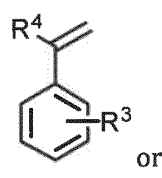
Formula 2d1



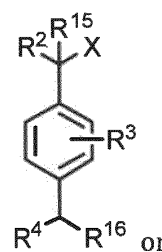
Formula 2d2



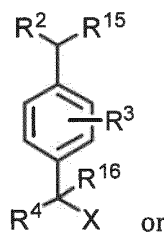
Formula 2d3



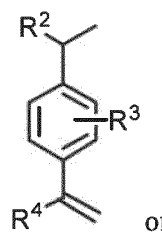
Formula 2d4



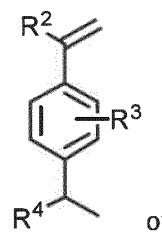
Formula 2d5



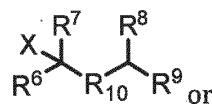
Formula 2d6



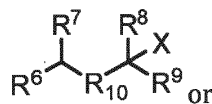
Formula 2d7



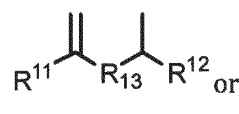
Formula 2d8



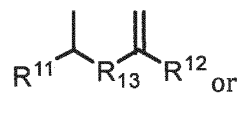
Formula 4d1



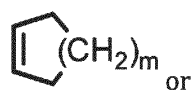
Formula 4d2



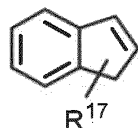
Formula 5d1



Formula 5d2



Formula 3d1



Formula 3d2

wherein R² to R¹³ have the meaning as explained before with view to the residues of formulae 2, 3, 4, and 5,

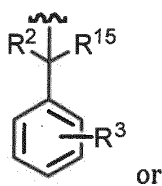
R¹⁵, R¹⁶, and R¹⁷ are independently from each other H or C₁₋₅ alkyl

10 m is an integer from 1 to 7 and

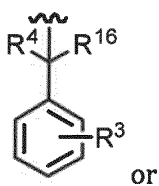
X is a hydroxyl group or a halogen selected of chlorine, bromine and iodine.

The end group E may also be obtained from a monomer having the meaning of a C₅₋₁₂ cycloolefinic compound with only one double bond optionally substituted with a methyl group or an ethyl group.

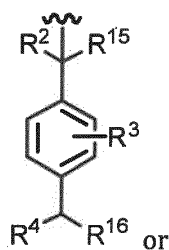
- 5 According to an embodiment, the end group E has the meaning of



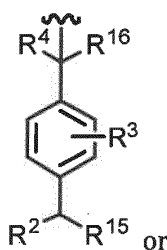
or



or



or



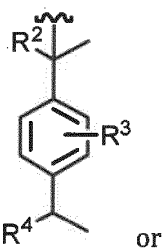
or

Formula 2c1

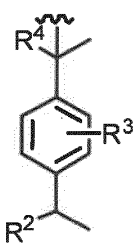
Formula 2c2

Formula 2c3

Formula 2c4



or



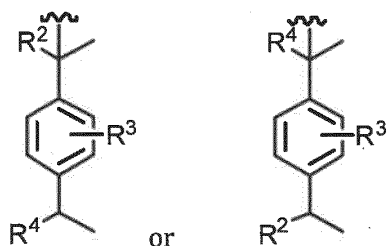
Formula 2c5

Formula 2c6

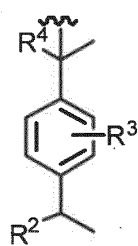
wherein R², R³, R⁴, R¹⁵, and R¹⁶ are independently from each other H or C₁₋₅ alkyl, preferably wherein independently from each other R³ is H, R² is H or CH₃, R⁴ is H or CH₃, R¹⁵ is C₁₋₅ alkyl, and R¹⁶ is C₁₋₅ alkyl. Preferably, the end group E has the meaning of formula 2c1, 2c3 or 2c5 as shown before, wherein R², R³, R⁴, R¹⁵, and R¹⁶ are independently from each other H or C₁₋₅ alkyl, more preferably wherein independently from each other R³ is H, R² is H or CH₃, R⁴ is H or CH₃, R¹⁵ is C₁₋₅ alkyl, and R¹⁶ is C₁₋₅ alkyl.

15

According to a preferred embodiment, the end group E has the meaning of



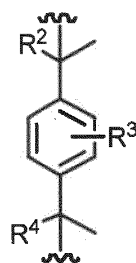
Formula 2c5



Formula 2c6,

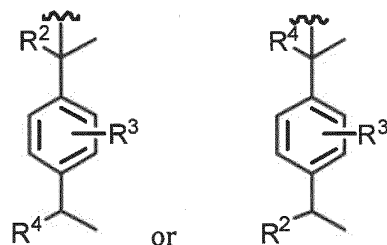
wherein R^2 , R^3 , and R^4 are independently from each other H or C₁₋₅ alkyl, preferably H.

- 5 According to a preferred embodiment, the linker group L has the meaning of

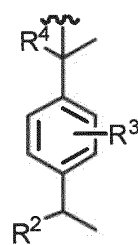


Formula 2,

and the end group E has the meaning of



Formula 2c5



Formula 2c6,

wherein R^2 , R^3 , and R^4 are independently from each other H or C₁₋₅ alkyl, preferably H.

The phenolic polymer may have a high OH content, preferably of 5 to 13 wt.%, in particular preferred 6 to 9 wt.% based on the weight of the phenolic polymer. The phenolic polymer preferably has a softening point according to ASTM 3461 up to 170 °C, more preferred 40 °C to 120 °C, most preferred 50 °C to 100 °C. The hydroxyl content of the phenolic polymer can be influenced by incorporating end groups E that are not H. High hydroxyl contents allow to improve the accelerating or hardening

effect of the phenolic polymer. Also the softening point of the phenolic polymer may be influenced by incorporating end groups E that are not H. A lower softening point allows to reduce the amount of thinner or diluent employed for providing the phenolic polymer of the epoxy system to customers because the viscosity of the solution decreases. A solvent may in particular escape entirely from the hardened product or has entirely escaped therefrom. A thinner may in particular remain in the hardened product. A low-boiling thinner point may in particular partially escape from the hardened product, e.g. up to 30 wt.% or up to 20 wt.% or up to 10 wt.% of the low-boiling point thinner, based on the total mass of the low-boiling point thinner.

10

While it is also possible to adjust the softening point by the reaction temperature used to manufacture the phenolic polymer, this is not preferred because higher temperatures lead to higher Gardner color numbers. According to an embodiment, the phenolic polymer has a Gardner color number, determined according to DIN EN ISO 4630:2016-05 using acetone instead of toluene for the measurement 0 to 5, preferably from 0 to 2, more preferably from 0 to 1. An epoxy system containing a phenolic polymer with a low Gardner color number allows to prepare coatings that are almost colorless or colorless.

15

20 Further properties of the epoxy system according to the invention are described below.

The epoxy systems may be one part epoxy systems or two part epoxy systems. In one part epoxy systems, the epoxy resin, the hardener, the accelerator and other components are in particular part of the same mixture. In one part epoxy systems the hardeners are latent reactive at ambient temperature and become active at high temperature. In one part epoxy systems, the hardener preferably comprises anhydride, thiol and/or phenol functionalities. Examples of latent hardeners are dicynamide, BF_3 complexes such as BF_3 monoethylamine complex, aromatic amines, and imidazoles such as 2-ethyl-4-methyl imidazole. However, also hardeners comprising carboxylic acid and/or isocyanate functionalities can be used in one part

25

30

systems. Accelerators or optional additional accelerators in one part epoxy systems can in particular be amines which reveal catalytic activity at curing temperature. In two part epoxy systems, the epoxy resin and the hardener are separate. The epoxy resin and the hardener are combined to effect cross-linking of the epoxy resin and the hardener. The hardeners in two part epoxy systems are preferably amines or their derivatives. Accelerators in two part epoxy systems may in particular be incorporated into the hardener part. Accelerators or optional additional accelerators in two part epoxy systems may in particular be compounds containing functionalities of amine, phenol, alcohol, thiol or carboxylic acid. In the one part or the two part epoxy systems, the epoxy resin may be present cross-linked with the hardener.

The epoxy system may in particular also comprise a hardener comprising amine, anhydride, phenolic, and/or thiol, in particular amine, functionalities. If the phenolic polymer according to the invention is used as an accelerator, the epoxy system preferably contains a hardener. If the phenolic polymer according to the invention is used as a hardener, the epoxy system may contain the hardener comprising amine, anhydride, phenolic, and/or thiol, in particular amine, functionalities as a co-hardener. In the epoxy systems, the epoxy resin may be present cross-linked with the hardener.

Examples of hardeners or co-hardeners comprising amine functionalities may be selected from, for example, but are not limited to, aliphatic amines, dicyandiamide, substituted guanidines, phenolic, amino, benzoxazine, anhydrides, amido amines, polyamides, polyamines, carbodiimides, urea formaldehyde and melamine formaldehyde resins, ethanolamine, ethylenediamine, diethylenetriamine (DETA), triethyleneaminetetramine (TETA), 1-(o-tolyl)-biguanide, amine-terminated polyols, aromatic amines such as methylenedianiline (MDA), toluenediamine (TDA), diethyltoluenediamine (DETDA), diaminodiphenylsulfone (DADS), and mixtures thereof.

Examples of hardeners or co-hardeners comprising anhydride functionalities are phthalic anhydride, trimellitic anhydride, nadic methyl anhydride (also referred to as

methyl-5-norbornene-2,3-dicarboxylic anhydride), methyl tetrahydrophthalic anhydride, methyl hexahydrophthalic anhydride and mixtures thereof.

- Examples of hardeners or co-hardeners comprising phenolic functionalities are
- 5 bisphenol A, bisphenol F, 1,1-bis(4-hydroxyphenyl)-ethane, hydroquinone, resorcinol, catechol, tetrabromobisphenol A, novolacs such as phenol novolac, bisphenol A novolac, hydroquinone novolac, resorcinol novolac, naphthol novolac, and mixtures thereof.
- 10 Examples of hardeners or co-hardeners comprising thiol functionalities are aliphatic thiols such as methanedithiol, propanedithiol, cyclohexanedithiol, 2-mercaptoethyl-2,3-dimercaptosuccinate, 2,3-dimercapto-1-propanol(2-mercaptoacetate), diethylene glycol bis(2-mercaptoacetate), 1,2-dimercaptopropyl methyl ether, bis(2-mercaptoethyl)ether, trimethylolpropane tris(thioglycolate), pentaerythritol
- 15 tetra(mercaptopropionate), pentaerythritol tetra(thioglycolate), ethyleneglycol dithioglycolate, trimethylolpropane tris(β -thiopropionate), tris-mercaptan derivative of tri-glycidyl ether of propoxylated alkane, and dipentaerythritol poly(β -thiopropionate); halogen-substituted derivatives of the aliphatic thiols; aromatic thiols such as di-, tris- or tetra-mercaptobenzene, bis-, tris- or tetra-
- 20 (mercaptoalkyl)benzene, dimercaptobiphenyl, toluenedithiol and naphthalenedithiol; halogen-substituted derivatives of the aromatic thiols; heterocyclic ring-containing thiols such as amino-4,6-dithiol-sym-triazine, alkoxy-4,6-dithiol-sym-triazine, aryloxy-4,6-dithiol-sym-triazine and 1,3,5-tris(3-mercaptopropyl) isocyanurate; halogen-substituted derivatives of the heterocyclic ring-containing thiols; thiol
- 25 compounds having at least two mercapto groups and containing sulfur atoms in addition to the mercapto groups such as bis-, tris- or tetra(mercaptoalkylthio)benzene, bis-, tris- or tetra(mercaptoalkylthio)alkane, bis(mercaptoalkyl) disulfide, hydroxyalkylsulfidebis(mercaptopropionate), hydroxyalkylsulfidebis(mercaptoacetate), mercaptoethyl ether
- 30 bis(mercaptopropionate), 1,4-dithian-2,5-diolbis(mercaptoacetate), thiodiglycolic acid bis(mercaptoalkyl ester), thiodipropionic acid bis(2-mercaptoalkyl ester), 4,4-

thiobutyric acid bis(2-mercaptoalkyl ester), 3,4-thiophenedithiol, bismuththiol and 2,5-dimercapto-1,3,4-thiadiazol, and mixtures thereof.

Exemplary epoxy resins may comprise at least one epoxy resin based on bisphenol A,
5 bisphenol F, novolac, phenol resin, epoxidized natural oils and any polyalcohols. These compounds may also have been reacted with for example epichlorohydrin. Other exemplary epoxy resins are described in US 9 074 041 B2, column 4, lines 24 to 46.

The epoxy resins mentioned herein can be pigmented and filled systems with
10 pigments and/or fillers, for example iron oxides, titanium dioxide, organic pigments, calcium carbonates, talcum, barium sulphonates, silica, mica, glas pearls, sand, alumina trioxide, magnesium oxides, or zinc phosphates.

The epoxy resins mentioned herein can contain reactive or non reactive diluents. The
15 diluents may also be referred to as thinners. The epoxy systems and/or the epoxy resins mentioned herein may in particular contain non-reactive solvents. As already explained above, a solvent may in particular escape entirely from the hardened product or has entirely escaped therefrom. A thinner may in particular remain in the hardened product. A low-boiling point thinner may in particular partially escape from
20 the hardened product, e.g. up to 30 wt.% or up to 20 wt.% or up to 10 wt.% of the low-boiling point thinner, based on the total mass of the low-boiling point thinner. Examples of reactive diluents are low molecular mass compounds with 1 to 5 glycidyl functionalities with linear or cyclic backbones with 2 to 20 carbon units or ether backbones or, ester backbones. Examples of non reactive solvents and/or diluents are
25 acetone, ketone, esters, ether, aromatic solvents or their mixtures.

Consequently, also the epoxy systems may contain the above-mentioned pigments and/or fillers and/or reactive diluents and/or non-reactive diluents.

30 The epoxy resins and the epoxy systems mentioned herein may be used for coatings, for example flooring coatings, construction coatings, metal coatings, for adhesives, for

sealants, particularly for structure adhesives in metal construction, in wood and concrete construction, for lamination, in particular for lamination of electronic circuits and equipments, for composites and casting applications, for chemical dowels, for electrical encapsulation. The same applies to the epoxy systems mentioned herein.

5

The phenolic polymer described herein as part of the epoxy system according to the invention may also be used as an accelerator for the curing of epoxy resins. When the phenolic polymer of the invention is used as an accelerator for the curing of epoxy resins a hardener comprising amine, anhydride, phenolic, and/or thiol functionalities is preferably present. More preferably, a hardener comprising amine functionalities is present.

10

The phenolic polymer described herein as part of the epoxy system according to the invention may also be used as a hardener for epoxy resins. When the phenolic polymer of the invention is used as a hardener for the curing of epoxy resins, a co-hardener comprising amine, anhydride, phenolic, and/or thiol functionalities, in particular comprising amine functionalities, may also be present.

15

All the details concerning the phenolic polymer, the epoxy resin, the hardener, the accelerator, optional additional accelerators, and optional additional compounds described above in the context of the epoxy system apply to the use of the phenolic polymer accordingly.

20

In particular, the phenolic polymer described herein as part of the epoxy system according to the invention may serve at room temperature or below as an accelerator. At higher temperatures, the phenolic polymer of the invention may also serve as a hardener. It was found that the phenolic polymer yields particularly good results as a hardener for epoxy resins at a temperature of from 50 to 200°C, preferably from 100 to 170°C, more preferably from 120 to 160°C.

25

30

Preferably, the phenolic polymer described herein as part of the epoxy system according to the invention is used at room temperature or below, in particular at -10°C to 40°C, more particularly at 15°C to 25°C as an accelerator for epoxy resins.

- 5 When the phenolic polymer is used as an accelerator or as a hardener for epoxy resins, the phenolic polymer is preferably part of an epoxy system, preferably an epoxy system according to the invention.

- 10 As hardener, the phenolic polymer may be used in different amounts depending on the desired degree of cross-linking. As hardener, the phenolic polymer is preferably used at a ratio of OH:epoxy groups of 0.5:1 to 10:1, preferably 1:1 to 10:1, based on the total mass of the epoxy system, in particular in casting, lamination and adhesive applications. As accelerator, the phenolic polymer is preferably used in an amount of 0.5 to 20 wt.%, more preferable 5 to 15 wt.% and even more preferably 8 to 12 wt.%,
15 or 0.5 to 30 wt.%, more preferably 0.5 to 25 wt.%, even more preferably 0.5 to 20 wt.%, 0.5 to 15 wt.%, most preferably 0.5 to 12 wt.%, based on the total mass of the epoxy system. As accelerator, the phenolic polymer is more preferably used in an amount of 0.5 to 20 wt.%, more preferable 5 to 15 wt.% and even more preferably 8 to 12 wt.%, or 0.5 to 30 wt.%, more preferably 0.5 to 25 wt.%, even more preferably 0.5
20 to 20 wt.%, 0.5 to 15 wt.%, most preferably 0.5 to 12 wt.%, based on the total mass of the epoxy resin. Preferably, the phenolic polymer is used as accelerator.

- Moreover, the invention also provides for a kit-of-parts comprising an epoxy resin and the phenolic polymer described herein as part of the epoxy system according to the
25 invention, and a hardener comprising amine, anhydride, phenolic, and/or thiol, in particular amine, functionalities. The kit-of-parts according to the invention is preferably a two part epoxy system.

- All the details concerning the phenolic polymer, the epoxy resin, the hardener, the
30 accelerator, optional additional accelerators, and optional additional compounds

described above in the context of the epoxy system apply to the kit-of-parts accordingly.

- In the kit-of-parts, the phenolic polymer and the hardener are preferably present as a mixture that optionally contains a solvent and/or a thinner.

The following examples serve to further explain the invention.

Examples

10 Abbreviations

SP = Softening point

DVB = Divinylbenzene

EVB = Ethylvinylbenzene

DIPB = Diisopropenylbenzene

15 DVBP = Divinylbenzene-phenol

DCPD = Dicyclopentadiene

Suppliers of chemicals:

Chemical	Purity	Supplier
DVB	62%	Sigma-Aldrich
DVB	80%	Sigma-Aldrich
DCPD	80%	Braskem
DIPB	>98%	Sigma-Aldrich
Phenol	99%	PanReac AppliChem
4-Tert-octylphenol	97%	Sigma-Aldrich
BF ₃ *OEt ₂	>98%	Bernd Kraft
Xylene	>98%	Bernd Kraft

20 Example 1

Phenol (282 g) was dissolved in toluene (138 g) in a three-neck flask equipped with a dimroth coil condenser and a dropping funnel at 70 °C followed by the addition of $\text{BF}_3 \cdot (\text{OEt}_2)$ (2.01 mL). Divinyl benzene (195 g, 62% purity) was added dropwise via the dropping funnel over a period of 30 minutes to the reaction mixture. After the addition the solution was stirred for 2 hours at a reaction temperature of 90 °C. The polymerization was quenched by addition of chalk. Filtration of the crude product and purification via steam distillation at 230 °C yielded the resin as colorless solid. The results of the characterization of the phenolic polymer are presented in the table below.

10

Table 1: Analysis values example 1

SP [°C] ASTM 3461	Tg [°C]	OH content [wt.%]	Mn [g/mol]	Mw [g/mol]	Mz [g/mol]
42	13	8.6	528	735	1066

Example 1a

Phenol (282 g) was dissolved in xylene (138 g) in a three-neck flask equipped with a dimroth coil condenser and a dropping funnel at 70 °C followed by the addition of $\text{BF}_3 \cdot (\text{OEt}_2)$ (2.01 mL). Divinyl benzene (195 g, 62% purity) was added dropwise via the dropping funnel over a period of 30 minutes to the reaction mixture. After the addition the solution was stirred for 2 hours at a reaction temperature of 120 °C. The polymerization was quenched by addition of chalk. Filtration of the crude product and purification via steam distillation at 230 °C yielded the resin as yellowish solid. The results of the characterization of the phenolic polymer are presented in the table below.

20

Table 1a: Analysis values comparison example 1

SP [°C] ASTM 3461	Tg [°C]	OH content [wt.%]	Mn [g/mol]	Mw [g/mol]	Mz [g/mol]
46	14	8.6	493	660	915

25

Example 1b

Phenol (282 g) was dissolved in xylene (138 g) in a three-neck flask equipped with a dimroth coil condenser and a dropping funnel at 70 °C followed by the addition of $\text{BF}_3 \cdot (\text{OEt}_2)$ (2.01 mL). Divinyl benzene (195 g, 62% purity) was added dropwise via the dropping funnel over a period of 30 minutes to the reaction mixture. After the addition the solution was stirred for 2 hours at a reaction temperature of 140 °C. The polymerization was quenched by addition of chalk. Filtration of the crude product and purification via steam distillation at 230 °C yielded the resin as yellowish solid. The results of the characterization of the phenolic polymer are presented in the table below.

Table 1b: Analysis values comparison example 2

SP [°C] ASTM 3461	Tg [°C]	OH content [wt.%]	Mn [g/mol]	Mw [g/mol]	Mz [g/mol]
45	13	8.5	494	656	907

15

Example 2

Phenol (254 g) was dissolved in toluene (138 g) in a three-neck flask equipped with a dimroth coil condenser and a dropping funnel at 70 °C followed by the addition of $\text{BF}_3 \cdot (\text{OEt}_2)$ (2.01 mL). Divinyl benzene (195 g, 62% purity) was added dropwise via the dropping funnel over a period of 30 minutes to the reaction mixture. After the addition the solution was stirred for 2 hours at a reaction temperature of 90 °C. The polymerization was quenched by addition of chalk. Filtration of the crude product and purification via steam distillation at 230 °C yielded the resin as colorless solid. The results of the characterization of the phenolic polymer are presented in the table below.

25

Table 2: Analysis values example 2

SP [°C]	Tg	OH content	Mn	Mw	Mz
ASTM 3461	[°C]	[wt.%]	[g/mol]	[g/mol]	[g/mol]
53	27	7.3	592	960	1683

Table 3: Summary of example 1-2

	Molar ratio Phenol : DVB : EVB			SP [°C] ASTM 3461	Tg [°C]	OH Content [wt. %]	Mn [g/mol]	Mw [g/mol]	Mz [g/mol]
Example 1	3.6	1.7	1.0	42	13	8,6	528	735	1066
Example 2	3.2	1.7	1.0	53	27	7.3	592	960	1683

5 Example 3

Phenol (94 g) was dissolved in toluene (61 g) in a three-neck flask equipped with a dimroth coil condenser and a dropping funnel at 40 °C followed by the addition of $\text{BF}_3 \cdot (\text{OEt}_2)$ (0.88 mL). Dicyclopentadiene (44 g, 80% purity, 5% vinyl aromatics (indene, methyl styrene isomers) provided by Braskem) was added dropwise via the dropping funnel over a period of 30 minutes to the reaction mixture. After the addition the solution was stirred for 3 hours at a reaction temperature of 120 °C. The polymerization was quenched by addition of chalk. Filtration of the crude product and purification via steam distillation at 250 °C yielded the resin as red solid. The results of the characterization of the phenolic polymer are presented in the table below.

15

Table 4: Analysis values example 3

SP [°C]	Tg	OH content	Mn	Mw	Mz
ASTM 3461	[°C]	[wt.%]	[g/mol]	[g/mol]	[g/mol]
98	65	7.8	487	702	1049

Example 4

Phenol (282 g) was dissolved in toluene (92 g) in a three-neck flask equipped with a dimroth coil condenser and a dropping funnel at 40°C followed by the addition of

20

BF₃·(OEt₂) (2,70 mL). Dicyclopentadiene (132 g, 80% purity, 5% vinyl aromatics (indene, methyl styrene isomers) provided by Braskem) was added dropwise via the dropping funnel over a period of 30 minutes to the reaction mixture. After the addition the solution was stirred for 3 hours at a reaction temperature of 120 °C. The polymerization was quenched by addition of chalk. Filtration of the crude product and purification via steam distillation at 250 °C yielded the resin as red solid. The results of the characterization of the phenolic polymer are presented in the table below.

Table 5: Analysis values example 4

SP [°C] ASTM 3461	Tg [°C]	OH content [wt.%]	Mn [g/mol]	Mw [g/mol]	Mz [g/mol]
109	72	7.0	510	761	1168

Example 5

4-Tert-octylphenol (255 g) was dissolved in xylene (255 g) in a three-neck flask equipped with a dimroth coil condenser and a dropping funnel at 70 °C followed by the addition of BF₃·(OEt₂) (0.921 mL). Divinylbenzene (195 g, 62% purity: divinylbenzene : ethylvinylbenzene = 62:38) was added dropwise via the dropping funnel over a period of 14 minutes to the reaction mixture. After the addition the solution was stirred for 2 hours at a reaction temperature of 90 °C. The polymerization was quenched by the addition of chalk. Filtration of the crude product and purification via steam distillation at 230°C yielded the resin as colorless solid. The results of characterization of the phenolic polymer are presented in the table below.

Table 6: Analysis values example 5

SP [°C] ASTM 3461	Tg [°C]	OH content [wt.%]	Mn [g/mol]	Mw [g/mol]	Mz [g/mol]
41	4.4	5.5	588	897	1321

Example 6

Phenol (254 g) and divinylbenzene (195 g, 62% purity: divinylbenzene : ethylvinylbenzene = 62:38) was dissolved in Xylene (138 g) in a three-neck flask equipped with a dimroth coil condenser and a dropping funnel at 30 °C followed by the portion wise addition of $\text{BF}_3 \cdot (\text{OEt}_2)$ (0.624 mL). The reaction mixture was cooled by an ice bath. After the addition the solution was stirred for 1 hour at a reaction temperature of 70 °C. The polymerization was quenched by the addition of chalk. Filtration of the crude product and purification via steam distillation at 230°C yielded the resin as colorless solid. The results of characterization of the phenolic polymer are presented in the table below.

Table 7: Analysis values example 6

SP [°C] ASTM 3461	Tg [°C]	OH content [wt.%]	Mn [g/mol]	Mw [g/mol]	Mz [g/mol]
68	31	7.7	711	1379	2564

Example 7

Phenol (203 g) and divinylbenzene (195 g, 62% purity: divinylbenzene : ethylvinylbenzene = 62:38) was dissolved in xylene (138 g) in a three-neck flask equipped with a dimroth coil condenser and a dropping funnel at 30 °C followed by the portion wise addition of $\text{BF}_3 \cdot (\text{OEt}_2)$ (0,624 mL). The reaction mixture was cooled by an ice bath. After the addition the solution was stirred for 1 hour at a reaction temperature of 70 °C. The polymerization was quenched by the addition of chalk. Filtration of the crude product and purification via steam distillation at 230°C yielded the resin as colorless solid. The results of characterization of the phenolic polymer are presented in the table below.

Table 8: Analysis values example 7

SP [°C] ASTM 3461	Tg [°C]	OH content [wt.%]	Mn [g/mol]	Mw [g/mol]	Mz [g/mol]
77	37	6.8	850	2014	4234

Example 8

Phenol (177 g) and divinylbenzene (195 g, 62% purity: divinylbenzene : ethylvinylbenzene = 62:38) was dissolved in xylene (138 g) in a three-neck flask equipped with a dimroth coil condenser and a dropping funnel at 30 °C followed by the portion wise addition of $\text{BF}_3 \cdot (\text{OEt}_2)$ (0.624 mL). The reaction mixture was cooled by an ice bath. After the addition the solution was stirred for 1 hour at a reaction temperature of 70 °C. The polymerization was quenched by the addition of chalk. Filtration of the crude product and purification via steam distillation at 230°C yielded the resin as colorless solid. The results of characterization of the phenolic polymer are presented in the table below.

Table 9: Analysis values example 8

SP [°C] ASTM 3461	Tg [°C]	OH content [wt.%]	Mn [g/mol]	Mw [g/mol]	Mz [g/mol]
84	40	6.0	953	2902	7177

Example 9

Phenol (141 g) and divinylbenzene (195 g, 62% purity: divinylbenzene : ethylvinylbenzene = 62:38) was dissolved in xylene (138 g) in a three-neck flask equipped with a dimroth coil condenser and a dropping funnel at 30 °C followed by the portion wise addition of $\text{BF}_3 \cdot (\text{OEt}_2)$ (0,624 mL). The reaction mixture was cooled by an ice bath. After the addition the solution was stirred for 1 hour at a reaction temperature of 70 °C. The polymerization was quenched by the addition of chalk. Filtration of the crude product and purification via steam distillation at 230°C yielded the resin as colorless solid. The results of characterization of the phenolic polymer are presented in the table below.

Table 10: Analysis values example 9

SP [°C] ASTM 3461	Tg [°C]	OH content [wt.%]	Mn [g/mol]	Mw [g/mol]	Mz [g/mol]
98	49	5.8	1228	6787	21520

Example 10

Phenol (141 g) and divinylbenzene (215 g, 62% purity: divinylbenzene : ethylvinylbenzene = 62:38) was dissolved in xylene (138 g) in a three-neck flask equipped with a dimroth coil condenser and a dropping funnel at 30 °C followed by the portion wise addition of $\text{BF}_3 \cdot (\text{OEt}_2)$ (0.624 mL). The reaction mixture was cooled by an ice bath. After the addition the solution was stirred for 1 hour at a reaction temperature of 70 °C. The polymerization was quenched by the addition of chalk. Filtration of the crude product and purification via steam distillation at 230°C yielded the resin as colorless solid. The results of characterization of the phenolic polymer are presented in the table below.

Table 11: Analysis values example 10

SP [°C] ASTM 3461	Tg [°C]	OH content [wt.%]	Mn [g/mol]	Mw [g/mol]	Mz [g/mol]
104	46	5.5	1405	9468	30130

Table 12: Summary of example 6-10

	Ratio phenol : DVB : EVB			SP [°C] ASTM 3461	Tg [°C]	OH Content [wt. %]	Mn [g/mol]	Mw [g/mol]	Mz [g/mol]
Example 6	3.2	1.7	1.0	68	31	7.7	711	1379	2564
Example 7	2.6	1.7	1.0	77	37	6.8	850	2014	4234
Example 8	2.3	1.7	1.0	84	40	6.0	953	2902	7177
Example 9	1.8	1.7	1.0	98	49	5.8	1228	6787	21520
Example 10	1.5	1.7	1.0	104	46	5.5	1405	9468	30130

Example 11

Phenol (254 g) and divinylbenzene (195 g, 80% purity: divinylbenzene : ethylvinylbenzene = 80:20) was dissolved in xylene (138 g) in a three-neck flask equipped with a dimroth coil condenser and a dropping funnel at 30 °C followed by the portion wise addition of $\text{BF}_3 \cdot (\text{OEt}_2)$ (0.234 mL). The reaction mixture was cooled by an ice bath. After the addition the solution was stirred for 1 hour at a reaction

temperature of 70 °C. The polymerization was quenched by the addition of chalk. Filtration of the crude product and purification via steam distillation at 230°C yielded the resin as colorless solid. The results of characterization of the phenolic polymer are presented in the table below.

5

Table 13: Analysis values example 11

SP [°C]	Tg	OH content	Mn	Mw	Mz
ASTM 3461	[°C]	[wt.%]	[g/mol]	[g/mol]	[g/mol]
93	53	7.2	963	2209	4628

Example 12

Phenol (207 g) and divinylbenzene (195 g, 80% purity: divinylbenzene : ethylvinylbenzene = 80:20) was dissolved in xylene (138 g) in a three-neck flask equipped with a dimroth coil condenser and a dropping funnel at 30 °C followed by the portion wise addition of $\text{BF}_3 \cdot (\text{OEt}_2)$ (0.234 mL). The reaction mixture was cooled by an ice bath. After the addition the solution was stirred for 1 hour at a reaction temperature of 70 °C. The polymerization was quenched by the addition of chalk. Filtration of the crude product and purification via steam distillation at 230°C yielded the resin as colorless solid. The results of characterization of the phenolic polymer are presented in the table below.

15

Table 14: Analysis values example 12

SP [°C]	Tg	OH content	Mn	Mw	Mz
ASTM 3461	[°C]	[wt.%]	[g/mol]	[g/mol]	[g/mol]
101	57	6.6	1149	3976	10400

20

Table 15: Comparison of example 6-7 and 11-12

	Molar ratio phenol : DVB : EVB			Molar ratio phenol : sum (DVB+EVB)		SP [°C] ASTM 3461	Tg [°C]	OH Content [wt. %]	Mn [g/mol]	Mw [g/mol]	Mz [g/mol]
Example 6	3.2	1.7	1.0	1.8	1.0	68	31	7.7	711	1379	2564
Example 11	6.1	4.1	1.0	1.8	1.0	93	53	7.2	963	2209	4628
Example 7	2.6	1.7	1.0	1.5	1.0	77	37	6.8	850	2014	4234
Example 12	5.0	4.1	1.0	1.5	1.0	101	57	6.6	1149	3976	10400

Example 13

- 5 Phenol (141 g) and diisopropenylbenzene (158 g) was dissolved in xylene (138 g) in a three-neck flask equipped with a dimroth coil condenser and a dropping funnel at 30 °C followed by the portion wise addition of $\text{BF}_3 \cdot (\text{OEt}_2)$ (0.234 mL). The reaction mixture was cooled by an ice bath. After the addition the solution was stirred for 1 hour at a reaction temperature of 70 °C. The polymerization was quenched by the
- 10 addition of chalk. Filtration of the crude product and purification via steam distillation at 230°C yielded the resin as colorless solid. The results of characterization of the phenolic polymer are presented in the table below.

Table 16: Analysis values example 13

SP [°C] ASTM 3461	Tg [°C]	OH content [wt.%]	Mn [g/mol]	Mw [g/mol]	Mz [g/mol]
140	82	3.6	1654	7567	21890

15

Example 14

- Phenol (141 g), styrene (52 g) and diisopropenylbenzene (79 g) was dissolved in xylene (138 g) in a three-neck flask equipped with a dimroth coil condenser and a dropping funnel at 30 °C followed by the portion wise addition of $\text{BF}_3 \cdot (\text{OEt}_2)$
- 20 (0.234 mL). The reaction mixture was cooled by an ice bath. After the addition the solution was stirred for 1 hour at a reaction temperature of 70 °C. The polymerization was quenched by the addition of chalk. Filtration of the crude product and purification

via steam distillation at 230°C yielded the resin as colorless solid. The results of characterization of the phenolic polymer are presented in the table below.

Table 17: Analysis values example 14

SP [°C] ASTM 3461	Tg [°C]	OH content [wt.%]	Mn [g/mol]	Mw [g/mol]	Mz [g/mol]
96	46	4.2	722	2110	4853

5

Example 15

Phenol (141 g), styrene (73 g) and diisopropenylbenzene (48 g) was dissolved in Xylene (138 g) in a three-neck flask equipped with a dimroth coil condenser and a dropping funnel at 30 °C followed by the portion wise addition of BF₃·(OEt₂) (0.234 mL). The reaction mixture was cooled by an ice bath. After the addition the solution was stirred for 1 hour at a reaction temperature of 70 °C. The polymerization was quenched by the addition of chalk. Filtration of the crude product and purification via steam distillation at 230°C yielded the resin as colorless solid. The results of characterization of the phenolic polymer are presented in the table below.

10
15

Table 18: Analysis values example 15

SP [°C] ASTM 3461	Tg [°C]	OH content [wt.%]	Mn [g/mol]	Mw [g/mol]	Mz [g/mol]
58	9	4,9	435	1138	2608

Table 19: Summary of example 13-15

	Ratio diisopropenyl benzene : styrene*		SP [°C] ASTM 3461	Tg [°C]	OH Content [wt. %]	Mn [g/mol]	Mw [g/mol]	Mz [g/mol]
Example 13	1.0	0	140	82	3.6	1654	7567	21890
Example 14	1.0	1.0	96	46	4.2	722	2110	4853
Example 15	0.4	1.0	58	9	4.9	435	1138	2608

*ratio of phenol to the sum of diisopropenyl benzene and styrene is kept constant

20

Example 16

Phenol (141 g), α -methylstyrene (59 g) and diisopropenylbenzene (79 g) was dissolved in xylene (138 g) in a three-neck flask equipped with a dimroth coil condenser and a dropping funnel at 30 °C followed by the portion wise addition of

5 $\text{BF}_3 \cdot (\text{OEt}_2)$ (0.234 mL). The reaction mixture was cooled by an ice bath. After the addition the solution was stirred for 1 hour at a reaction temperature of 70 °C. The polymerization was quenched by the addition of chalk. Filtration of the crude product and purification via steam distillation at 230°C yielded the resin as colorless solid. The results of characterization of the phenolic polymer are presented in the table below.

10

Table 20: Analysis values example 16

SP [°C]	Tg	OH content	Mn	Mw	Mz
ASTM 3461	[°C]	[wt.%]	[g/mol]	[g/mol]	[g/mol]
81	40	3.4	590	1444	3244

As can be seen from the exemplary syntheses above, the properties of the polymeric phenolic polymer can be varied in a wide range.

15

As can be seen from the results above, material characteristics can be influenced by chain stopper (the end group E). Further experiments concerning the influence of the chain stopper are presented hereinbelow.

20 Influence of the chain stopper content on the material characteristics and workability

Epoxy systems are in general cured by mixing two liquid substances (epoxy prepolymer and a curing agent) and modified by various additives and fillers. Normally, the viscosity of both, prepolymer and curing agent, have an immense impact

25 on the handling as well as the curing process and thus on the final properties of the cured resin. The viscosity of the single components as well as the final composition is related to the physical and chemical properties (e.g. softening point, Tg, polarity and functional groups) of the single ingredients, such as the compounds synthesized

- herein. Another aspect, which is directly influenced by those physical and chemical properties is the solubility and the dissolving behavior at given temperatures in the curing agent or common thinners. Especially the solving temperature is often critical due to the temperature sensitivity of a great variety of curing agents. Consequently,
- 5 the control of the softening point of the accelerator shown in this invention has a drastic impact on its applicability.

Table 20a: Comparison of example 6-7 and 11-12

	Molar ratio: DVB : EVB		Molar ratio phenol : sum (DVB + EVB)		SP [°C] ASTM 3461	Tg [°C]	OH Content [wt. %]	Mn [g/mol]	Mw [g/mol]	Mz [g/mol]
Example 6	1.7	1.0	1.8	1.0	68	31	7.7	711	1379	2564
Example 11	4.1	1.0	1.8	1.0	93	53	7.2	963	2209	4628
Example 7	1.7	1.0	1.5	1.0	77	37	6.8	850	2014	4234
Example 12	4.1	1.0	1.5	1.0	101	57	6.6	1149	3976	10400

- 10 As shown in Table 20b (example 13 – 15) and Table 20a (example 6 vs 11 & example 7 vs 12) the ratio of monovinyllic (EVB and styrene) to divinyllic (DVB and DIPB) compound has a crucial impact on the molecular weight distribution as well as on the softening point and Tg of the resulting resin.

- 15 Table 20b: Comparison of example 13-15

	Molar ratio diisopropenyl benzene : styrene*		SP [°C] ASTM 3461	Tg [°C]	OH Content [wt. %]	Mn [g/mol]	Mw [g/mol]	Mz [g/mol]
Example 13	1.0	0	140	82	3.6	1654	7567	21890
Example 14	1.0	1.0	96	46	4.2	722	2110	4853
Example 15	0.4	1.0	58	9	4.9	435	1138	2608

*ratio of phenol to the sum of diisopropenyl benzene and styrene is kept constant

Under equal reaction conditions and constant phenol content the molecular weight, softening point and Tg declines with increasing content of the monovinyl compound. Additionally, this variation only marginally influences the OH content of the final resin, unlike the variation of the phenol content (see Table 12 above). An increase of the ratio of phenol to the sum of the mono- and divinyl compound increases the OH content and reduces the softening point, Tg and the molecular weight as does the use of the monovinyl compound.

Contrary to the monomer ratios (monovinyl vs divinyl aromatics vs phenol) the reaction temperature shows marginal to no influence on the product properties with color as only exception (Table 20c). With increasing reaction temperature yellowing of the product increases. Those results once more emphasize the necessity of molecular weight control by a chain stopper, as the molecular weight cannot be controlled by reaction temperature like for example common cationic polymerization reactions.

Table 20c: Influence of reaction temperature on the product properties

	Reaction temperature	Gardner Color	SP	Tg	Mn	Mw	Mz
Example 1	90	0.3	42	13	528	735	1066
Comparison example 1	120	1.9	46	14	493	660	915
Comparison example 2	140	2.2	45	13	494	656	907

As mentioned above the softening point and the molecular weight have a crucial impact on the solubility and workability of a resin as well as the viscosity of the formulation in epoxy applications. This effect and its connection to the chain stopper content is shown in Table 20d, Table 20f and Table 20g. Resins, which were prepared under equal reaction conditions and equal phenol content (example 6 vs 11; example

13 vs 14 vs 14), were dissolved in a variety of solvents and thinners commonly used in the coatings industry as well as in a curing agent.

General procedure: Dissolving of resins

- 5 50 g resin and 100 g thinner/solvent were submitted to a 300 mL three-neck round bottom flask equipped with a dimroth coil condenser and an overhead stirrer. The mixture was stirred at room temperature for one hour. Afterwards, if no complete dissolution occurred the temperature of the mixture was increased by 10°C/5 min until the resin was completely dissolved. Although for at least some of the resins, a
- 10 lower amount of thinner would have sufficed to effect solubilization upon heating, in particular when heating beyond the softening point of the resin, the protocol above was followed and 100 mL of the solvent/thinner were employed.

Table 20d: Dissolving temperatures

	Dissolving example 1	Dissolving example 2	Dissolving example 3	Dissolving example 4	Dissolving example 5
Resin	example 11	example 6	example 13	example 14	example 15
Molar ratio of DIPB : Styrene	-	-	1.0 : 0.0	1.0 : 1.0	0.4 : 1.0
Molar ratio of DVB : EVB	4.1 : 1.0	1.7 : 1.0	-	-	-
SP of resin [°C]	93	68	140	96	58
Thinner/solvent*	Dissolving temperature [°C]				
Butan-2-on	rt	rt	rt	rt	rt
Xylene	rt	rt	rt	rt	rt
Benzyl alcohol	80	60	80	80	50
L40	130	80	insoluble	140	70
Epicure Agent 548	130	80	insoluble	140	70

- 15 *Weight ration thinner : resin = 2 : 1

Low viscosity solvents Butan-2-on and Xylene were able to dissolve all resins already at room temperature. However, with declining dissolving power (Benzyl alcohol, L40, Epicure Agent 548) the influence of the softening point und thus the chain stopper content becomes more inherent.

5

Table 20e: Thinner/ solvent viscosity

Thinner/solvent	Compound	Viscosity [mPas]
Solvent	Butan-2-on	0.2 @ 20°C
Solvent	Xylene	0.6 @ 20°C
Low-boiling point thinner	Benzyl alcohol	6.6 @ 20°C
Thinner	Novares® L40 (aromatic oligomer)	37.5 @ 25°C
Curing agent	Epicure® Agent 548	467.1 @ 25°C

The results show that with decreasing chain stopper content and thus increasing softening point the dissolving process becomes more difficult and the dissolving temperature had to be increased accordingly. Notably, in case of example 13 (dissolving example 3), which was prepared without additional chain stopper, no complete dissolution could be achieved in L40 and in the curing agent Epicure Agent 548.

10

Table 20f: Viscosities of mixtures of DVB-EVB-Phenol resins and thinners / solvents

		Dissolving example 1	Dissolving example 2
Resin		example 11	example 6
Molar ratio of DVB : EVB		4.1 : 1.0	1.7 : 1.0
SP of resin [°C]		93	68
	Thinner/Solvent		
viscosity (resin : thinner 1:2) @ 25 [mPas]	Butan-2-on	2.8	2.0
	Xylene	12.5	5
	Benzyl alcohol	89.1	51.1
viscosity (resin : thinner 1:2) @ 30°C [mPas]	L40	12250	1485
	Epicure Agent 548	98280	21750

The viscosity measurements show a comparable tendency. The influence of the softening point of the resin on the viscosity of the resin-thinner mixture increases drastically with increasing viscosity of the thinner / solvent (Table 20f). On increasing the softening point, the viscosity of the resin/thinner shows a much more pronounced increase (dissolving example 1 and 2; dissolving example 3 – 5, Tables 20f and 20g).

Table 20g: Viscosities of mixtures of DIPB-Styrene-Phenol resins and thinners / solvents

		Dissolving example 3	Dissolving example 4	Dissolving example 5
Resin		example 13	example 14	example 15
Molar ratio of DIPB : Styrene		1.0 : 0.0	1.0 : 1.0	0.4 : 1.0
SP of resin [°C]		140	96	58
	Thinner/Solvent			
viscosity (resin : thinner 1:2) @ 25 [mPas]	Butan-2-on	4.6	2.2	1.6
	Xylene	18.1	7.9	4.2
	Benzyl alcohol	220.0	68.5	37.2
viscosity (resin : thinner 1:2) @ 30°C [mPas]	L40	insoluble	2640	431
	Epicure Agent 548	insoluble	43360	11090

Influence of the Softening point on dosing amount of resin under constant mixture
5 viscosity

Generally industry requires coating formulations to have a distinct viscosity or viscosity range. Hence, the possible dosing amount of an additive, like the accelerator shown in this invention, is directly linked to its influence on viscosity.

- 10 To demonstrate the influence of the softening point, and thus the chain stopper content on the dosing amount of an accelerator, the resins of example 6 and 11 were dissolved in the thinner L40. The viscosity of both mixtures was adjusted to the same level by addition of further L40 (Table 20h) as follows:
- 15 50 g resin and 50 g L40 were added to a 300 mL three-neck round bottom flask equipped with a dimroth coil condenser and an overhead stirrer. The mixture was heated up to the temperatures established in the previous dissolving examples (see Table 20d; 80°C for dissolving the resin of example 6, 130°C for dissolving the resin of example 7) until a complete dissolution occurred. Afterwards, the viscosity of both

mixtures was measured. Then the viscosity of dissolving example 7 was set as target value and the viscosity of dissolving example 6 was adjusted to the same value by addition of 26.6 g L40.

5 Table 20h: Influence of the softening point on the dosing amount

	Dissolving example 6	Dissolving example 7
Resin	example 11	example 6
Molar ratio of DVB : EVB	4.1 : 1.0	1.7 : 1.0
SP of resin [°C]	93	68
Weight ratio of thinner (L40) : resin	60.5 : 39.5	50.0 : 50.0
Viscosity of L40	43950	43500
resin mixture @ 25 [mPas]		
OH content of L40	2.8	3.9
-resin mixture [%]		

The results of the dosing experiments demonstrate that by a distinct control of the molecular weight and the softening point the dosing amount in formulations can be improved. Especially the differing OH content, which is a main indicator for the acceleration activity of the solution, points out this beneficial effect induced by the differing EVB content. Further, it is possible by adjusting the end group content to tailor the softening point such that so-called "high solids" systems containing for example up to 80 wt.% of solids or even "no-solvent" systems that are free from solvent and/or thinner can be obtained which are interesting because the amount of thinner can be decreased to such a low level that it does not need to be removed at the end or the use of a thinner or solvent may even entirely be avoided. High solids systems are mainly prepared using diluents or thinners. As already explained above, a solvent normally escapes or has escaped from the hardened product. A thinner normally remains in the hardened product.

Explanation of the analytical methods

Molar mass Distribution via GPC

- 5 The molar mass distribution (M_n , M_w , M_z) was estimated via gel permeation chromatography (GPC) with a SECcurity²-System supplied by the company PSS-Polymers. The used column system consists of a 3 μm precolumn and three 3 μm 1000 Å main columns filled with a styrene divinylbenzene copolymer as column material. For substance detection a refraction index (RI) detector was used. Unstabilized
- 10 ULC/MS-grade THF was used as eluent supplied by the company Biosolve. Each measurement run was performed isothermal at 40°C. ReadyCal-Kit Poly(styrene) low (M_p 266 - 66 000 Da) was used as external standard supplied by PSS-Polymer.

Glas Transition Temperature via DSC

- 15 The glass transition temperature (T_g) was estimated with a DSC 2/400 with intra cooler supplied by the company Mettler Toledo. Aluminum crucibles with pin hole with a volume of 40 μl (Me-26763 AL-Crucibles) were used as sample vessels. The sample weight amounted to 10 - 20 mg. For the evaluation of the thermal properties, a heating-cooling-heating-cooling sequence was chosen as analytical method with a
- 20 heating / cooling rate of 10 K/min within a measuring window between -40 °C to 150 °C. The T_g evaluation was performed in accordance to DIN 53765.

Softening point (SP) via Mettler Ring & Ball

- 25 The softening points were estimated via the method „Ring & Ball“ in accordance to ASTM D 3461 „Softening point of asphalt and pitch - Mettler cup and ball method“. A FP 90 Central Processor in combination with a FP 83 HT Dropping Point Cell supplied by Mettler Toledo was used a testing device.

Hydroxyl content

The hydroxyl content was estimated via a potentiometric titration in accordance to DIN 53240-2 (1-methylimidazol catalyzed acetylation of free OH-groups with acetic anhydride followed by a titration with 0.5 M NaOH). The measurement was performed
5 with an automated titration unite (Titrande in combination with Titroprozessor 840 Touch Control and Dosimate 6.2061.010) supplied by Deutsche Metrohm GmbH & Co. KG.

Viscosity measurement via Rheometer

10 The viscosity of the resin thinner/solvent mixtures were measured with an Anton Paar MCR301 rheometer. Either a double gap geometry (DG26.7) for viscosities below 250 mPas or a concentric cylinder (CC27) for viscosities above 250 mPas were used. The measurement was performed isotherm at 25 or 30 °C in rotation mode with a
15 shear rate of 25 s⁻¹.

Application of the Accelerator in Epoxy Systems

The phenolic polymer, for example the DVBP resins prepared in the examples above, is suitable as modifier in coatings, adhesives, and composite formulations. Particularly
20 in epoxy-based systems it is usable as accelerator and chemical resistance enhancer.

To investigate its effect in epoxy systems the divinylbenzene phenol (DVBP) resin derived from the synthetis example 2 was tested in the curing of the commercially available epoxy resin Epikote 828 with the curing agent Epicure Agent 548. For
25 comparison purposes the epoxy system without additional accelerator (Std.) as well as the influence of a styrenated phenol, Novares LS500 a commonly applied accelerator for the curing of epoxy resins, were tested with epoxy resin Epikote 828® and curing agent Epicure Agent 548. Furthermore, the influence on the mechanical properties and chemical resistance of cured epoxy resins was investigated.

30

General Procedure for the Curing of Epoxy Resins

- Epikote 828 and a mixture of Epicure Agent 548 and the corresponding accelerator as shown in table 21 were added to a 100 mL plastic cup at room temperature and mixed
- 5 in a speed mixer at 2500 rpm for 1 min.

Table 21: Formulation of tested epoxy systems

Curing example	Epikote 828®[g]	Epicure Agent 548® [g]	Accelerator [g]
1	62	38	example 2: 15 g
2 (comparative)	62	38	styrenated phenol: 15 g
3 (comparative)	62	38	-

- Afterwards the corresponding amounts of sample were extracted for the different
- 10 application tests. Curing was conducted at room temperature.

Effects of acceleration

- 20g of the above shown mixture were extracted for a rheological analysis, which was
- 15 directly started after the mixing of the substances and transferred to the rheometer.
- The curing process was analyzed via a rheometer in accordance with the general procedure at 40°C. The time-dependent results of the rheological analysis are shown in Table 22 and Figure 1. Table 22 displays representative time points of the time-viscosity relationship during the rheology measurement. Figure 1 show the complete
- 20 complete development of the viscosity over time.

Table 22: Complex viscosity in dependence of time of the tested expoy systems

Curing example 3		Curing example 2		Curing example 1	
	complex viscosity		complex viscosity		complex viscosity
time [s]	[mPas]	time [s]	[mPas]	time [s]	[mPas]
125,7	1429,3	64,97	2243,4	67,02	6385

Curing example 3		Curing example 2		Curing example 1	
time [s]	complex viscosity [mPas]	time [s]	complex viscosity [mPas]	time [s]	complex viscosity [mPas]
515,7	2003,1	455	3296,9	457	14134
995,7	3337,3	935	8002,3	937	39695
1536	6260,9	1475	22198	1477	1,27E+05
2016	11179	1955	52853	1957	3,04E+05
2526	20766	2465	1,28E+05	2467	6,05E+05
3006	36972	2945	2,87E+05	2947	1,37E+06
3576	72520	3515	7,33E+05	3517	3,57E+06
4056	1,27E+05	3995	1,47E+06	3997	7,60E+06
5016	3,82E+05	4955	5,20E+06	4957	2,72E+07
5496	6,64E+05	5435	8,94E+06	5437	4,52E+07
6096	1,27E+06	6035	1,61E+07	6037	7,88E+07
6576	2,06E+06	6515	2,40E+07	6517	1,18E+08
7056	3,29E+06	6995	3,43E+07	6997	1,72E+08
7536	5,18E+06	7475	4,69E+07	7477	2,45E+08
8016	8,03E+06	7955	6,23E+07	7957	3,43E+08
8496	1,22E+07	8435	8,07E+07	8437	4,74E+08
9096	1,97E+07	9035	1,09E+08	9037	6,78E+08
9576	2,83E+07	9515	1,36E+08	9517	8,24E+08
1,01E+04	3,97E+07	9995	1,67E+08	9997	9,87E+08
1,05E+04	5,46E+07	1,05E+04	2,02E+08	1,05E+04	1,14E+09
1,10E+04	7,41E+07	1,10E+04	2,43E+08	1,10E+04	1,30E+09
1,15E+04	9,87E+07	1,14E+04	2,88E+08	1,14E+04	1,45E+09
1,20E+04	1,30E+08	1,19E+04	3,40E+08	1,19E+04	1,59E+09
1,25E+04	1,71E+08	1,24E+04	3,98E+08	1,24E+04	1,74E+09
1,26E+04	1,83E+08	1,25E+04	4,13E+08	1,25E+04	1,78E+09
1,31E+04	2,37E+08	1,30E+04	4,78E+08	1,30E+04	1,88E+09

Curing example 3		Curing example 2		Curing example 1	
time [s]	complex viscosity [mPas]	time [s]	complex viscosity [mPas]	time [s]	complex viscosity [mPas]
1,35E+04	3,07E+08	1,35E+04	5,50E+08	1,35E+04	2,01E+09
1,40E+04	3,96E+08	1,40E+04	6,28E+08	1,40E+04	2,07E+09
1,45E+04	5,07E+08	1,44E+04	7,04E+08	1,44E+04	2,15E+09
1,49E+04	6,05E+08	1,48E+04	7,61E+08	1,48E+04	2,19E+09
1,50E+04	6,37E+08	1,49E+04	7,81E+08		
1,51E+04	6,68E+08	1,50E+04	8,00E+08		
1,55E+04	7,68E+08	1,54E+04	8,56E+08		
1,56E+04	8,09E+08	1,55E+04	8,75E+08		
1,61E+04	9,77E+08	1,60E+04	9,46E+08		
1,65E+04	1,17E+09	1,65E+04	1,01E+09		
1,70E+04	1,34E+09	1,70E+04	1,09E+09		
1,75E+04	1,51E+09	1,74E+04	1,16E+09		
1,80E+04	1,70E+09	1,79E+04	1,22E+09		
1,81E+04	1,74E+09	1,80E+04	1,24E+09		
1,85E+04	1,86E+09	1,84E+04	1,29E+09		
1,86E+04	1,90E+09	1,85E+04	1,31E+09		
1,91E+04	2,04E+09	1,90E+04	1,37E+09		

- As shown above the viscosity in each experiment increased exponentially after a distinct amount of time. Both, the viscosities of the epoxy systems of curing example 2 with styrenated phenol and curing example 1 increased faster than the standard system in curing example 3 without additional additives indicating an acceleration effect. Furthermore, the effect of the phenolic polymer exemplified by the synthesis example 2 on the acceleration of the curing process in curing example 1 exceeds the styrenated phenol in curing example 2.

Complex viscosity via rheometer

The complex viscosity of the epoxy curing was measured with an Anton Paar MCR302 rheometer. An aluminum plate system (PP15 Geometry) was used. The measurement was performed isotherm at 40°C in oscillation mode at a frequency of 10 rads^{-1} with a shear gap of 1 mm. The deformation was started at 10% and was reduced to 1% with 0.2%/min. After the deformation reduction to 1% the rest of the measurement was performed at this deformation level until a torque of 100 mNm was reached.

Impact on mechanical properties of epoxy systemPendulum Hardness via Pendulum Hardness Tester

The pendulum hardness of the cured epoxy resins was measured with an BYK-Gardner pendulum hardness tester according to König (DIN 53 157). 10 g each of the different mixtures were poured in a defined mold and stored at room temperature for 1 day prior to the initial measurement. The prepared samples were clamped in the tester and the pendulum was locked in the starting position. The measurement was initiated by the pendulum release. The measurements were repeated after 1, 2, 6 and 13 weeks storage time. The results of the measurements are shown in Table 23.

Table 23: Pendulum hardness

Time [weeks]	0	1	2	6	13
	Pendulum Hardness [s]				
Curing example 3	129	179	187	203	203
Curing example 2	75	115	133	152	155
Curing example 1	136	171	185	192	196

As follows from Table 23, the epoxy system containing the phenolic polymer as accelerator of curing example 1 reached a high pendulum hardness value already at the beginning of the measurement (0 weeks). By contrast, the epoxy system without any accelerator had a lower pendulum hardness at the beginning of the measurement and the epoxy system containing the styrenated phenol as accelerator displayed an

even lower initial pendulum hardness. After the first week, all of the curing examples displayed higher pendulum hardness values. Thereafter, the pendulum hardness remained fairly constant for the curing example 1 containing the phenolic polymer of synthesis example 2 as accelerator while the curing example 3 without any
5 accelerator displayed a larger increase in the pendulum hardness after the first week. By contrast, the epoxy system containing the styrenated phenol accelerator displayed a significant increase in the pendulum hardness even from week 2 to week 13.

Tensile strength and maximum elongation via tensile testing

10 The tensile strength and elongation at break of the cured epoxy resins were measured via a Shimadzu Autograph AGS-X tensile testing machine. Each of the different mixtures were poured in defined bone shaped molds and stored at room temperature for 2 weeks. Prior to the measurement the dimensions of the samples were determined. The measurements were performed with a starting gauge length of
15 130.0 mm at room temperature with a speed of 10 mm/min. The results of the measurements and calculated average values are shown in Table 24.

Table 24: Tensile tests

ITEMS	THICKNESS	WIDTH	GAUGE LENGTH	TENSILE STRENGTH	ELOGANTION AT BREAK
unit	mm	mm	mm	MPa	(%)
Curing example 3 (no accelerator)					
Sample 3-1	4.05	10.14	130.0	43.22	2.92
Sample 3-2	4.06	10.16	130.0	46.71	3.26
Sample 3-3	4.02	10.16	130.0	45.33	2.85
Sample 3-4	4.09	10.10	130.0	50.36	3.57
average				46.4	3.15
Curing example 2 (styrenated phenol accelerator)					
Sample 2-1	3.88	10.16	130.00	43.60	7.32
Sample 2-2	3.91	10.18	130.00	44.09	6.19
Sample 2-3	3.88	10.21	130.00	42.24	8.12
Sample 2-4	3.83	10.17	130.00	40.50	6.60
Sample 2-5	3.83	10.17	130.00	39.71	6.56
average				42.03	6.96
Curing example 1 (synthesis example 2 as accelerator)					
Sample 1-1	3.89	10.16	130	51.02	3.36
Sample 1-2	3.85	10.17	130	39.76	2.69
Sample 1-3	3.99	10.17	130	40.13	2.70
Sample 1-4	3.89	10.16	130	52.02	3.49
average				45.73	3.06

Low molecular mass accelerators like styrenated phenols but also benzylalcohol or nonylphenol often cause softening of the epoxy systems that are exemplified by a high elongation at break. The phenolic polymer of synthesis example 2 has only a small effect on the mechanical properties compared to the epoxy system without any accelerator as shown in the tensile tests (Table 24).

10 Impact on chemical resistance

General procedure for the chemical resistance test

10 g of each of the different mixtures were poured in 5 defined molds, which were stored at room temperature for 2 weeks. Afterwards the sample weight was determined followed by the immersion of the respective sample in a 100 mL closed

glass bottle filled with 90mL of the distinct test media. The following test media were employed:

1. aqueous solution of acetic acid (10 w%),
2. aqueous solution of sodium hydroxide (5 w%),
- 5 3. xylene,
4. water

Every week the samples were taken out from the glass bottles, cleaned from residual test media and weighed. After the weighing the samples were returned to the glass bottle. The process was repeated for 6 weeks.

10

Table 25: Water uptake

Time	1 week	2 weeks	3 weeks	6 weeks
	Weight change [%]			
Curing example 3 (no accelerator)	0.48	0.74	0.94	1.30
Curing example 2 (styrenated phenol accelerator)	0.44	0.65	0.81	1.11
Curing example 1 (phenolic polymer of synthesis example 2 as accelerator)	0.37	0.55	0.69	0.96

- Both curing example 2 and curing example 3 show an improvement to the storage stability of the cured epoxy resins under aqueous conditions (Table 25), which is indicated by reduced weight gain caused by swelling effects. When employing an accelerator, the weight gain was reduced to 0.96 wt. % (curing example 1) and 1.11 wt. % (curing example 2) in contrast to 1.30 wt. % (curing example 3).

Table 26: Acetic acid (10%) uptake

Time	1 week	2 weeks	3 weeks	6 weeks
	Weight change [%]			
Curing example 3 (no accelerator)	2.38	3.41	4.20	5.63
Curing example 2 (styrenated phenol accelerator)	0.81	1.16	1.44	1.96
Curing example 1 (phenolic polymer of synthesis example 2 as accelerator)	0.95	1.39	1.71	2.67

Both under acidic (Table 26) and under basic (Table 27) conditions, the hydrophilization properties of the accelerator of synthesis example 2 become evident. The swelling has been reduced under acidic conditions from 5.63 wt. % (curing example 3) to 2.67 wt. % (curing example 1) and under basic conditions from 1.06 wt. % (curing example 3) to 0.83 wt. % (curing example 1). In both cases the effect is comparable to the styrenated phenol of curing example 2 (acidic 1.96 wt. %; basic 0.90 wt. %).

Table 27: Sodium hydroxid (5%) uptake

Time	1 week	2 weeks	3 weeks	6 weeks
	Weight change [%]			
Curing example 3 (no accelerator)	0.39	0.59	0.75	1.06
Curing example 2 (styrenated phenol accelerator)	0.36	0.52	0.65	0.90
Curing example 1 (phenolic polymer of synthesis example 2 as accelerator)	0.30	0.45	0.57	0.83

Table 28: Xylene uptake

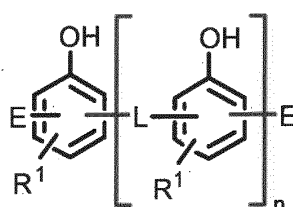
Time	1 week	2 weeks	3 weeks	6 weeks
	Weight change [%]			
Curing example 3 (no accelerator)	0.02	0.05	0.07	0.11
Curing example 2 (styrenated phenol accelerator)	0.19	0.71	1.30	2.43
Curing example 1 (phenolic polymer of synthesis example 2 as accelerator)	-0.03	0.00	-0.06	0.08

Both the cured epoxy system of curing example 1 (phenolic polymer of synthesis example 2 as accelerator) and of curing example 3 (no accelerator) showed very high chemical resistance to xylene. Almost no swelling effects (0.11 wt. % curing example 3; 0.08 wt. % curing example 1) could be observed during the test period (Table 28). In comparison, the styrenated phenol accelerator of curing example 2 deteriorated the resistance significantly. After 6 weeks a weight gain of 2.43 w% was detected for curing example 2.

The shown chemical resistance tests demonstrate DVBP resin is a modifier for coatings systems with an around improvement against aqueous as well as organic impact.

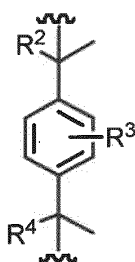
Claims

1. An epoxy system comprising
an epoxy resin and
a phenolic polymer having a number average molar mass (M_n) of from 200 to
1,500 g/mol comprising a phenol compound, a linker group L and end group E,
said phenolic polymer having the structure as presented in formula 1 below:

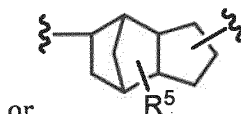


Formula 1

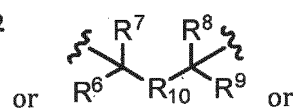
wherein the linker group L has the meaning of



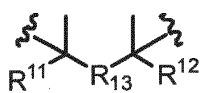
Formula 2



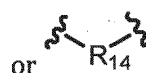
Formula 3



Formula 4

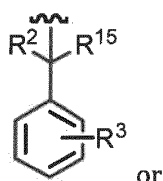


Formula 5

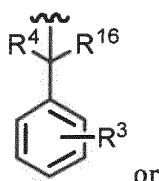


Formula 6

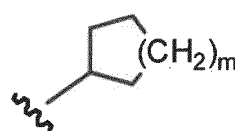
each end group E has the meaning of H or is a group of formula 2, 3, 4, 5 or 6 with only one bond to a phenol compound in formula 1 or has the meaning of



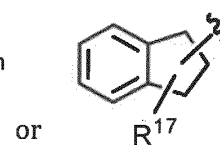
Formula 2c1



Formula 2c2



Formula 3c1



Formula 3c2

5 and wherein

R¹ is H, C₁₋₁₅ alkyl, or C₁₋₁₅ oxyalkyl, or C₆H₅(CR¹⁸R¹⁹)_o-Z-, preferably H, C₁₋₁₅ alkyl, or C₁₋₁₅ oxyalkyl,

R², R⁴, R⁶, R⁷, R⁸, R⁹, R¹¹ and R¹² are independently from each other H or C₁₋₅ alkyl, R³ and R⁵ are H, OH, NO₂, halogen, C₁₋₅ alkyl or C₁₋₅ oxyalkyl,

10 R₁₀ and R₁₃ are C₁₋₅ alkyl or C₅₋₆ cycloalkyl,

R₁₄ is C₅₋₁₂ cycloalkyl, optionally substituted with a methyl or an ethyl group,

R¹⁵, R¹⁶, and R¹⁷ are independently from each other H or C₁₋₅ alkyl, preferably -CH₃,

R¹⁸ and R¹⁹ are independently of each other H or CH₃

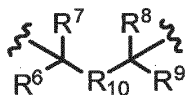
Z is a covalent bond or -O-,

15 o is 1 or 0,

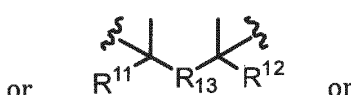
m is an integer from 1 to 7 and

n is an integer of from 2 to 21.

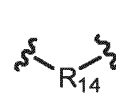
2. The epoxy system of claim 1, wherein said phenolic polymer comprises 50 wt.% to 70 wt.% phenol compound, 20 wt.% to 50 wt.% of the linker group L, in particular of difunctional monomers selected from a divinylbenzene compound, dicyclopentadiene compound or a compound of formula 4, 5 or 6,



Formula 4



Formula 5



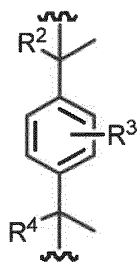
Formula 6

25

wherein the residues R^6 to R^{14} have the same meaning as defined before,
 and/or 0 wt.% to 50 wt.%, in particular 5 wt.% to 40 wt.%, more particularly 10
 wt.% to 40 wt.%, of the end group E, in particular of a monofunctional monomer
 having only one bond to a phenol compound in the phenolic polymer, based on the
 mass of the phenolic polymer.

3. The epoxy system of claims 1 or 2, wherein in the phenolic polymer R^1 is H, C_{1-10}
 alkyl, in particular C_{1-8} alkyl, more particularly C_{1-5} alkyl, or C_{1-10} oxyalkyl, in
 particular C_{1-8} oxyalkyl, more particularly C_{1-5} oxyalkyl.

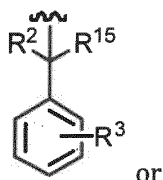
4. The epoxy system of claims 1 to 3, wherein in the phenolic polymer the linker
 group L has the meaning of



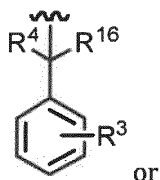
Formula 2,

wherein R^2 , R^3 , and R^4 are as defined in claim 1, in particular H.

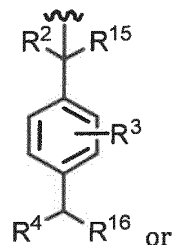
5. The epoxy system of claims 1 to 4, wherein in the phenolic polymer the end group E has the meaning of



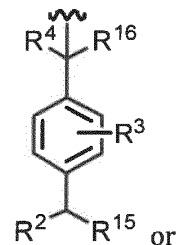
Formula 2c1



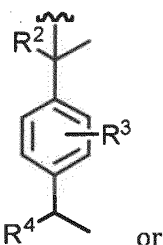
Formula 2c2



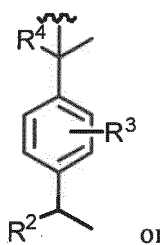
Formula 2c3



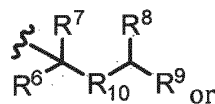
Formula 2c4



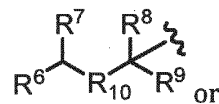
Formula 2c5



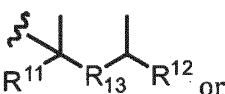
Formula 2c6



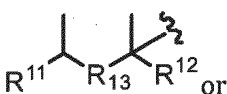
Formula 4c1



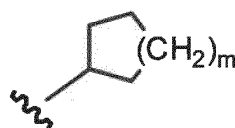
Formula 4c2



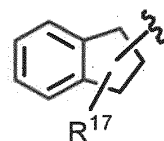
Formula 5c1



Formula 5c2



Formula 3c1



Formula 3c2

5

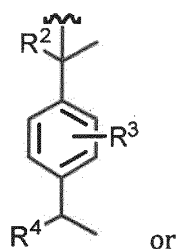
wherein R^2 to R^{13} are as defined in claim 1

m is an integer from 1 to 7 and

R^{15} , R^{16} , and R^{17} are independently from each other H or C_{1-5} alkyl, preferably $-CH_3$.

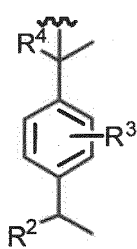
10

6. The epoxy system of claims 1 to 5, wherein in the phenolic polymer the end group E has the meaning of



Formula 2c5

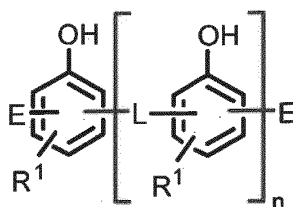
or



Formula 2c6,

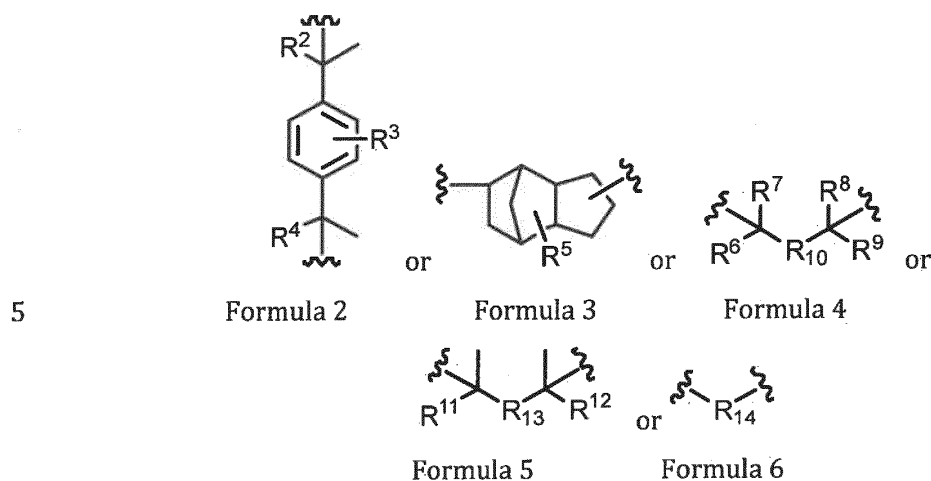
wherein R^2 , R^3 , and R^4 are as defined in claim 1, in particular H.

- 5 7. The epoxy system of claims 1 to 6, wherein in the phenolic polymer the OH content is 5 to 13 wt.%, in particular 6 to 9 wt.% based on the mass of the phenolic polymer.
8. The epoxy system of claims 1 to 7, wherein the phenolic polymer has a softening point according to ASTM 3461 up to 170 °C, more preferred 40°C to 120°C, more preferred 50°C to 100°C, and/or a Gardner color number, determined according to DIN EN ISO 4630:2016-05 using acetone instead of toluene for the measurement from 0 to 5, preferably from 0 to 2, more preferably from 0 to 1.
- 15 9. The epoxy system of claims 1 to 8, wherein the epoxy system comprises a hardener comprising amine, anhydride, phenolic, and/or thiol, in particular amine, functionalities.
10. Use of a phenolic polymer having a number average molar mass (M_n) of from 200 to 1,500 g/mol comprising a phenol compound, a linker group L and end group E, said phenolic polymer having the structure as presented in formula 1 below:

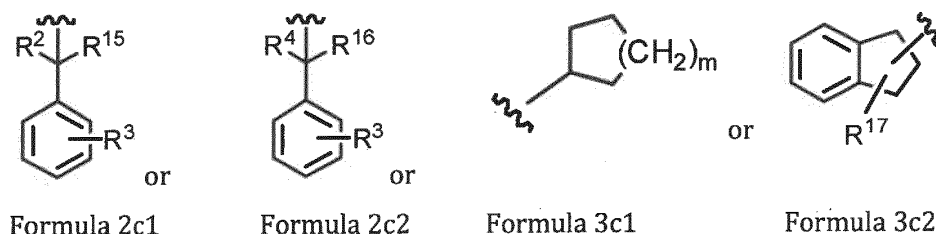


Formula 1

wherein the linker group L has the meaning of



10 each end group E has the meaning of H or is a group of formula 2, 3, 4, 5 or 6 with only one bond to a phenol compound in formula 1 or has the meaning of



and wherein

15 R^1 is H, C₁₋₁₅ alkyl, or C₁₋₁₅ oxyalkyl, or C₆H₅(CR¹⁸R¹⁹)_o-Z-, preferably H, C₁₋₁₅ alkyl, or C₁₋₁₅ oxyalkyl,
 R^2 , R^4 , R^6 , R^7 , R^8 , R^9 , R^{11} and R^{12} are independently from each other H or C₁₋₅ alkyl,
 R^3 and R^5 are H, OH, NO₂, halogen, C₁₋₅ alkyl or C₁₋₅ oxyalkyl,
 R^{10} and R^{13} are C₁₋₅ alkyl or C₅₋₆ cycloalkyl,
 R^{14} is C₅₋₁₂ cycloalkyl, optionally substituted with a methyl or an ethyl group,
 20 R^{15} , R^{16} , and R^{17} are independently from each other H or C₁₋₅ alkyl, preferably

-CH₃,

R¹⁸ and R¹⁹ are independently of each other H or CH₃

Z is a covalent bond or -O-,

o is 1 or 0,

5 m is an integer from 1 to 7 and

n is an integer of from 2 to 21

as an accelerator for the curing of epoxy resins, in particular in the presence of a hardener comprising amine functionalities

or

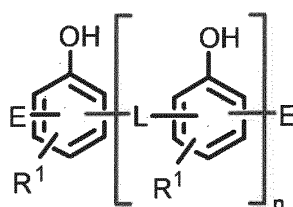
10 as a hardener for epoxy resins, in particular in the presence of a co-hardener comprising amine functionalities.

11. Use according to claim 10, wherein the phenolic polymer is further characterized by at least one of the features defined in any one of claims 2 to 8.

15

12. Kit-of-parts comprising an epoxy resin and a phenolic polymer having a number average molar mass (M_n) of from 200 to 1,500 g/mol comprising a phenol compound, a linker group L and end group E, said phenolic polymer having the structure as presented in formula 1 below:

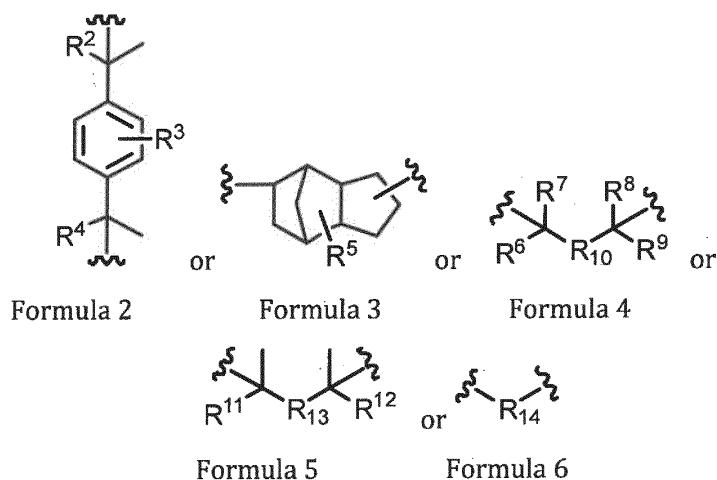
20



Formula 1

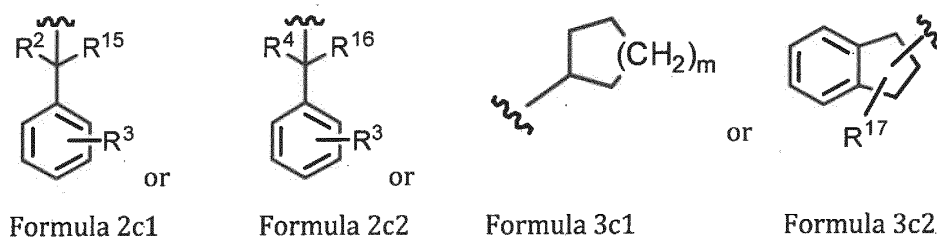
wherein the linker group L has the meaning of

25



5

each end group E has the meaning of H or is a group of formula 2, 3, 4, 5 or 6 with only one bond to a phenol compound in formula 1 or has the meaning of



10

and wherein

R¹ is H, C₁₋₁₅ alkyl, or C₁₋₁₅ oxyalkyl, or C₆H₅(CR¹⁸R¹⁹)_o-Z-, preferably H, C₁₋₁₅ alkyl, or C₁₋₁₅ oxyalkyl,

R², R⁴, R⁶, R⁷, R⁸, R⁹, R¹¹ and R¹² are independently from each other H or C₁₋₅ alkyl, R³ and R⁵ are H, OH, NO₂, halogen, C₁₋₅ alkyl or C₁₋₅ oxyalkyl,

15

R₁₀ and R₁₃ are C₁₋₅ alkyl or C₅₋₆ cycloalkyl,

R₁₄ is C₅₋₁₂ cycloalkyl, optionally substituted with a methyl or an ethyl group,

R¹⁵, R¹⁶, and R¹⁷ are independently from each other H or C₁₋₅ alkyl, preferably -CH₃,

R¹⁸ and R¹⁹ are independently of each other H or CH₃

20

Z is a covalent bond or -O-,

o is 1 or 0,
m is an integer from 1 to 7 and
n is an integer of from 2 to 21, and
a hardener comprising amine, anhydride, phenolic, and/or thiol, in particular
amine, functionalities.

5

13. Kit-of-parts according to claim 12, wherein the phenolic polymer and the hardener are present as a mixture that optionally contains a solvent and/or a thinner.

10