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(54) Title: GEL TIME CONTROLLABLE TWO PART EPOXY ADHESIVE

(57) Abstract: The present invention provides a gel time controllable two part epoxy adhesive, which includes a first part comprising an epoxy resin containing two or more epoxy groups in one molecule, and a peroxide; and a second part comprising a thiol curing agent and a curing accelerator.



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Gel time controllable two part epoxy adhesive

FIELD OF THE INVENTION

This invention relates to a two part epoxy adhesive, and a method for preparing
5 the same.

BACKGROUND OF THE INVENTION

Compounds having two or more thiol groups in one molecule readily react with epoxy resins, urethane resins or the like by mixing them with such resins and become
10 cured products, and therefore, they have been widely used for sealing materials, coating materials, adhesives, etc. For example, various polythiol-based curing agents are described as low-temperature curing agents on page 204 of "Sosetsu Epokishi Jushi (General Reviews Epoxy Resins)" (Vol. 1, Basic Edition, published on Nov. 19, 2003). Conventional polythiol-based epoxy adhesives with tertiary-amine curing
15 agents, however, have a clear shortcoming that when such a curing agent is mixed with an epoxy compound and a curing assistant at ordinary temperature to form an epoxy resin composition, the gel time of the composition is as short as 3 minutes to 5 minutes and curing is initiated in the course of preparation of the composition, though the curing agent shows excellent curability at low temperatures. Thus, it was rather
20 difficult to control the gel time of adhesives based on epoxy-thiol systems. The gel time is either so long in case of not using curing accelerator, or so short when using curing accelerator. As a result, the working conditions of epoxy-thiol adhesives were restricted.

There are not related references reported about how to control the gel time of
25 the thiol-amine curing system, some patents have mentioned this problem as following:

In US patent No. US 2010/0273940 A1, there is disclosed a curing agent for epoxy resins, which contains a thiol compound having a branch (substituent) on a carbon atom at the α position to a thiol group (-SH), and one compound epoxy resin
30 composition using the curing agent. This invention relates to an epoxy resin curing agent having a pot life from 5min to 15min and having storage stability.

In Japanese Patent No. 269203/1996, there is disclosed a thiol group-containing polyether polymer obtained by allowing a halogen-terminated polyether polymer which is obtained by addition of epihalohydrin to a polyol having a polyether moiety
35 in the main chain and having 3 or more hydroxyl groups at the ends to react with an alkali hydrosulfide and/or an alkali polysulfide in amides. It is indicated that an epoxy

resin composition containing this polyether polymer has favorable curability, but when this epoxy resin composition is used as a curing agent for epoxy resins, the gel time is so short that curing is initiated while the epoxy resin and a thiol compound that is a curing agent are being mixed with each other, and hence, the working conditions are restricted.

An epoxy resin curing composition using a hetero ring-containing compound, which is described in WO99/54373, has low-temperature curability and rapid curability at ordinary temperature, but the workability is poor because its gel time is short.

In Japanese patent No. 21693/1992, there is disclosed a liquid polysulfide polymer for epoxy resin curing, which is a copolymer obtained by allowing a mixture of a tri- or tetrafunctional alkyl halide and a bifunctional alkyl halide to react with an alkali polysulfide, the amount of said polyfunctional monomers in the polymerization being 20 to 60% by mol based on all the monomers, and which contains 2 to 30% by mass of end thiol groups. It is indicated that by using this liquid sulfide polymer in combination with an amine, the curing rate becomes higher as compared with that of conventional polysulfide polymers. However, the gel time is short, and the resulting cured product has a problem of workability because it develops odor, though it is excellent in impact resistance, chemical resistance, etc.

Thus, despite all these prior arts, there is still a need for a two part epoxy adhesive system, whose gel time is controllable and suitable for satisfying different gel time requirements from customers.

The present invention provides a novel epoxy based adhesive system, which allows a controllable gel time ranging from 5min to more than 24 hours.

SUMMARY OF THE INVENTION

This invention is directed to a two part epoxy adhesive, which includes a first part comprising an epoxy resin containing two or more epoxy groups in one molecule, and a peroxide containing a -O-O- structure; and a second part comprising a thiol curing agent and an curing accelerator.

In one embodiment of the inventive adhesive, the peroxide has a formula of R1-O-O-R2, wherein R1 and R2 are each independently selected from hydrogen atom, alkyl group of 1~10 carbon atoms and aromatic group including one or more phenyl group, and optionally there is a carbonyl group between R1, R2 and -O-O-.

In a further embodiment of the inventive adhesive system, the thiol curing agent containing one or more R₃-SH groups in one molecule, wherein R₃ is an alkyl group which includes 2~16 carbon atoms or aromatic group.

A preferred embodiment of the inventive adhesive comprises:

5 a first part comprising 100 parts by weight of an epoxy resin containing two or more epoxy groups in one molecule; 0.03~3 parts by weight of a peroxide containing a -O-O- structure; and a second part comprising 110~120 parts by weight of a thiol curing agent, 0.05~5 parts by weight of an curing accelerator.

10 Advantages and unique features of the inventive adhesive system include:
the gel time of the epoxy based compositions can be easily controlled;
peroxide is for the first time used to delay the reaction of thiol-amine curing
system; and
this adhesive system is suitable for satisfying different gel time requirements
15 from customers.

Various other features, aspects, and advantages of the present invention will become more apparent with reference to the following description, examples, and
20 appended claims.

DETAILS OF THE INVENTION

All publications, patent applications, patents and other references mentioned herein, if not otherwise indicated, are explicitly incorporated by reference herein in their entirety for all purposes as if fully set forth.

25 Unless otherwise defined, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this invention belongs. In case of conflict, the present specification, including definitions, will control.

Unless stated otherwise, all percentages, parts, ratios, etc., are by weight.

30 When an amount, concentration, or other value or parameter is given as either a range, preferred range or a list of upper preferable values and lower preferable values, this is to be understood as specifically disclosing all ranges formed from any pair of any upper range limit or preferred value and any lower range limit or preferred value, regardless of whether ranges are separately disclosed. For example, when a range of
35 "1 to 5" is recited, the recited range should be construed as including ranges "1 to 4", "1 to 3", "1-2", "1-2 & 4-5", "1-3 & 5", and the like. Where a range of numerical values is recited herein, unless otherwise stated, the range is intended to include the endpoints thereof, and all integers and fractions within the range.

When the term "about" is used in describing a value or an end-point of a range, the disclosure should be understood to include the specific value or end-point referred to.

Further, unless expressly stated to the contrary, "or" refers to an inclusive "or" and not to an exclusive "or". For example, a condition A "or" B is satisfied by any one of the following: A is true (or present) and B is false (or not present), A is false (or not present) and B is true (or present), and both A and B are true (or present).

Also, the indefinite articles "a" and "an" preceding an element or component of the invention are intended to be nonrestrictive regarding the number of instances (i.e. occurrences) of the element or component. Therefore, "a" or "an" should be read to include one or at least one, and the singular word form of the element or component also includes the plural unless the number is obviously meant to be singular.

The materials, methods, and examples herein are illustrative only and, except as specifically stated, are not intended to be limiting. Although methods and materials similar or equivalent to those described herein can be used in the practice or testing of the present invention, suitable methods and materials are described herein.

The invention is described in detail hereinafter.

As used herein, all concentration shall be expressed as percentages by weight unless otherwise specified.

Upon extensive experimentation, the inventors found that desirable effects were achieved using a two part epoxy adhesive comprising:

- a first part comprising 100 parts by weight of an epoxy resin containing two or more epoxy groups in one molecule; 0.03~3 parts by weight of a peroxide containing a -O-O- structure;
- and a second part comprising 110~120 parts by weight of a thiol curing agent, 0.05~5 parts by weight of an curing accelerator.

A preferred embodiment of the inventive adhesive comprises:

- a first part comprising 100 parts by weight of an epoxy resin containing two or more epoxy groups in one molecule; 0.2~2 parts by weight of a peroxide containing a -O-O- structure; 6~7 parts by weight of silane, and 4~5 parts by weight of thixotropic agent;
- and a second part comprising 113~118 parts by weight of a thiol curing agent, 0.2~5 parts by weight of an accelerator, and 12~16 parts by weight of filler.

In this invention, the epoxy resin containing two or more epoxy group in molecule, examples of the epoxy resins include polyhydric phenols, such as bisphenol A, halogenated bisphenol A, bisphenol F, halogenated bisphenol F, resorcinol,

hydroquinone, pyrocatechol, 4,4'-dihydroxybiphenyl and 1,5-hydroxynaphthalene, polyhydric alcohols, such as ethylene glycol, propylene glycol and glycerol, and epoxy resins obtained by the addition of epichlorohydrin to aromatic dicarboxylic acids such as oxybenzoic acid and phthalic acid, but the epoxy resins are not limited to these resins. Examples of commercially available epoxy resin products include Epon 828, 826, 862, 1001, 1002, 1071 (from Hexion Co. Ltd), DER 331, 332, 354, 671, 431, 731 (from Dow Chemical Co.Ltd), Epicoat 828, 1001, 801, 806, 807, 152, 604, 630, 871, YX8000, YX8034, YX4000 and Cardura E10P (from Japan Epoxy Resins Co., Ltd.), Epichlon 830, 835LV, HP4032D, 703, 720 and HP820 (from Dainippon Ink & Chemicals, Inc.), EP4100, EP4000, EP4080, EP4085, EP4088, EPU6, EPR4023, EPR1309 and EP49-20 (from ADEKA Corporation), Denachol EX411, EX314, EX201, EX212, EX252, EX111, EX146 and EX721 (from Nagase ChemteX Corporation), and KBM403 and KBE402 (from Shin-Etsu Chemical Co., Ltd.), but the epoxy resin products are not limited to these products. These resins can be used singly or can be used in combination of two or more kinds in arbitrary proportions.

The peroxide used in the invention has such structure as R1-O-O-R2, in which R1 and R2 are each independently selected from hydrogen atom, alkyl group of 1~10 carbon atoms and aromatic group including one or more phenyl group, and optionally there is a carbonyl group between R1, R2 and -O-O-. Examples of commercially available products include Benzoyl peroxide (CAS No. 94-36-0), TRIGONOX C-50D, TRIGONOX P-50S, PERKADOX L-50S, PERKADOX PD-50S (from Akzonobel Chemical Co. Ltd), tert-amylperoxy-3,5,5-trimethylhexanoate, tert-butylperoxyacetate, 1,1-di-(tert-butylperoxy)cyclohexane, 1,1-di-(tertbutylperoxy)-3,3,5-trimethylcyclohexane, methyl ethyl ketone peroxides, 2,5-dimethyl-2,5-di-(tert-butylperoxy)hexyne-3, tert-butyl-monoperoxymaleate. 3-chloroperoxybenzoic acid, dibenzoyl peroxide, di-4-chlorobenzoyl peroxide, 2,2-dihydroperoxypropane, 2,5-dimethyl-2,5-di-(benzoylperoxy)hexane, di-(2-phenoxyethyl) peroxydicarbonate, disuccinic acid peroxide, 3,3,6,6,9,9-hexamethyl-1,2,4,5-tetraoxacyclononane, 2,5-dimethyl-2,5-di-(benzoylperoxy)hexane, di-(2-phenoxyethyl) peroxydicarbonate, disuccinic acid peroxide, tert-amyl peroxybenzoate, n-butyl-4,4-di-(tert-butylperoxy)valera, tert-butyl hydroperoxide, di-tert-butylperoxide, tert-butyl-monoperoxymaleate, tert-butyl peroxyacetate, tert-butyl peroxybenzoate, tert-butylperoxy isopropylcarbonate, tert-butylperoxy-2-methylbenzoate, 1,1-di-(tert-amylperoxy)cyclohexane,

2,2-di-(tert-butylperoxy)butane, 1,1-di-(tert-butylperoxy)-3,3,5-trimethylcyclohexane,
 2,5-dimethyl-2,5-di-(tert-butylperoxy)hexyne-3-ethyl,
 3,3-di-(tert-butylperoxy)butylate, cyclohexanone peroxide,
 2,5-dimethyl-2,5-di(benzoylperoxy)hexane, 2,5-dimethyl-2,5-dihydroperoxyhexane
 5 acetyl acetone peroxide, acetyl benzoyl peroxide(from Aldrich chemical company).
 Suitable peroxides are not limited to these compounds. Preferably, in the peroxide
 R1-O-O-R2, there is a carbonyl group between R1, R2 and -O-O-. The peroxide was
 used as solution when preparing the inventive adhesives, and the used solvent
 includes ethyl acetate, acetone, chloroform and the like.

10 The reason for using silane in this invention is to increase the crosslink degree
 for cured compound and used as a coupling agents between fillers and resin
 substrates.

15 Optionally, the silane can be used in this invention, and these silane can be
 ended by amine, alkyl, or epoxy groups. Commercially products include KH550,
 KH560 (from Chinese Chemical Company), Glymo, Wetlink 78 (from Evonik),
 A-1106, A-1702, A-1002 (from Momentive Co.Ltd). The silane products are not
 limited to these products. These resins can be used singly or can be used in
 combination of two or more kinds in arbitrary proportions.

20 Optionally, thixotropic agent can be used in invention to control the thixotropic
 and viscosity properties of the adhesive, common used is fumed silica, the
 commercially products that can be used in invention include Cabosil TS-720, Cabosil
 M5 (from Cabot Company).

25 The curing accelerator can be a nucleophilic substance such as an amine, a
 tertiary phosphine, quaternary ammonium salt with a nucleophilic anion, a quaternary
 phosphonium salt with a nucleophilic anion, an imidazole, tertiary arsenium salt with
 a nucleophilic anion and a tertiary sulfonium salt with a nucleophilic anion. Possible
 30 amine catalysts include primary, secondary and tertiary amines. Various mixtures of
 catalysts can be used. Tertiary amine accelerator are preferred and are described, for
 examples: trimethylamine, triethylamine, tetraethylmethylenediamine,
 tetramethylpropane-1,3-diamine, tetramethylhexane-1,6-diamine,
 pentamethyldiethylenetriamine, pentamethyldipropylenetriamine,
 35 bis(2-dimethylaminoethyl)ether, ethylene glycol (3-dimethyl)aminopropyl ether,
 dimethylaminoethanol, dimethylaminoethoxyethanol,
 N,N,N'-trimethylaminoethylethanolamine, dimethylcyclohexylamine,

N,N-dimethylaminomethylphenol, N,N-dimethylpropylamine,
 N,N,N',N'-tetramethylhexamethylenediamine, N-methylpiperidine,
 N,N'-dimethylpiperazine, N,N-dimethylbenzylamine, dimethylaminomethylphenol,
 2,4,6-tris(dimethylaminomethyl)phenol, 1,8-diazabicycloundecene-7,
 5 1,5-diazabicyclo-nonene-5, 6-dibutylamino-1,8-diazabicycloundecene-7,
 1,2-dimethylimidazole, dimethylpiperazine,
 N-methyl-N'-(2-dimethylamino)-ethylpiperazine, N-methylmorpholine,
 N-(N',N'-(dimethylamino)ethyl)morpholine,
 N-methyl-N'-(2-hydroxyethyl)morpholine, triethylenediamine and
 10 hexamethylenetetramine. Of these, tertiary amines are preferable, and
 N,N-dimethylbenzylamine and 2,4,6-tris (dimethylaminomethyl) phenol are
 particularly preferable. These can be used singly or can be used in combination of two
 or more kinds in arbitrary proportions.

15 The thiol used in invention contains one or more R3-SH group in molecules, R3
 is an alkyl group includes 2~16 carbon atoms or aromatic group. Examples for the
 commercially products include Polythiol QE 340M, GMP 800 (CAS No. 100-53-8),
 Didodecanethiol (CAS No. 112-55-0), 1,3-dimercaptopropane (CAS No. 109-80-8),
 Capcure 3-800 (Cognis Chemical company).

20

Optionally, fillers can be used in the invention, and it is not specifically
 restricted. Examples for commonly used fillers include CaCO₃, SiO₂, BaSO₄, Al₂O₃,
 CaSiO₄.

25 The process for preparing the epoxy resin composition of the invention is not
 specifically restricted as long as the materials used can be mixed and dispersed, and
 for example, the following processes can be used.

(1) The components are mixed by a stirring rod, a spatula or the like in an
 appropriate container, such as a glass beaker, a can, a plastic cup or an aluminum cup.

30 (2) The components are mixed by a double helical ribbon impeller, a gate
 impeller or

(3) The components are mixed by a planetary mixer.

(4) The components are mixed by a bead mill.

(5) The components are mixed by a three-roll mill.

35 (6) The components are mixed by an extruder type kneading extrusion
 machine.

These preparation process can be used but the preparation process is not limited these process. These preparation processes can be used singly or can be used in combination of two or more process in preparing two components separately.

5 Tests

Gel Time Measurement

The gel time measurements were based on the standard ASTM D3532-99. The gel time is considered as the time when the viscosity of the adhesive increased to
10 twice time of the original compound.

Lap Shear Strength Measurement

The lap shear strength measurements were based on the testing standard ASTM D 3161. The substrates used are cold rolled steel, and the the bonding line is
15 10mm*25 mm. The surface of the substrates were washed by ethylacetate or actone. The data show in table 1 is the average value for at least 5 measurement data.

EXAMPLES

To illustrate the advantages of the inventive adhesives, different two-part
20 epoxy adhesives were prepared and tested in gel time measurements and lap shear strength measurements.

In the examples provided below, the following materials were used.

Trade names	Compound names or formulae	Suppliers
Epon828	Bis phenol A Epoxy resin	Hexio
Epon862	Bis phenol F Epoxy resin	Hexion
DER331	Bis phenol A Epoxy resin	DOW
DER671	Solid Bis phenol A Epoxy resin	DOW
YX8000	Hydrogenated Epoxy resin	JER
Perkadox L-50S	Dibenzoyl peroxide, paste 50% in silicone oil	Akzonobel
Trigonox P-50S	Acetyl benzoyl peroxide	Akzonobel
A1106	3-aminopropyltriethoxysilane aqueous solution	Momentive
Wetlink 78	Epoxy functional silane	Evonik
Glymo	Epoxy functional silane	Evonik
M5	Fumed silica	Cabot
TS-720	Fumed silica	Cabot

Polythiol QE340M	Polythiol	Akzonobel
Capcure 3-800	Difunctional thiol polymer	Akzonobel
GMP 800	Difunctional thiol polymer	Momentive
DMP-30	Tertiaryamine	Aldrich

Example 1~14: (Useful embodiment for the invention including the key performance principles)

The ingredients listed in Table 1 were combined to provide gel-time
 5 controllable epoxy based adhesives. Fixing other components in formulation, only
 varying the concentration of peroxide in the formulation, the gel time can be adjusted
 from 5min to more than 24h. The procedure for preparation of the first part as follows:
 peroxide was dissolved into acetone to form a solution with peroxide concentration
 0.12g/ml. Epoxy resin was weighed out in a speedmixer cup at room temperature and
 10 then peroxide solution was weighed out in the mixing container, mixing the two
 components under 2000rpm THINKY Speedmixer for 1min at room temperature. The
 silane and thixotropic agent were weighed out in the mixing container. The combined
 four components were mixed with 2000 rpm rate for 1 minute under room
 temperature and 0.2 kPa vacuum in THINKY Speedmixer. After mixing and taking
 15 out from speedmixer, the liquid mixture was dropped in to a one part of 2K cartridge.
 The procedure for preparation of the second part as follows: firstly, thiol used as
 curing agent was weighed out in a mixing container and then amine catalyst was
 weighed out in mixing container, mixing the two components under 2000rpm
 THINKY Speedmixer for 30 seconds at room temperature, and then fillers were
 20 weighed and added into the mixture. The combined three components were mixed
 with 2000 rpm rate for 1 minute under room temperature and 0.2 kPa vacuum in
 THINKY Speedmixer. After mixing and taking out from speedmixer, the liquid
 mixture was dropped in to another one part of 2K cartridge. Samples for gel time
 measurements or mechanical properties measurements were prepared by using a
 25 mechanical or air pressure adhesive gun to extrude the two parts out and mixing, then
 apply it onto substrates.

The gel time measurements were based on the standard ASTM D3532-99, and
 the results were listed in Table 1. From it we can find that the gel time will increase
 from 4.2 min to 24 hours by increasing the benzoyl peroxide from 0.03~2.99 weight%
 30 in formulations. The lap shear strength measurements were based on the testing
 standard ASTM D 3161, The used substrates are cold rolled steel. The measurement
 results were shown in Table 1. From it we can find that the addition of peroxide in the
 formulation will not have negative influence on the mechanical performance of the
 adhesives.

TABLE 1

Component s	Trade names	Suppliers	Ex.1	Ex.2	Ex.3	Ex.4	Ex.5	Ex.6	Ex.7	Ex.8	Ex.9	Ex.10	Ex.11	Ex.12	Ex.13	Ex.14
epoxy resin	Epon828	Hexio	100	100	100	100	100	100	100	100	100	100	100	100	100	100
peroxide	Benzoyl peroxide	Aldrich	0.03	0.3	0.58	1.04	1.35	1.58	1.90	2.34	2.68	1.82	2.14	2.48	2.99	2.79
silane	A1106	Momentiv e	5.2	5.2	5.2	5.2	5.2	5.2	5.2	5.2	5.2	5.2	5.2	5.2	5.2	5.2
thixotropic agent	TS-720	Cabot	4	4	4	4	4	4	4	4	4	4	4	4	4	4
thiol curing agent	Capcure 3-800	Cognis	112	112	112	112	112	112	112	112	112	112	112	112	112	112
Curing accelerator	Dimethyl benzoyl amine (DMBA)	Aldrich	4.33	4.36	4.41	4.48	4.53	4.57	4.62	4.68	4.73	2.28	2.3	2.33	2.36	0.23
fillers	CaCO ₃	Ankerpoo rt	18	18	18	18	18	18	18	18	18	18	18	18	18	18
Gel time			4.2 min	6.6 min	11.7 min	28.8 min	36.3 min	47.6 min	1.1 h	1.7 h	2.2 h	3.3 h	4.6 h	6.3h	9h	24 h
Lap shear substrates	strength on CRS		14.9 MP a	14.8 MPa	15.2 MPa	14.9 MPa	15.1 Mpa	14.6 MPa	14.2 MPa	14.7 MPa	14.5 MPa	15.2M Pa	14.8M Pa	14.2M Pa	15.0M Pa	14.2M Pa

* unit for ingredients is grams.

Example 15~35

The weight of components were listed in Table 2, and the procedure processes for examples 11~20 are similar as examples 1~10. The used peroxides including Perkadox L-50S, Trigonox P-50S were dissolved in acetone with a concentration of 0.12g/ml. In the first part, Epoxy resin was weighed out in a speedmixer cup at room temperature and then peroxide solution was weighed out in the mixing container, mixing the two components under 2000rpm THINKY Speedmixer for 1 min at room temperature. The silane and thixotropic agent were weighed out in the mixing container. The combined four components were mixed with 2000 rpm rate for 1 minute under room temperature and 0.2 kPa vacuum in THINKY Speedmixer. After mixing and taking out from speedmixer, the liquid mixture was dropped in to a one part of 2K cartridge. The procedure for preparation of the second part as follows: firstly, thiol used as curing agent was weighed out in a mixing container and then amine catalyst was weighed out in a mixing container, mixing the two components under 2000rpm THINKY Speedmixer for 30 seconds at room temperature. The fillers were weighed and added into the mixture, then the combined three components were mixed with 2000 rpm rate for 1 minute under room temperature and 0.2 kPa vacuum in THINKY Speedmixer. After mixing and taking out from speedmixer, the liquid mixture was dropped in to another one part of 2K cartridge.

TABLE 2

Components	Trade names	Suppliers	Ex. 15	Ex. 16	Ex. 17	Ex. 18	Ex. 19	Ex. 20	Ex. 21	Ex. 22	Ex. 23	Ex. 24	Ex.25	Ex. 26	Ex. 27	Ex. 28
epoxy resin	Epon828	Hexion				100					50	20	100			
	Epon862	Hexion	100		100					100		80		100	100	
	DER331	DOW		100				100	100		50					
	DER671	DOW					100									
	YX8000	JER														100
peroxide	Benzoyl peroxide	Aldrich			0.89		1.53		1.67	0.87	0.74		2.25			3
	Perkadox L-50S	Akzonobel	0.73	1.04				0.89				0.74		2.78	0.21	
	Trigonox P-50S	Akzonobel				1.13										
silane	A1106	Momentive	5	5	5	5							5	1		
	Wetlink 78	Evonik					5	6	7	8			2	5	2	
	Glymo	Evonik									6	6			3	5
thixotropic agent	M5	Cabot	3	3	3	3	3				6	6		4		5
	TS-720	Cabot						5	5	5			4		5	

thiol curing agent	Polythiol QE340M	Toray	115															
	Capcure 3-800	Cognis		115	100	100	115			113				112	90		115	112
	GMP 800	Lunqi			20			115							20	110		
	1,3-dimer captopropane	Aldrich				20					120							
tertiary amine	DMP-30	Aldrich	2.5	2.5					5						2.4			3.5
	Dimethyl benzoyl amine (DMBA)	Aldrich			1.2	0.5	0.3	4.8			1.6	1.8				2.9	4.1	
fillers	CaCO ₃	Ankerpoort	15		15			10	15							15		10
	SiO ₂	Ankerpoort		15		15	20				15	15	15				20	10
Gel time			37.2min	1.0 h	1.5 h	3.1 h	6 h	16.6 min	43.7min	1.2 h	52.2 min	39.6 min	3.8 h	3.2 h	9.4 min	6.1 h		

* unit for ingredients is grams.

TABLE 2 continued

Components	Trade names	Suppliers	Ex. 29	Ex. 30	Ex. 31	Ex. 32	Ex. 33	Ex. 34	Ex. 35
epoxy resin	Epon828	Hexion	100	100	100	100			
	Epon862	Hexion							
	DER331	DOW					100	100	100
	DER671	DOW							
	YX8000	JER							
peroxide	Benzoyl peroxide	Aldrich			0.03			3	2.5
	Perkadox L-50S	Akzonobel							
	Trigonox P-50S	Akzonobel				2			
silane	A1106	Momentive	5			5	5	5	
	Wetlink 78	Evonik		5	5				5
	Glymo	Evonik							
thixotropic agent	M5	Cabot	3		3	3	3	3	3
	TS-720	Cabot		3					

thiol curing agent	Polythiol QE340M	Toray								
	Capcure 3-800	Cognis	110	115	100	110				115
	GMP 800	Lunqi			20		110	110		
	1,3-dimer captopropane	Aldrich								
tertiary amine	DMP-30	Aldrich								
	Dimethyl benzoyl amine (DMBA)	Aldrich	2.2			2.13	0.05	4.9		5
fillers	CaCO ₃	Ankerpoort	15		15					
	SiO ₂	Ankerpoort		15		15		18	20	
Gel time			11.2min	72 h	120 h	4.5 h	4 h	3.3h		1.2h

*unit for ingredients is grams.

As is shown in the above test results, by introducing a peroxide into the two-part epoxy-thiol based adhesives, desirable control on gel time was achieved. Depending on the amounts of peroxide added, the gel times of the adhesive are adjustable in a wide range from 5min to more than 24h.

Using peroxide additive for delaying gel time in the epoxy-thiol curing systems is a total innovation and the effects are rather surprising. This finding together with the present invention will have a deep influence on design of the future epoxy-thiol based adhesives. For example, it can be used to design a series of specially products with different gel time for satisfying the requirements from customers.

While the invention has been illustrated and described in typical embodiments, it is not intended to be limited to the details shown, since various modifications and substitutions are possible without departing from the spirit of the present invention. As such, modifications and equivalents of the invention herein disclosed may occur to persons skilled in the art using no more than routine experimentation, and all such modifications and equivalents are believed to be within the spirit and scope of the invention as defined by the following claims.

CLAIMS

What is claimed is:

1. A two part epoxy adhesive, which includes
a first part comprising an epoxy resin containing two or more epoxy groups in one molecule, and a peroxide containing a -O-O- structure; and
a second part comprising a thiol curing agent and an curing accelerator.
2. The two part epoxy adhesive of claim 1, wherein the peroxide has a formula of R1-O-O-R2, wherein R1 and R2 are each independently selected from hydrogen atom, alkyl group of 1~10 carbon atoms and aromatic group including one or more phenyl group, and optionally there is a carbonyl group between R1, R2 and -O-O-.
3. The two part epoxy adhesive of claim 1 or 2, wherein the thiol curing agent containing one or more R3-SH group in one molecule, R3 is an alkyl group includes 2~16 carbon atoms or aromatic group.
4. The two part epoxy adhesive of anyone of claims 1-3, wherein the first part further comprises silane as a coupling agent.
5. The two part epoxy adhesive of anyone of claims 1-4, wherein the first part further comprises a thixotropic agent.
6. The two part epoxy adhesive of anyone of claims 1-5, wherein the second part further comprises filler.
7. The two part epoxy adhesive of claim 1, wherein
the first part comprises 100 parts by weight of an epoxy resin containing two or more epoxy groups in one molecule; 0.03~3 parts by weight of a peroxide containing a -O-O- structure;
and the second part comprises 110~120 parts by weight of a thiol curing agent, 0.05~5 parts by weight of an curing accelerator.
8. The two part epoxy adhesive of claim 7, wherein
the first part comprises 100 parts by weight of an epoxy resin containing two or more epoxy groups in one molecule; 0.2~2 parts by weight of a peroxide containing a -O-O- structure; 6~7 parts by weight of silane, and 4~5 parts by weight of thixotropic agent;
and the second part comprises 113~118 parts by weight of a thiol curing agent, 0.2~5 parts by weight of an accelerator, and 12~16 parts by weight of filler.
9. The two part epoxy adhesive of claim 7 or 8, wherein the peroxide has a formula of R1-O-O-R2, wherein R1 and R2 are each independently selected from hydrogen atom, alkyl group of 1~10 carbon atoms and aromatic group including one or more phenyl group, and optionally there is a carbonyl group between R1, R2 and -O-O-.

10. The two part epoxy adhesive of any one of claims 7-9, wherein the thiol curing agent containing one or more R3-SH group in one molecule, R3 is an alkyl group includes 2~16 carbon atoms or aromatic group.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2011/080626

A. CLASSIFICATION OF SUBJECT MATTER

See the extra sheet

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC: C09J163/-; C08G 59/-; C08L63/-

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

CNKI, CNPAT, WPI, EPODOC, epoxy adhesive?, epoxy binder?, epoxy resin?, thiol, mercapto, peroxide, hydroperoxide, organoperoxide, organo peroxide, initiator?, two part?, two component?, accelerator?, catalyst?, accelerating agent, curing agent?, crosslinking agent?, crosslinker?, hardening agent?, hardener?, Henkel

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	CN 1993399 A (SHOWA DENKO KK) 04 Jul. 2007 (04.07.2007), see its claims 1-4 and 8, lines 19-20 page 4, lines 10-20 page 7 and lines 17-20 page 12 of its description	1-10
Y	CN 101698787 A (ZHENJIANG ELECTROCHEMICAL MATERIAL ENG RES CENT) 28 Apr. 2010 (28.04.2010), see its claim 1	1-10
A	US 2005/0143496 A1 (HENKEL KGAA) 30 Jun. 2005 (30.06.2005), see the whole document	1-10
A	JP 2003-231736 A (NAGASE CIBA KK) 19 Aug. 2003 (19.08.2003), see the whole document	1-10

☐ Further documents are listed in the continuation of Box C.☒ See patent family annex.

* Special categories of cited documents:	“T” later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
“A” document defining the general state of the art which is not considered to be of particular relevance	“X” document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
“E” earlier application or patent but published on or after the international filing date	“Y” document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
“L” document which may throw doubts on priority claim (S) or which is cited to establish the publication date of another citation or other special reason (as specified)	“&” document member of the same patent family
“O” document referring to an oral disclosure, use, exhibition or other means	
“P” document published prior to the international filing date but later than the priority date claimed	

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06 Jul. 2012 (06.07.2012)

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/CN2011/080626

Patent Documents referred in the Report	Publication Date	Patent Family	Publication Date
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		JP 2006045406 A	16.02.2006
		JP 4707981 B2	22.06.2011
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US 2005/0143496 A1	30.06.2005	EP 1541610 A	15.06.2005
		DE 10357355 A	14.07.2005
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INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2011/080626

Continuation of A CLASSIFICATION OF SUBJECT MATTER in the second sheet:

C09J 163/00 (2006.01) i

C09J 11/04 (2006.01) i

According to International Patent Classification (IPC) or to both national classification and IPC: