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.

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 $-C(CH_3)_2C_6H_5$ group or a $-C(CH_3)_2C_6H_4OH$ group with a benzene compound substituted with two independent occurrences of $-C(CH_3)CH_2$ or $-C(CH_3)_2OH$ in the presence of an acidic catalyst.

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.

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.

SUMMARY

The object of the disclosure 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.

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

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,

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,

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,

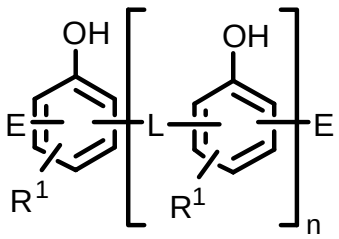
m is an integer from 1 to 7 and

n is an integer of from 2 to 21.

In one aspect, the disclosure is directed to an epoxy system comprising

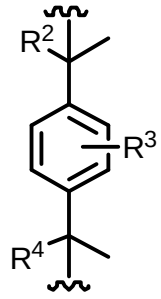
an epoxy resin and

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:

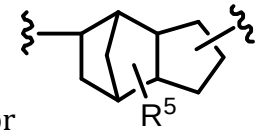


Formula 1

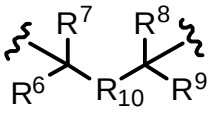
wherein the linker group L has the meaning of



or

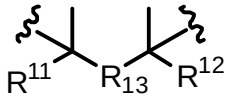


or

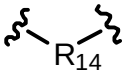


or

Formula 2 Formula 3 Formula 4

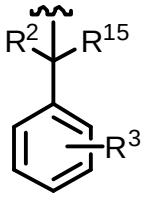


or

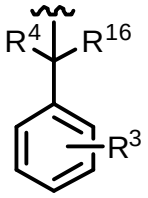


Formula 5 Formula 6

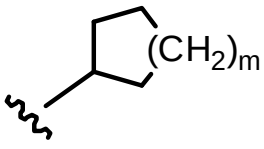
each end group E is a group of formula 2, 3, 4, 5 or 6 with only one bond to a phenol compound in formula 1 and the remaining bond to a hydrogen atom or has the meaning of



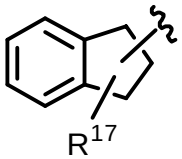
or



or



or



Formula 2c1 Formula 2c2 Formula 3c1 Formula 3c2

and wherein

R^1 is H, $C_{1\text{-}15}$ alkyl, or $C_{1\text{-}15}$ oxyalkyl, or $C_6H_5(CR^{18}R^{19})_o$-Z-, preferably H, $C_{1\text{-}15}$ alkyl, or $C_{1\text{-}15}$ 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 $C_{1\text{-}5}$ alkyl,

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

R_{10} and R_{13} are $C_{1\text{-}5}$ alkyl or $C_{5\text{-}6}$ cycloalkyl,

R_{14} is $C_{5\text{-}12}$ cycloalkyl, optionally substituted with a methyl or an ethyl group,

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

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

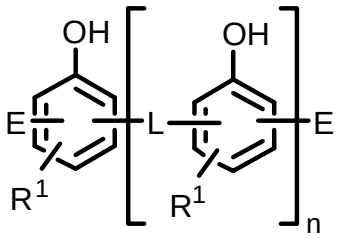
Z is a covalent bond or –O-,

o is 1 or 0,

m is an integer from 1 to 7 and

n is an integer of from 2 to 21.

The disclosure is furthermore directed to the use of a phenolic polymer comprising 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

o is 1 or 0,

m is an integer from 1 to 7 and

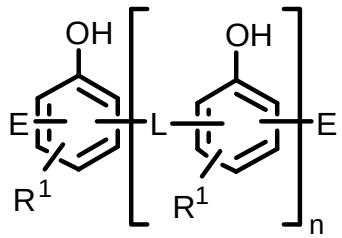
n is an integer of from 2 to 21

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

or

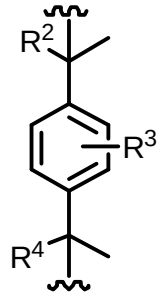
as a hardener for epoxy resins, in particular in the presence of a co-hardener comprising amine functionalities.

In another aspect, the disclosure is furthermore directed 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:

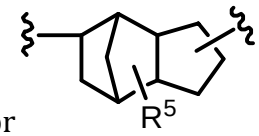


Formula 1

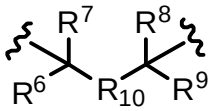
wherein the linker group L has the meaning of



or

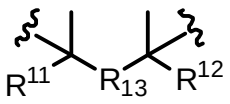


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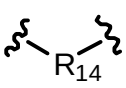


or

Formula 2 Formula 3 Formula 4

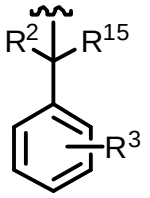


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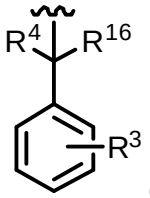


Formula 5 Formula 6

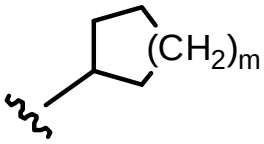
each end group E is a group of formula 2, 3, 4, 5 or 6 with only one bond to a phenol compound in formula 1 and the remaining bond to a hydrogen atom or has the meaning of



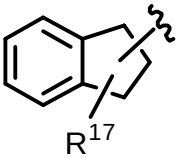
or



or



or



Formula 2c1 Formula 2c2 Formula 3c1 Formula 3c2

and wherein

R^1 is H, $C_{1\text{-}15}$ alkyl, or $C_{1\text{-}15}$ oxyalkyl, or $C_6H_5(CR^{18}R^{19})_o$-Z-, preferably H, $C_{1\text{-}15}$ alkyl, or $C_{1\text{-}15}$ 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 $C_{1\text{-}5}$ alkyl,

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

R_{10} and R_{13} are $C_{1\text{-}5}$ alkyl or $C_{5\text{-}6}$ cycloalkyl,

R_{14} is $C_{5\text{-}12}$ cycloalkyl, optionally substituted with a methyl or an ethyl group,

R^{15}, R^{16}, and R^{17} are independently from each other H or $C_{1\text{-}5}$ 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

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

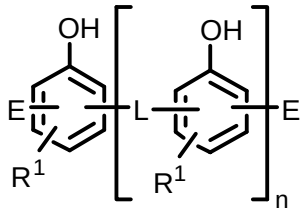
or

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

The disclosure is furthermore directed to a kit of parts comprising

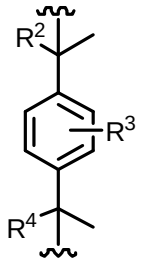
an epoxy resin and

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:

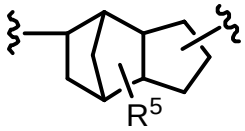


Formula 1

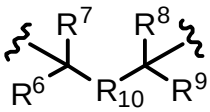
wherein the linker group L has the meaning of



or

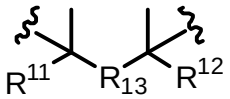


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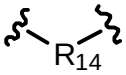


or

Formula 2 Formula 3 Formula 4

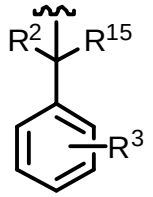


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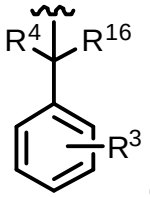


Formula 5 Formula 6

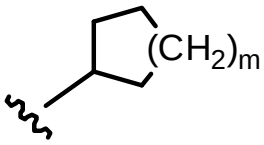
each end group E has the meaning of H or is a group of formula 2, 3, 4, 5 or 6 with only one bond to a phenol compound in formula 1 or has the meaning of



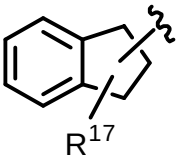
or



or



or



Formula 2c1 Formula 2c2 Formula 3c1 Formula 3c2

and wherein

R^1 is H, $C_{1\text{-}15}$ alkyl, or $C_{1\text{-}15}$ oxyalkyl, or $C_6H_5(CR^{18}R^{19})_o$-Z-, preferably H, $C_{1\text{-}15}$ alkyl, or $C_{1\text{-}15}$ 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 $C_{1\text{-}5}$ alkyl,

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

R_{10} and R_{13} are $C_{1\text{-}5}$ alkyl or $C_{5\text{-}6}$ cycloalkyl,

R_{14} is $C_{5\text{-}12}$ cycloalkyl, optionally substituted with a methyl or an ethyl group,

R^{15}, R^{16}, and R^{17} are independently from each other H or $C_{1\text{-}5}$ 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,

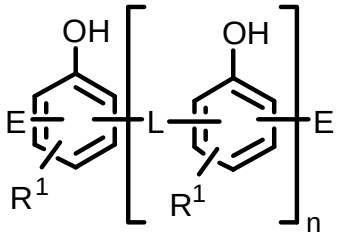
m is an integer from 1 to 7 and

n is an integer of from 2 to 21, and

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

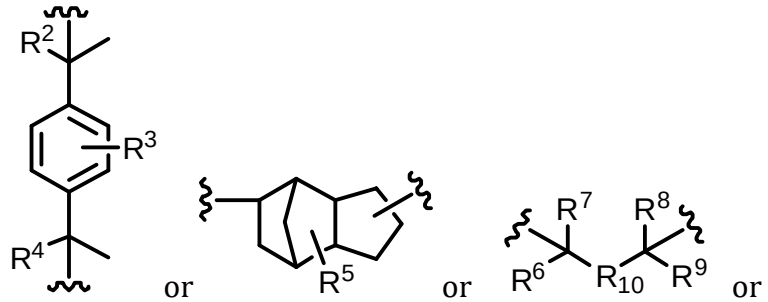
In another aspect, the disclosure is directed to kit-of-parts comprising an epoxy resin and a phenolic polymer having a number average molar mass (M_n) of from 200 to

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:

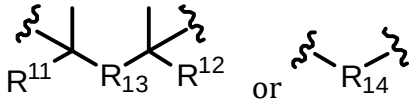


Formula 1

wherein the linker group L has the meaning of

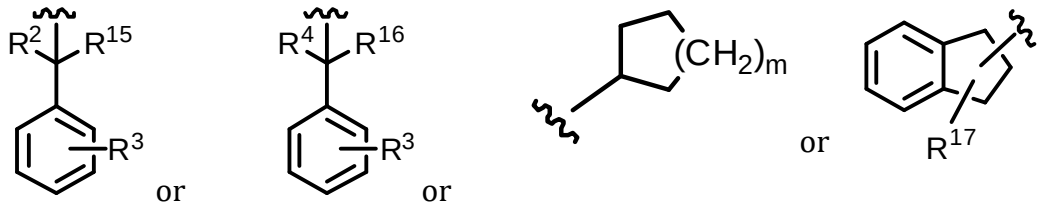


Formula 2 Formula 3 Formula 4



Formula 5 Formula 6

each end group E is a group of formula 2, 3, 4, 5 or 6 with only one bond to a phenol compound in formula 1 and the remaining bond to a hydrogen atom 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 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,

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

n is an integer of from 2 to 21, and

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

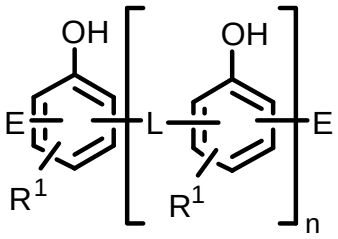
The phenolic polymer according to the disclosure accelerates the curing of epoxy resins, for example in adhesive systems or in coatings. The hardened epoxy resins have good mechanical properties and also good chemical resistivity.

C l a i m s

1. An epoxy system comprising

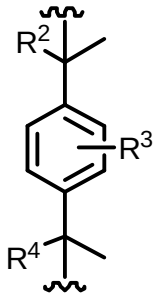
an epoxy resin and

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:

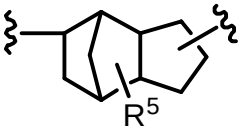


Formula 1

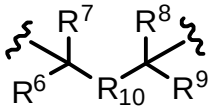
wherein the linker group L has the meaning of



or

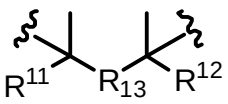


or

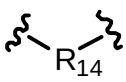


or

Formula 2 Formula 3 Formula 4



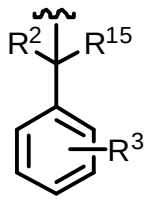
or



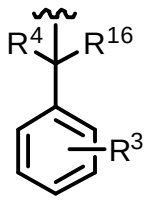
Formula 5 Formula 6

each end group E is a group of formula 2, 3, 4, 5 or 6 with only one bond to a phenol compound in formula 1 and the remaining bond to a hydrogen atom or

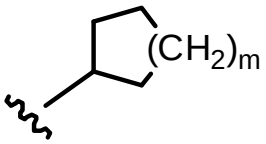
has the meaning of



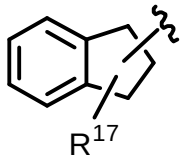
or



or



or



Formula 2c1 Formula 2c2 Formula 3c1 Formula 3c2

and wherein

R^1 is H, $C_{1\text{-}15}$ alkyl, or $C_{1\text{-}15}$ oxyalkyl, or $C_6H_5(CR^{18}R^{19})_o$-Z-, preferably H, $C_{1\text{-}15}$ alkyl, or $C_{1\text{-}15}$ 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 $C_{1\text{-}5}$ alkyl,

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

R_{10} and R_{13} are $C_{1\text{-}5}$ alkyl or $C_{5\text{-}6}$ cycloalkyl,

R_{14} is $C_{5\text{-}12}$ cycloalkyl, optionally substituted with a methyl or an ethyl group,

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

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

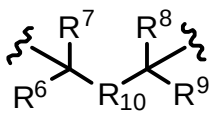
Z is a covalent bond or –O-,

o is 1 or 0,

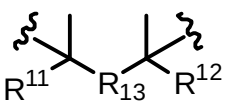
m is an integer from 1 to 7 and

n is an integer of from 2 to 21.

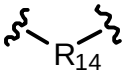
2. The epoxy system of claim 1, wherein said phenolic polymer comprises 50 wt.% to 70 wt.% phenol compound, 20 wt.% to 50 wt.% of the linker group L, in particular of difunctional monomers selected from a divinylbenzene compound, diclyclopentadiene compound or a compound of formula 4, 5 or 6,



or



or

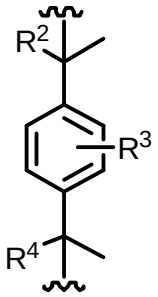


Formula 4 Formula 5 Formula 6

wherein the residues R^6 to R^{14} have the same meaning as defined before, and/or 5 wt.% to 40 wt.%, in particular 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.

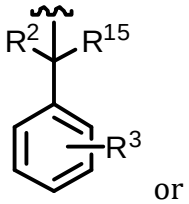
4. The epoxy system of claims 1 to 3, wherein in the phenolic polymer the linker group L has the meaning of



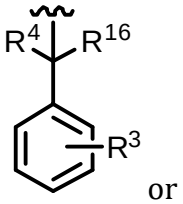
Formula 2,

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

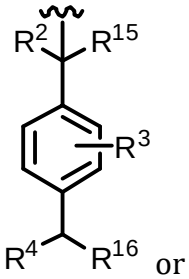
5. The epoxy system of claims 1 to 4, wherein in the phenolic polymer the end group E has the meaning of


or

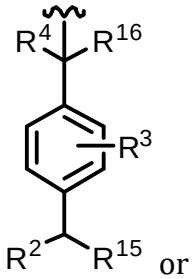
Formula 2c1


or

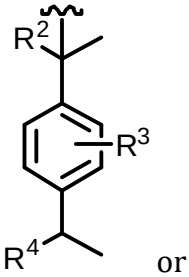
Formula 2c2


or

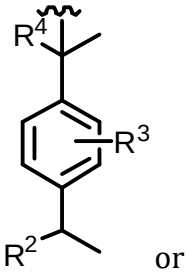
Formula 2c3


or

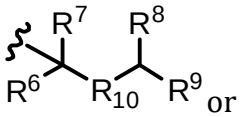
Formula 2c4


or

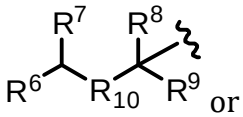
Formula 2c5


or

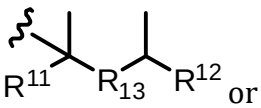
Formula 2c6


or

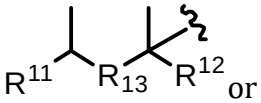
Formula 4c1


or

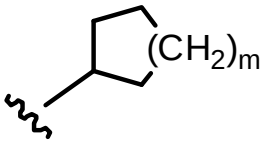
Formula 4c2


or

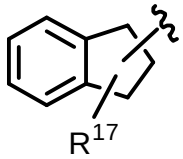
Formula 5c1


or

Formula 5c2


or

Formula 3c1



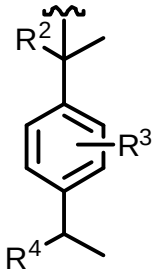
Formula 3c2

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

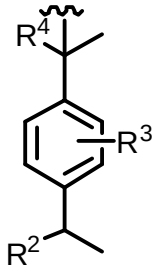
m is an integer from 1 to 7 and

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

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



or



Formula 2c5 Formula 2c6,

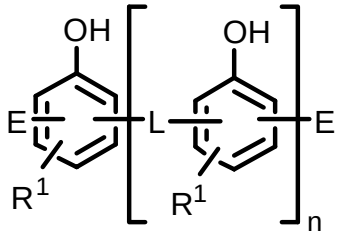
wherein R^2, R^3, and R^4 are as defined in claim 1, in particular H.

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.

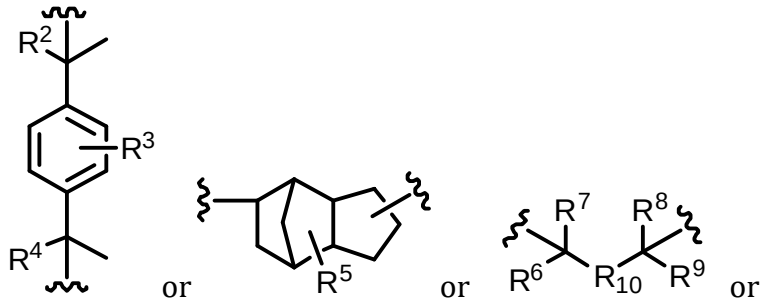
9. The epoxy system of claims 1 to 8, wherein the epoxy system comprises a hardener comprising amine, anhydride, phenolic, and/or thiol, in particular amine, functionalities.

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:

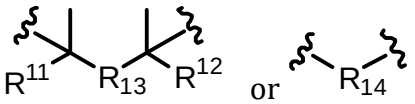


Formula 1

wherein the linker group L has the meaning of

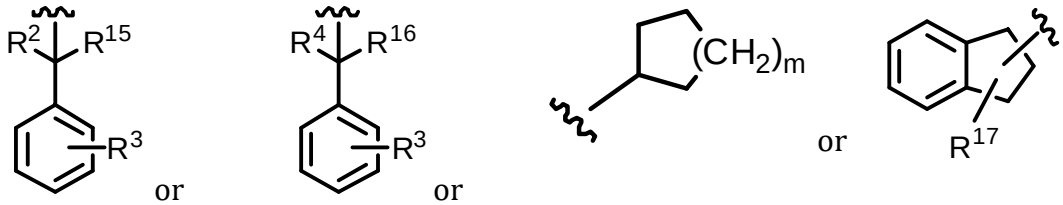


Formula 2 Formula 3 Formula 4



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 compound in formula 1 and the remaining bond to a hydrogen atom or has the meaning of



Formula 2c1 Formula 2c2 Formula 3c1 Formula 3c2

and wherein

R^1 is H, $C_{1\text{-}15}$ alkyl, or $C_{1\text{-}15}$ oxyalkyl, or $C_6H_5(CR^{18}R^{19})_o$-Z-, preferably H, $C_{1\text{-}15}$ alkyl, or $C_{1\text{-}15}$ 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 $C_{1\text{-}5}$ alkyl,

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

R_{10} and R_{13} are $C_{1\text{-}5}$ alkyl or $C_{5\text{-}6}$ cycloalkyl,

R_{14} is $C_{5\text{-}12}$ cycloalkyl, optionally substituted with a methyl or an ethyl group,

R^{15}, R^{16}, and R^{17} are independently from each other H or $C_{1\text{-}5}$ 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

n is an integer of from 2 to 21

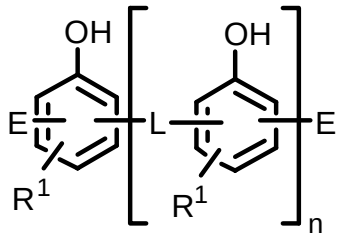
as an accelerator for the curing of epoxy resins, in particular in the presence of a hardener comprising amine functionalities

or

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

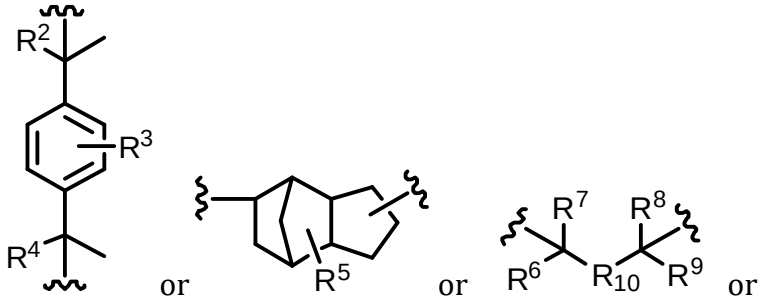
11. Use according to claim 10, wherein the phenolic polymer is further characterized by at least one of the features defined in any one of claims 2 to 8.

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:

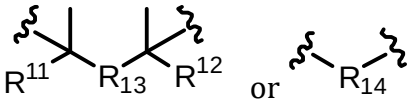


Formula 1

wherein the linker group L has the meaning of

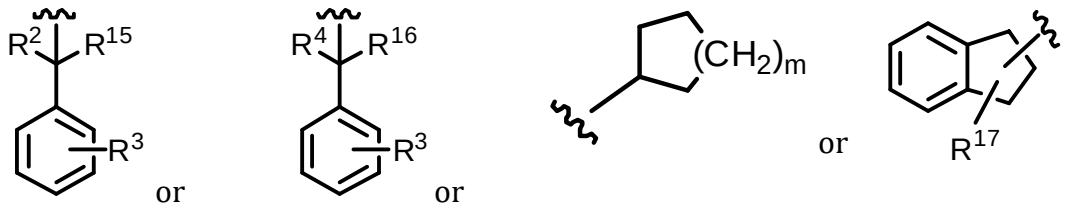


Formula 2 Formula 3 Formula 4



Formula 5 Formula 6

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



Formula 2c1 Formula 2c2 Formula 3c1 Formula 3c2

and wherein

R^1 is H, $C_{1\text{-}15}$ alkyl, or $C_{1\text{-}15}$ oxyalkyl, or $C_6H_5(CR^{18}R^{19})_o$-Z-, preferably H, $C_{1\text{-}15}$ alkyl, or $C_{1\text{-}15}$ 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 $C_{1\text{-}5}$ alkyl,

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

R_{10} and R_{13} are $C_{1\text{-}5}$ alkyl or $C_{5\text{-}6}$ cycloalkyl,

R_{14} is $C_{5\text{-}12}$ cycloalkyl, optionally substituted with a methyl or an ethyl group,

R^{15}, R^{16}, and R^{17} are independently from each other H or $C_{1\text{-}5}$ 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
n is an integer of from 2 to 21, and
a hardener comprising amine, anhydride, phenolic, and/or thiol, in particular amine, functionalities.

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.