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(54) **Title:** A LATENT CURING ACCELERATOR COMPOSITION AND A ONE-PART CURABLE ADHESIVE COMPOSITION COMPRISING THE SAME

(57) **Abstract:** A latent curing accelerator composition, comprising: an aromatic polyisocyanate, a chain extender, a chain stopper, and a non-latent curing accelerator having at least one tertiary amine group. In particular, a one-part epoxy-thiol adhesive composition has improved curing performance and improved storage stability.



A latent curing accelerator composition and a one-part curable adhesive composition comprising the same

Technical Field

The present invention relates to a latent curing accelerator composition and a one-part curable adhesive composition. In particular, the present invention relates to a one-part epoxy-thiol adhesive composition having improved curing performance and improved storage stability.

Background

Curable epoxy-based compositions are well known. Such compositions are used as adhesives, coating agents, sealing agents and may also be used as casting agents. Epoxy-based compositions are also used in the electronics industry for the fabrication of heat resistant printed circuit laminates for printed circuit boards (PCBs). One use of curable epoxy compositions is to bond surface mount components to PCBs.

Epoxy/polythiol-containing compositions conventionally have been used as two-part compositions. This was due at least in part to the instability of a one-part composition, having an epoxy resin and a polythiol component and a liquid (soluble) tertiary amine curing agent or hardener. One-part compositions of this sort where the epoxy resin-polythiol and the curing agent or hardener were admixed at room temperature had working or “pot” lives on the order of minutes to a few hours. Such short “pot lives” are undesirable as they impose practical restrictions on end-use applications of such compositions. Accordingly, many traditional epoxy/polythiol compositions have been formulated as two-part compositions.

Commercially available latent curing agents used in one-part epoxy resin adhesive formulations ordinarily provide such formulations with a combination of good storage stability and moderate reactivity at elevated temperatures. Examples of such commercially available latent curing agents include dicyandiamide and dibasic

acid dihydrazide. These curing agents are useful in formulating epoxy resin compositions with excellent storage stability. However to achieve cure, these curing agents ordinarily require heating to temperatures greater than 150°C for extended periods of time.

U.S. Pat. No. 5,430,112 (Sakata) discloses epoxy resin/polythiol compositions which are reported to display enhanced stability, i.e. an extended pot life, if (a) a solid dispersion-type amine adduct latent curing accelerator composition, or (b) the product of a reaction between a compound which contains one or more isocyanate groups in its molecule and a compound which has two or more primary and/or secondary amino groups in its molecule, is used. The compounds (a) and (b) above are each reported to act as a "latent hardener", being activatable at higher temperatures. In particular, the composition disclosed in the '112 patent contains (1) an epoxy resin which has two or more epoxy groups in its molecule, (2) a polythiol compound which has two or more thiol groups in its molecule and (3) an accelerator which is (a) a solid dispersion-type amine adduct latent curing accelerator composition, or (b) the product of a reaction between a compound which contains one or more isocyanate groups in its molecule and a compound which has at least one primary and/or secondary amino groups in its molecule. Examples given of commercially available solid dispersion-type amine adduct latent curing accelerator compositions are those sold under the trade names Ajicure PN-H or Ajicure PN-23 (commercially available from Ajinomoto Co., Inc., Tokyo, Japan). The compositions containing these amine adduct latent curing accelerator compositions show improved room temperature stability over conventional formulations based on liquid or soluble tertiary amine curing agents. However, in practice such compositions with a pot life of in excess of 1 week at room temperature, show a poor ability to cure, i.e. their ability to cure in less than 30 mins at 80°C is poor.

The stability of an epoxy resin/polythiol composition of the '112 patent is reported to be improved by the use of a solid dispersion-type amine adduct latent curing accelerator composition and/or the product of a reaction between an isocyanate and an amine containing group, though compositions containing Ajicure PN-23 are

not described. However, improved stability, for at least the commercially available Ajicure PN-H, is achieved at the expense of gel time, i.e. greater stability is achieved only with an undesirable effect of increase in gel time.

The '112 patent also describes the use of liquid or solid organic or inorganic acids for surface treating the latent hardener (the amine adduct) and for use in making the latent hardener. The treatment of the hardener with an acid is designed to neutralise active basic materials on the surface of the hardener particles as the hardener is ordinarily in a solid state. The organic or inorganic acid is often in a liquid state or in a solution to allow for the surface treatment, or for making the latent hardener.

U.S. Pat. No. 6,872,762 describes epoxy/polythiol compositions comprising (a) an epoxy compound which has two or more epoxy groups per molecule, (b) a polythiol compound which has two or more thiol groups per molecule, (c) a latent hardener, and (d) at least one solid organic acid which is substantially insoluble in a mixture of (a), (b) and (c) above, at room temperature. The composition described is used to bond surface mount devices to the surface of a PCB.

Notwithstanding state-of-the-art compositions, there is a need for a latent curing accelerator composition which is stable at room temperature, becomes active at relatively lower curing temperature, and in turn contributes to an improved, more ready-to-use adhesive composition, especially epoxy-polythiol composition. It would be desirable to provide adhesive compositions with improved rheological properties such as improved storage stability, particularly with respect to viscosity maintenance over time.

Summary of the Invention

To achieve the above objects, one aspect of the present invention is a latent curing accelerator composition, comprising:

- (a) an aromatic polyisocyanate,
- (b) a chain extender,
- (c) a chain stopper, and

- (d) a non-latent curing accelerator having at least one tertiary amine group.

Another aspect of the present invention is a one-part curable adhesive composition, comprising:

- (A) an epoxy resin,
- (B) a compound having at least one group reactive towards the epoxy resin, in particular a polythiol compound,
- (C) the latent curing accelerator according to the present invention or prepared by the method according to the present invention,
- (D) optionally an impact modifier and/or a toughener, and
- (E) optionally a filler.

Yet another aspect of the present invention is a method of bonding substrates together which comprises applying the one-part curable adhesive composition according to the present invention to a first substrate, bringing a second substrate in contact with the adhesive composition applied to the first substrate, and subjecting the applied composition to conditions which allow the applied composition to be cured.

Yet another aspect of the present invention is a cured product of the one-part curable adhesive composition according to the present invention or prepared by the method of bonding substrates together according to the present invention.

Yet, another aspect is the use of the one-part curable adhesive composition according to the present invention or the cured product according to the present invention in bonding substrates together.

Other features and aspects of the subject matter are set forth in greater detail below.

Detailed Description

It is to be understood by one of ordinary skill in the art that the present discussion is

a description of exemplary embodiments only, and is not intended as limiting the broader aspects of the present invention.

Herein, "comprising" means that other steps and other components which do not affect the end result can be added. This term encompasses the terms "consisting of" and "consisting essentially of".

The term "aliphatic" as used herein refers to C₁-C₄₀, suitably C₁-C₃₀ straight or branched chain alkenyl, alkyl, or alkynyl which may or may not be interrupted or substituted by one or more heteroatoms such as O, N or S.

The term "aromatic" refers to C₃-C₄₀ suitably C₃-C₃₀ aromatic groups including heterocyclic aromatic groups containing one or more of the heteroatoms, O, N, or S, and fused ring systems containing one or more of these aromatic groups fused together.

The term "derivatives" refers to substitutions at one or more positions (including directly on a heteroatom) with one or more of the following:

C₁-C₂₀ alkoxy, C₁-C₂₀ alkyl, C₂-C₂₀ alkenyl, a carbonyl group, a thiocarbonyl group such as a -C=S group, a carboxylic group, a C₁-C₄ alkyl group further containing up to three N atoms, phenyl, C₁-C₄ alkylphenyl, or C₂-C₄ alkenylphenyl; OR, NR, SR, or SSR, where R is phenyl, an aliphatic, cycloaliphatic or aromatic group, each of which may be optionally further substituted in any position with one or more, of C₁-C₄ alkyl, OH, halogen (F, Br, Cl, or I), phenyl, a C₁-C₄ alkylphenyl, a C₂-C₄ alkenylphenyl, or OR, where R is phenyl, a carboxylic group, carbonyl, or an aromatic group and R is optionally substituted with C₁-C₄ alkyl, OH, or halogen; or nitro, nitrile, or halogen.

Latent curing accelerator composition

In one aspect, the present disclosure is generally directed to a latent curing accelerator composition, comprising:

- (a) an aromatic polyisocyanate,

- (b) a chain extender,
- (c) a chain stopper, and
- (d) a non-latent curing accelerator having at least one tertiary amine group.

In another aspect, the present disclosure relates to a latent curing accelerator produced by the latent curing accelerator composition according to the present invention.

The inventor has surprisingly found that the latent curing accelerator, produced by the latent curing accelerator composition according to the present invention, contributes to a one-part curable adhesive composition possesses an excellent storage stability under room temperature and a relatively low curing temperature as well as other curing performance.

Without wishing to be bound by any theory, it is believed that the aromatic polyisocyanate comprised in the latent curing accelerator composition reacts with the chain extender at room temperature and preferably forms polyurea compounds having suitable molecule weight and density in the presence of the chain stopper. The significant amount of N-H bonds on the polyurea compounds interacts with the tertiary amine groups on the non-latent curing accelerator. Therefore, the non-latent curing accelerator is stabilized and inactive in the latent curing accelerator composition under room temperature and renders active when the adhesive composition containing the latent curing accelerator is heated to suitable curing temperature.

It is understood by a person skilled in the art that the latent curing accelerator composition itself is not a ready to use adhesive. To have the properties of an adhesive the latent curing accelerator composition or the so produced latent curing accelerator has to be incorporated into an adhesive composition containing a reactive system being able to be activated by this latent curing accelerator, like an epoxy system, as described in detail further below. In this context it is preferred that the latent curing accelerator composition of the present invention is substantially

free of epoxides. Preferably the latent curing accelerator composition consist only of the components (a) to (d) and optionally a solvent. The term "substantially free" means that the improved curable composition of the present invention comprises less than 1 wt.-%, preferably less than 0.1 wt.-%, more preferably less than 0.01 wt.-%, and particularly preferably less than 0.001 wt.-% of these compounds, each based on the total amount of the curable composition.

Aromatic polyisocyanate

The latent curing accelerator composition of the present invention comprises an aromatic polyisocyanate as isocyanate compound containing at least two isocyanate groups linked to aromatic rings, such as benzene ring, naphthalene ring, etc. Examples of the aromatic polyisocyanate are tolylene diisocyanates such as tolylene 2,4-diisocyanate, tolylene 2,6-diisocyanate, diphenylmethane 4,4'-diisocyanate, diphenylmethane 2,4'-diisocyanate, diphenylmethane 2,2'-diisocyanate, 4,4'-diisocyanato-1,2-diphenylethane, triisocyanatotoluene, phenylene 1,3-diisocyanate, phenylene 1,4-diisocyanate, toluene diisocyanate, biphenyl diisocyanate, 4,4'-diphenylmethane diisocyanate, 2,2-diphenylpropane-4,4'-diisocyanate, xylylene diisocyanate, 1,4-naphthylene diisocyanate, 1,5-naphthylene diisocyanate, m-phenylene diisocyanate, p-phenylene diisocyanate, diphenyl-4,4'-diisocyanate, azobenzene-4,4'-diisocyanate, diphenylsulphone-4,4'-diisocyanate, 2,4-toluene diisocyanate, 4,4',4''-triisocyanatotriphenylmethane, 1,3,5-triisocyanato-benzene, 2,4,6-triisocyanato-toluene, 4,4'-dimethyldiphenyl-methane-2,2',5,5-tetraisocyanate, the derivatives thereof, and combination thereof.

Preferably, the aromatic polyisocyanate is selected from the group consisting of tolylene 2,4-diisocyanate, tolylene 2,6-diisocyanate, diphenylmethane 4,4'-diisocyanate, diphenylmethane 2,4'-diisocyanate, diphenylmethane 2,2'-diisocyanate, and combination thereof.

The aromatic polyisocyanate comprised in the latent curing accelerator composition is present in an amount of 35% to 90%, preferably 40% to 80%, more preferably

50% to 75% by weight, based on the total weight of the components (a) to (d) of the latent curing accelerator composition.

If the amount of the aromatic polyisocyanate is too low, the latent curing accelerator composition cannot form enough polyurea compounds to well stabilize the non-latent curing accelerator.

If the amount of the aromatic polyisocyanate is too high, the amount of the non-latent curing accelerator is not enough for curing the adhesive composition.

Although it is not preferred, the latent curing accelerator composition of the present invention may also contain less than 10% by weight, preferably less than 5%, more preferably less than 1% by weight of an aliphatic polyisocyanate, such as ethylene diisocyanate, ethylidene diisocyanate, propylene diisocyanate, butylene diisocyanate, trimethylene diisocyanate, hexamethylene diisocyanate.

If the amount of aliphatic polyisocyanate is too large, the storage stability of the one-part curable adhesive composition comprising the latent curing accelerator composition may be comprised.

In one preferred embodiment, the latent curing accelerator composition of the present invention is substantially free of aliphatic polyisocyanate, preferably contains no aliphatic polyisocyanate.

Chain extender

The latent curing accelerator composition of the present invention also comprises a chain extender to react with aromatic polyisocyanate under an elevated temperature and form preferred polyurea compounds.

The chain extender contains at least two active hydrogen-containing groups per molecule, and is preferably selected from the group consisting of water, a polyamine having at least two primary amino groups, and the combination thereof.

According to the present invention, the polyamine having at least two primary amino groups preferably further contains an additional acid group. The examples of such polyamine are amino acids selected from the group consisting of lysine, arginine, glutamine, ornithine and the combination thereof.

In the latent curing accelerator composition according to the present invention, the chain extender is preferably present in an amount of 0.5% to 35%, preferably 1% to 30%, more preferably 2% to 25% by weight, based on the total weight of components (a) to (d) of the latent curing accelerator composition.

If the amount of the chain extender is too low, the storage stability of the adhesive composition might be negatively influenced since a polyurea polymer with a sufficiently high molecular weight fails to form.

If the amount of the chain extender is too large, the formed polyurea polymer might have overly large molecular weight and thus the accelerating capacity will be decreased.

Chain stopper

The latent curing accelerator composition of the present invention also comprises a chain stopper to terminate the polymerization of the polyurea polymer and keep the molecular weight of the polyurea polymer in a suitable range.

According to the present invention, the chain stopper contains one active hydrogen-containing group per molecule, and is preferably selected from the group consisting of monohydric alcohol, monohydric phenol, monohydric secondary amine, monohydric thiol, monohydric carboxylic acid, and the combination thereof. Preferably, the chain stopper is a monohydric alcohol, and more preferably is ethanol.

In the latent curing accelerator composition according to the present invention, the

chain stopper is preferably present in an amount of 1% to 20%, preferably 3% to 18%, more preferably 4% to 15% by weight, based on the total weight of components (a) to (d) of the latent curing accelerator composition.

If the amount of the chain stopper is too low, the polymerization of the polyurea compounds may not be terminated efficiently, resulting in an overly high molecular weight of reaction product which decrease the accelerating capacity of the latent curing accelerator.

Non-latent curing accelerator

The latent curing accelerator composition according to the present invention also contains a non-latent curing accelerator having at least one tertiary amine group.

In one embodiment, the non-latent curing accelerator having at least one tertiary amine group is preferably selected from the group consisting of trimethylamine, triethylamine, tetraethylmethylenediamine, benzyldimethylamine, N,N'-dimethylpiperazine, tetramethyl-1,3-diaminopropane, N,N,N',N'-tetramethyl-1,6-hexanediamine, pentamethyldiethylenetriamine, 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-methyl-N'-(2-dimethylamino)-ethylpiperazine, N-methylmorpholine, N-(N',N'-(dimethylamino)ethyl)morpholine, N-methyl-N'-(2-hydroxyethyl)morpholine, N,N-dimethylbenzylamine, dimethylaminomethylphenol, tris(dimethylaminomethyl)phenol (DMP-30), triethylenediamine, 1,4-diazabicyclo[2.2.2]octane (DABCO), hexamethylenetetramine, 1,8-diazabicyclo (5,4,0)-undecene-7 (DBU), 1,5-diazabicyclo (4,3,0)-nonene-5 (DBN), imidazole, 1-methylimidazole, 1-vinylimidazole, 2-methylimidazole, 2-ethylimidazole, 2-ethyl-4-methylimidazole, 2-undecylimidazole, 2-heptadecylimidazole,

2-phenylimidazole, 2,4-dimethylimidazoline, 2-ethyl-4-methylimidazoline, and the combination thereof.

Preferably, the non-latent curing accelerator having at least one tertiary amine group is selected from the group consisting of tris(dimethylaminomethyl)phenol, triethylenediamine, hexamethylenetetramine, 1,4-diazabicyclo[2.2.2]octane, 1,8-diazabicyclo (5,4,0)-undecene-7, 1,5-diazabicyclo (4,3,0)-nonene-5, 2-ethyl-4-methylimidazole, 2-ethyl-4-methylimidazoline, triethylenediamine, and combination thereof.

In the latent curing accelerator composition according to the present invention, the non-latent curing accelerator having at least one tertiary amine group is preferably present in an amount of 1% to 50%, preferably 3% to 45%, more preferably 5% to 40% by weight, based on the total weight of components (a) to (d) of the latent curing accelerator composition.

If the amount of the non-latent curing accelerator is too low, the accelerating capacity of the latent curing accelerator may be decreased.

If the amount of the non-latent curing accelerator is too large, a polyurea polymer having a sufficiently high molecular weight may not be achieved.

Solvent

The latent curing accelerator composition according to the present invention may optionally contain a solvent.

Suitable examples of the solvent are esters such as ethyl acetate, n-butyl acetate, and n-pentyl-acetate; ketones such as acetone, methyl ethyl ketone (MEK), and methyl isobutyl ketone; chlorinated hydrocarbons such as dichloromethane, chloroform, 1,2-dichloroethane; and the combination.

Preferably, ketones such as acetone, methyl ethyl ketone, and methyl isobutyl

ketone are suitable as the solvent used in the latent curing accelerator composition.

If present, the weight ratio of the solvent to total weight of the other components contained in the latent curing accelerator composition is in the range of 1:1 to 40:1, preferably 5:1 to 30:1, more preferably 10:1 to 20:1.

In one preferred embodiment, the latent curing accelerator composition according to the present invention comprises:

- (a) 40% to 80%, preferably 50% to 75% by weight of an aromatic polyisocyanate,
- (b) 1% to 30%, preferably 2% to 25% by weight of a chain extender,
- (c) 3% to 18%, preferably 4% to 15% by weight of a chain stopper, and
- (d) 3% to 45%, preferably 5% to 40% by weight of a non-latent curing accelerator having at least one tertiary amine group,

in which the weight percentages are based on the total weight of components (a) to (d) of the latent curing accelerator composition.

In another preferred embodiment, the latent curing accelerator composition according to the present invention consists of:

- (a) 40% to 80%, preferably 50% to 75% by weight of an aromatic polyisocyanate,
- (b) 1% to 30%, preferably 2% to 25% by weight of a chain extender,
- (c) 3% to 18%, preferably 4% to 15% by weight of a chain stopper, and
- (d) 3% to 45%, preferably 5% to 40% by weight of a non-latent curing accelerator having at least one tertiary amine group, in which the weight percentages are based on the total weight of components (a) to (d) of the latent curing accelerator composition.
- (e) optionally a solvent, preferably in a range of 1:1 to 40:1, preferably 5:1 to 30:1, more preferably 10:1 to 20:1 based on a weight ratio of the solvent to total weight of the components (a) to (d).

In another aspect, the present invention relates to a latent curing accelerator

produced by the latent curing accelerator composition.

In yet another aspect, the present invention relates to method for preparing a latent curing accelerator, comprising:

- (1) reacting an aromatic polyisocyanate with a chain stopper at 25 to 80 ° C for 1 to 8 hours, and obtaining a mixture;
- (2) adding a chain extender to the mixture of step (1), and keeping the reaction at room temperature for 0.5 to 12 hours, and obtaining a mixture; and
- (3) adding a non-latent curing accelerator having at least one tertiary amine group to the mixture of step (2), and keeping the reaction under room temperature for 0.5 to 5 hours, and obtaining a latent curing accelerator.

One-part curable adhesive composition

In another aspect, the present invention is directed to a one-part curable adhesive composition comprising:

- (A) an epoxy resin,
- (B) a compound having at least one group reactive towards the epoxy resin,
- (C) the latent curing accelerator according to the present invention or prepared by the method according to the present invention,
- (D) optionally an impact modifier and/or a toughener, and
- (E) optionally a filler.

Epoxy resin

According to the present invention, the one-part curable adhesive composition contains at least one epoxy resin having preferably at least two or more glycidyl groups in one molecule. Preferably the epoxy resin is a non-toughened epoxy resin (A1).

The term “non-toughened epoxy resin” as used herein, refers generally to an epoxy resin, which does not undergo a toughening treatment, either physically or chemically. The “non-toughened epoxy resin” is thus different to the “toughened epoxy resin” also used in the present invention. Toughened epoxy resins refers to

those have undergone a toughening treatment. As an example, they can be modified by core-shell rubber particles or a carboxyl-terminated butadiene nitrile polymer.

The non-toughened epoxy resin used in the present invention includes non-toughened difunctional epoxy resin and non-toughened multifunctional epoxy resin, for example non-toughened trifunctional or tetrafunctional epoxy resin.

The non-toughened difunctional epoxy resin to be used in the present invention is selected from bisphenol A based diglycidyl ethers, bisphenol F based diglycidyl ethers, bisphenol S based diglycidyl ethers, bisphenol Z based diglycidyl ethers, N,N,O-triglycidyl-m-aminophenol, N,N,O-triglycidyl-p-aminophenol, fluoroglycinol triglycidyl ether, trihydroxybiphenyl triglycidyl ether, triglycidylaminophenol, tetraglycidyl-diaminodiphenylmethane, tetraglycidyl-m-xylenediamine, tetraglycidylbis(aminomethylcyclohexane), tetraglycidylbenzophenone, bisresorcinol tetraglycidyl ether, tetraglycidyl ether of methylene dianiline, halides thereof and hydrides thereof, and combination thereof.

Examples of commercially available products of non-toughened difunctional epoxy resin include Epon 828, Epon 826, Epon 862, Epon 1001, Epon 1002, Epon 1071 (all from Hexion Co., Ltd.), DER 330, DER 331, DER 383, DER 332, DER 330-EL, DER 331-EL, DER 354, DER 321, DER 324, DER 29, DER 353 (all from Dow Chemical Co., Ltd.), JER YX8000, JER RXE21, JER YL 6753, JER YL6800, JER YL980, JER 825, JER 630 (all from Japan Epoxy Resins Co., Ltd.), EP 4300E, EP 4901, EP 4901E, EP 4100HF, EP 490HF, EP 4088S, EP 4000S, EP 4080E, EP4080 (all from ADEKA Corporation), Epichlon 830, Epichlon 830S, Epichlon 835, Epichlon E830CRP, Epichlon E830LVP, Epichlon E835LV (all from DIC Corporation).

The non-toughened trifunctional epoxy resin, suitable to be used in the present invention is a triglycidyl ether or triglycidyl amine, preferably triglycidyl amine, selected from the group consisting of N,N,O-triglycidyl-m-aminophenol,

N,N,O-triglycidyl-p-aminophenol, fluoroglycinol triglycidyl ether, trihydroxybiphenyl triglycidyl ether, triglycidylaminophenol, and combination thereof.

The non-toughened epoxy resin having four glycidyl groups in one molecule suitable to be used in the present invention is a tetraglycidyl ether or tetraglycidyl amine, preferably tetraglycidyl amine. Suitable examples of tetraglycidyl amines are tetraglycidyl-diaminodiphenylmethane, tetraglycidyl-m-xylenediamine, tetraglycidylbis(aminomethylcyclohexane), tetraglycidylbenzophenone, bisresorcinol tetraglycidyl ether, tetraglycidyl ether of methylene dianiline, which may be used individually or as a combination of two or more of them.

Examples of suitable commercially available non-toughened multifunctional epoxy resins include LY 5056, MY 720, MY 721, XB 9721, MY 9512, MY 9612, MY 9634, MY 9655, MY 9663 (all from Huntsman Corporation), AG 80 (from Shanghai Institute of Organic Synthesis), and Jeh 011 (from Changshu Jiafa Chemical Company).

Preferably, the non-toughened epoxy resin is selected from the group consisting of bisphenol A based diglycidyl ethers, bisphenol F based diglycidyl ethers, and combination thereof.

The non-toughened epoxy resin is preferably present in an amount of 5% to 60%, preferably 10% to 50%, more preferably 15 to 40% by weight, based on the total weight of all components (A) to (E) of the one-part curable adhesive composition.

If the amount of the non-toughened epoxy resin is too low, the curing with polythiol may not be enough.

If the amount of the non-toughened epoxy resin is too large, the uncured resin may disperse in the cured product, which will decrease the properties, such as the tensile strength and modulus of the cured product. In addition, the curability of the adhesive composition may be negatively influenced.

In one preferred embodiment the one-part curable adhesive composition according to the present invention preferably also comprises a toughened epoxy resin (A2), preferably an epoxy resin having two or more glycidyl groups modified by core-shell rubber particles or a carboxyl-terminated butadiene nitrile polymer.

As used herein, the term “toughened epoxy resin” refers to an epoxy resin, which undergoes toughening modification or treatment by a toughening agent based on either physical or chemical mechanism and is used in the adhesive composition according to the present invention. For example, the toughening agent may be physically pre-dispersed in the epoxy resin matrix. The toughening agent may be reactive and capable of reacting substantially completely to form chemical bonds to the epoxy resin matrix.

Suitable examples of the epoxy resin having two or more glycidyl groups used for the toughened epoxy resin are the di-, tri-, or tetra-functional epoxy resins described as above, preferably the difunctional epoxy resins, for example bisphenol A based diglycidyl ethers and bisphenol F based diglycidyl ethers.

Core-shell rubber (CSR) particles are incorporated in the toughened epoxy resin to act as toughening agent, which allow for the toughening of the epoxy resin, and in turn the one-part curable adhesive upon curing. The particles may have an average particle size of from 10 nm to 300 nm, preferably from 50 nm to 200 nm. The particle size as used herein refers to the particle diameter or the largest dimension of a particle in a distribution of particles as determined by laser light scattering such that 50% by weight of the particles in the distribution are smaller than the particle and 50% by weight of the particles in the distribution are larger than the particle. The particle size was measured via dynamic light scattering using a Horiba LA-910 or LA-920 particle size distribution analyzer per manufacturer's recommendations.

Preferably, two types of particles with different particle size are used in the composition. The smaller particles may have an average particle size of less than or equal to 100 nm, preferably from 50 to 90 nm and the larger particles may have

an average size of greater than 100 nm, preferably from 150 to 300 nm. The weight ratio of smaller CSR particles to larger CSR particles may be in the range of 3:1 to 5:1. By having different particle sizes, the balance of the key properties such as shear strength, peel strength, and resin fracture toughness can be well controlled.

The core-shell rubber particles may have a soft core comprised of a polymeric material having elastomeric or rubbery properties (i.e., a glass transition temperature less than about 0° C, e.g., less than about -30° C) surrounded by a hard shell comprised of a non-elastomeric polymeric material (i.e., a thermoplastic or thermoset/crosslinked polymer having a glass transition temperature greater than ambient temperatures, e.g. greater than about 50° C). For example, the core may be comprised of, for example, a diene homopolymer or copolymer (for example, a homopolymer of butadiene or isoprene, a copolymer of butadiene or isoprene with one or more ethylenically unsaturated monomers such as vinyl aromatic monomers, (meth)acrylonitrile, (meth)acrylates, or the like) while the shell may be comprised of a polymer or copolymer of one or more monomers such as (meth)acrylates (e.g., methyl methacrylate), vinyl aromatic monomers (e.g., styrene), vinyl cyanides (e.g., acrylonitrile), unsaturated acids and anhydrides (e.g., acrylic acid), (meth)acrylamides, and the like having a suitably high glass transition temperature. The polymer or copolymer used in the shell may have acid groups that are crosslinked ionically through metal carboxylate formation (e.g., by forming salts of divalent metal cations). The shell polymer or copolymer may also be covalently crosslinked by monomers having two or more double bonds per molecule. Other elastomeric polymers may also be suitably be used for the core, including polybutylacrylate or polysiloxane elastomer (e.g., polydimethylsiloxane, particularly crosslinked polydimethylsiloxane). The particle may be comprised of more than two layers (e.g., a central core of one elastomeric material may be surrounded by a second core of a different elastomeric material or the core may be surrounded by two shells of different composition or the particle may have the structure of soft core/hard shell/soft shell/hard shell). Typically, the core comprises from about 50 to about 95 percent by weight of the particle while the shell comprises from about 5 to about 50 percent by weight of the particle.

The core-shell rubber particles may be pre-dispersed in a liquid resin matrix system such as those available from Kaneka Corporation under the trademarks Kane Ace MX.

In addition, elastomeric polymers with epoxy functional groups are also particularly suitable for the use in the present invention as the toughened epoxy resin. Specific examples include epoxy-elastomer adduct formed by reacting epoxy resin with carboxyl-terminated butadiene nitrile (CTBN) elastomer (formed for example from the reaction of the bisphenol A based diglycidyl ether and a carboxyl-terminated butadiene-acrylonitrile elastomer).

Suitable commercial examples of the toughened epoxy resins include MX 120 (liquid Bisphenol A epoxy with about 25 wt% CSR), MX 125 (liquid Bisphenol A epoxy with about 25 wt% CSR), MX 153 (liquid Bisphenol A epoxy with about 33 wt% CSR), MX 156 (liquid Bisphenol A epoxy with about 25 wt% CSR), MX 130 (liquid Bisphenol F epoxy with about 25 wt% CSR), MX 136 (liquid Bisphenol F epoxy with about 25 wt% CSR), MX 257 (liquid Bisphenol A epoxy with about 37 wt% CSR), MX 416 and MX 451 (liquid multifunctional epoxy with about 25 wt% CSR), MX 215 (Epoxidized Phenol Novolac with about 25 wt% CSR), and MX 551 (cycloaliphatic epoxy with about 25 wt% CSR), all from Kaneka Corporation, Albidur 2240A (reactive organosiloxane particles dispersed in bisphenol A glycidyl ether), Albidur 5340A (reactive organosiloxane particles dispersed in cycloaliphatic epoxide), and Albidur 5640, all from Evonik Corporation, Struktol 3652, Struktol 3619, Struktol 3614 (about 60 percent bisphenol A based diglycidyl ethers and about 40 percent CTBN type acrylonitrile-butadiene-rubber containing about 26 percent acrylonitrile), Struktol 3604, Struktol 3605, Struktol 3606, Struktol 3652, and Struktol 3710, all from Struktol Corporation, Hyprox RA95, Hyprox RA840, Hyprox RA1340, Hyprox RF928, Hyprox RM20, and Hyprox RK84L, all from CVC Corporation, ERS-172, EPR-21, EPR-1309, EPR-4026, EPR-4023, and EPR-4030, all from Adeka Corporation), DER 852, DER 791, DER 732, and DER 736, all from Dow Chemical Co., Ltd.

In the one-part curable adhesive composition according to the present invention, the toughened epoxy resin (A2) is preferably present in an amount of 1% to 60%, preferably 10% to 50%, more preferably 20% to 40% by weight based on the total weight of components (A) to (E) of the one-part curable adhesive composition. In the event that the toughened epoxy resin (A2) is mandatory included into the adhesive composition, these are not counted or belong anymore the amount of epoxy resin, and only contribute to the amount of compound (A2).

If the amount of the toughened epoxy resin is too low, the cured product may not be sufficiently toughened, and may tend to be brittle during the application.

If the amount the amount of the toughened epoxy resin is too large, the cured product may be too soft and the cost efficiency of the product may be lower.

Compound having at least one group reactive towards the epoxy resin

One further compound of the one-part curable adhesive composition is a compound having at least one, preferably two groups reactive towards the epoxy resin. Preferably, the reactive group is selected from phenol groups, amino groups and/or thiol groups, especially selected from amino groups and/or thiol groups, most preferred thiol groups. Therefore, in one preferred embodiment the compound (B) is a phenol resin. Yet, in another preferred embodiment, the compound (B) is a polyamine. In an especially preferred embodiment compound (B) is a polythiol.

Preferably, the polythiol compound comprised in the one-part curable adhesive composition may be selected from any mercapto compound which has two or more thiol groups per molecule, such as trimethylolpropane tris(β -mercaptopropionate), trimethylolpropane tris(thioglycolate), pentaerythritol tetrakis(thioglycolate), pentaerythritol tetrakis(β -mercaptopropionate), dipentaerythritol poly(β -mercaptopropionate), ethylene glycol bis(β -mercaptopropionate) and alkyl polythiols such as butane-1,4-dithiol, hexane-1,6-dithiol, and aromatic polythiols such as p-xylenedithiol, 1,3,5-tris(mercaptomethyl) benzene, and combination

thereof.

Preferably, the polythiol compound is selected from trimethylolpropane tris(β -mercaptopropionate) (TMPMP) (commercially available from Sinopharm Chemical Reagent Co., Ltd.), pentaerythritol tetrakis(β -mercaptopropionate) (commercially available under the trade name of Karenz MT PE-1 from Showa Denko Corporation).

In the one-part curable adhesive composition, the compound (B), especially the polythiol compound is preferably present in an amount of 1% to 40%, preferably 5% to 30%, more preferably 10 to 20% by weight, based on the total weight of components (A) to (E) of the one-part curable adhesive composition.

If the amount of the compound (B), especially the polythiol is too low, the curing with the non-toughed epoxy resin may not be enough.

If the amount of the compound (B), especially the polythiol is too large, the uncured material may disperse in the cured product, which will decrease the properties, such as the tensile strength and modulus of the cured product. In addition, the curability of the adhesive composition may be negatively influenced.

Latent curing accelerator

The latent curing accelerator comprised in the one-part curable adhesive composition is produced by the latent curing accelerator composition the corresponding preparation method as described above.

In the one-part curable adhesive composition according to the present invention, the latent curing accelerator is preferably present in an amount of 1% to 20%, preferably 3% to 18%, more preferably 4% to 15% by weight, based on the total weight of components (A) to (E) of the one-part curable adhesive composition.

If the amount of the latent curing accelerator is too low, the curing of polythiol

compounds with epoxy resin may not be well accelerated.

If the amount of the latent curing accelerator is too large, the properties of the polythiol-epoxy composition may be deteriorated.

Impact modifier and/or a toughener

Optionally, one or more impact modifier and/or a toughener can be used in this invention, and it is not specifically restricted. Such tougheners are known to the person skilled in the art in the field of epoxy adhesives. They can be selected for example from: thermoplastic isocyanates or polyurethanes, rubber particles, in particular those having a core-shell structure, and block copolymers, in particular those containing a first polymer block having a glass transition temperature of less than 15°C and a second polymer block having a glass transition temperature of greater than 25°C. Such block copolymers are preferably selected from those in which a first polymer block is selected from a polybutadiene or polyisoprene block and a second polymer block is selected from a polystyrene or a polymethyl methacrylate block. Specific examples thereof are block copolymers having the following block structure: styrene-butadiene-(meth)acrylate, styrene-butadiene-(meth)acrylic acid ester, ethylene-(meth)acrylic acid ester-glycidyl (meth)acrylic acid ester, ethylene-(meth)acrylic acid ester-maleic anhydride, methyl methacrylate-butyl acrylate-methyl methacrylate.

Tougheners that are especially preferred according to the invention are furthermore rubber particles having a core-shell structure, preferably those described above. In addition rubber particles having a core-shell structure are preferred with a core made from a polymer material having a glass transition temperature of less than 0°C and a shell made from a polymer material having a glass transition temperature of greater than 25°C. Particularly suitable rubber particles having a core-shell structure can have a core made from a diene homopolymer, a diene copolymer or a polysiloxane elastomer and/or a shell made from an alkyl (meth)acrylate homopolymer or copolymer. In this context such particles having a core-shell structure are preferably introduced as the mentioned toughened epoxy resin, but

the particles having a core-shell may also be incorporated into the adhesive composition as such.

In the one-part curable adhesive composition according to the present invention, the impact modifier and/or a toughener (D) is preferably present in an amount of 1% to 60%, preferably 10% to 50%, more preferably 20% to 40% by weight based on the total weight of components (A) to (E) of the one-part curable adhesive composition. In the event, that the toughened epoxy resin (A2) is mandatory included into the adhesive composition, these are not counted or belong anymore the amount of impact modifier and/or a toughener, and only contribute to the amount of compound (A2).

Filler

Suitable filler, which can be optionally used in the present invention includes, but not limited to silica, such as fumed silica, diatomaceous earth, alumina, zinc oxide, iron oxide, magnesium oxide, tin oxide, titanium oxide, magnesium hydroxide, aluminium hydroxide, magnesium carbonate, barium sulphate, gypsum, calcium silicate, talc, glass bead, sericite activated white earth, bentonite, aluminum nitride, silicon nitride, and the like.

The one-part curable adhesive composition according to the present invention may contain a filler in an amount of 0% to 30%, preferably 1% to 20%, more preferably 1% to 20% by weight, based on the total weight of components (a) to (e) of the composition.

Other components

According to the present invention, the one-part curable adhesive composition may optionally comprises a non-reactive or reactive diluent, a thixotropic agent, a silane coupling agent, and combination thereof.

Suitable examples of the reactive diluents are monoglycidyl ethers, such as phenyl glycidyl ether, alkyl phenol monoglycidyl ether, aliphatic monoglycidyl ether,

alkylphenol mono glycidyl ether, alkylphenol monoglycidyl ether, 3-glycidoxypropyl trimethoxysilane, 3-glycidoxypropyl trimethoxysilane, 3-glycidoxypropylmethyldimethoxysilane, 1-(3-glycidoxypropyl) 1,1,3,3,3-pentamethyl disiloxane; diglycidyl ethers, such as 1,4-butanediol diglycidyl ether; 1,4-cyclohexane-dimethanol; the diglycidyl ether of resorcinol; diglycidyl ether of cyclohexane dimethanol; diglycidyl ether of neopentyl glycol; triglycidyl ether of trimethylolpropane dipentene; and the divinyl ether of cyclohexanedimethanol; and tri- or tetra- glycidyl ethers, such as trimethylolpropane triglycidyl ether, glycerin triglycidyl ether, and pentaerythritol tetraglycidyl ether.

Suitable commercially available reactive diluents are for example under the trade name of NC-513, Lite 2513HP (both from Cardolite Corporation), ED-502S, ED-509, ED-529, ED-506, ED-503, ED-523T, ED-505, ED-505R, ED-507 (all from Adeka Corporation), DY-C, DY-D, DY-E, DY-F, DY-H, DY-K, DY-L, DY-P, DY-T, DY 3601, and DY-CNO (all from Air Product Corporation).

Suitable thixotropic agent, which can be optionally used in the present invention includes, but is not limited to, talc, superfine surface-treated calcium carbonate, fine particle alumina, plate-like alumina; layered compound such as montmorillonite, spicular compound such as aluminium borate whisker, and the like.

Suitable silane coupling agent, which can be optionally used in the present invention include, but is not limited to, γ -aminopropyltriethoxysilane, γ -mercaptopropyltrimethoxysilane, γ -methacryloxypropyltrimethoxysilane, γ -glycidoxypropyltrimethoxysilane, phenyltrimethoxysilane, and the like.

Examples of commercial examples of silane coupling agents KH550 and KH560 from Danyang City Chenguang Coincident Dose Co., Ltd.

In one preferred embodiment, the one-part curable adhesive composition according to the present invention comprises:

- (A1) 10% to 50%, preferably 15 to 40% by weight of an epoxy resin, especially a non-toughened epoxy resin,
 - (A2) optionally additional 10% to 50%, preferably 20% to 40% by weight of a toughened epoxy resin,
 - (B) 5% to 30%, preferably 10 to 20% by weight of a polythiol compound,
 - (C) 3% to 18%, preferably 4% to 15% by weight of the latent curing accelerator according to the present invention or prepared by the method according to the present invention,
 - (D) optionally 1% to 60%, preferably 10% to 50%, more preferably 20% to 40% of an impact modifier and/or a toughener, and
 - (E) optionally 1% to 20%, preferable 1% to 20% by weight a filler,
- in which the weight percentages are based on the total weight of components (A) to (E) of the one-part curable adhesive composition.

The one-part curable adhesive composition according to the present invention can be prepared by the steps of (1) mixing together all the components except the polythiol compounds by mechanical stirring; and (2) adding the polythiol compounds in the mixture obtained in step (1), and further mixing the mixture by mechanical stirring to obtain a homogeneous composition.

Another aspect of the present invention is a method of bonding substrates together which comprises applying the one-part curable adhesive composition according to the present invention to a first substrate, bringing a second substrate in contact with the adhesive composition applied to the first substrate, and subjecting the applied composition to conditions which allow the applied composition to be cured. A variety of application methods can be utilized, for example spraying, flow-coating, blade-coating, brushing, pouring, immersion, impregnation, dripping, rolling, sprinkle coating, or immersion coating. Examples of the material comprised of each substrate include metals, glasses, resin-based composite materials or ceramics. After applied, the one-part adhesive composition is subjected to a temperature range of about 130 °C to about 180 °C by heating for about 10 min to about 120 min, and then cured.

The present invention likewise relates to a cured product of the one-part curable adhesive composition according to the present invention or prepared by the method of bonding substrates together according to the present invention, and to the use of the one-part curable adhesive composition in bonding substrates together.

The following examples are intended to assist one skilled in the art to better understand and practice the present invention. The scope of the invention is not limited by the examples but is defined in the appended claims. All parts and percentages are based on weight unless otherwise stated.

Examples

Materials:

Raw material	Commercial Supplier	Function
Diphenylmethane diisocyanate (MDI)	Wanhua Chemical Group Co., Ltd	Aromatic polyisocyanate
Tolylene diisocyanate (TDI)	Wanhua Chemical Group Co., Ltd	Aromatic polyisocyanate
Hexamethylene diisocyanate (HDI)	Wanhua Chemical Group Co., Ltd	Aliphatic polyisocyanate
Water (deionized)	--	Chain extender
Lysine	Sinoparm Chemical Reagent Co., Ltd.	Chain extender
Arginine	Sinoparm Chemical Reagent Co., Ltd.	Chain extender
Ethanol	Sinoparm Chemical Reagent Co., Ltd.	Chain stopper
DMP-30	Sinoparm Chemical Reagent Co., Ltd.	Non-latent curing accelerator
2-ethyl-4-methyl-	Sinoparm Chemical Reagent Co.,	Non-latent curing accelerator

imidazole	Ltd.	
Triethylenediamine	Sinoparm Chemical Reagent Co., Ltd.	Non-latent curing accelerator
DABCO	Sinoparm Chemical Reagent Co., Ltd..	Non-latent curing accelerator
DBU	Sinoparm Chemical Reagent Co., Ltd.	Non-latent curing accelerator
MEK	Sinoparm Chemical Reagent Co., Ltd.	Solvent
Ajicure PN 23	Ajinomoto Corporation	Latent Curing accelerator
Epon 828	Hexion Co., Ltd.	Non-toughened epoxy resin
DER 354	Dow Chemical Corporation	Non-toughened epoxy resin
MY721	Huntsman Corporation	Non-toughened epoxy resin
MX154	Kaneka Corporation	Toughened epoxy resin
SS3614	Struktol Corpoaration	Toughened epoxy resin
TMPMP	Sinoparm Chemical Reagent Co., Ltd.	Polythiol compound
Karenz MT PE-1	SHOWA DENKO Corporation	Polythiol compound
CaCO ₃	Changzhou Calcium Carbonate company	Filler
TS 720 (Fumed Silica)	Cabot Corporation	Filler

The preparation of Examples 1 to 9 (E1 to E9) and Comparative Examples (CE1 to CE3):

The amount and type of components of latent curing accelerator compositions including inventive examples and comparative examples are shown in Table 1.

The preparation of the latent curing accelerators of E1 to E9 is as follows:

In a flask, an aromatic polyisocyanate and a chain stopper were added into the solvent, then the mixture was allowed to react at 50° C for 2 hours under stirring. Cool down to room temperature, then a chain extender was added to the mixture and reacted for additional 1 hour. Finally, a non-latent curing accelerator was added

into the mixture and reacted for another 4 hours. The resulting latent curing accelerator was precipitated, filtered, washed by the solvent, dried under vacuum, and ground, and thus a powdery non-latent curing accelerator was obtained.

The preparation of the latent curing accelerators of CE1 is as follows:

In a flask, an aromatic polyisocyanate and a chain stopper were added into the solvent, then the mixture was allowed to react at 50° C for 2 hours under stirring. Cool down to room temperature, then a chain extender was added to the mixture and reacted for additional 5 hours. The resulting polyurea compounds was precipitated, filtered, washed by the solvent, dried under vacuum, and ground to a powdery product.

The preparation of the non-latent curing accelerators of CE2 is as follows:

In a flask, an aromatic polyisocyanate and a chain extender were added into the solvent, then the mixture was allowed to react at room temperature for 1 hour under stirring. Then, a non-latent curing accelerator was added into the mixture and reacted for another 4 hours. The resulting latent curing accelerator was precipitated, filtered, washed by the solvent, dried under vacuum, and ground, and thus a powdery non-latent curing accelerator was obtained.

The preparation of one-part curable adhesive compositions

The preparation of the one-part curable adhesive compositions containing the latent curing accelerators of E1 to E9 and CE1 to CE3 is as follows:

32 parts by mass of Epon 828, 21 parts by mass of MX 154, 15 parts by mass of latent curing accelerator (E1 to E9, CE1 to CE3, and Ajicure PN23 for CE4), 2 parts by mass of fumed silicon dioxide (TS720) were dispersed by Speedmixer at 2000 rpm at room temperature for 1 min, then 30 parts by mass of TMPMP was added to the mixture, further dispersed by Speedmixer at 2000 rpm at room temperature for 30s. A one-part polythiol-epoxy resin composition was obtained.

Table 2. The formulations of one-part curable adhesive composition (parts by mass)

[illegible]

Table 3. The formulations of one-part curable adhesive composition (parts by mass)

Component	Adhesive Example			
	AE-10	AE-11	AE-12	AE-13
Epon 828	25	-	17	12
DER 354	10	30	-	-
MY721	-	10	-	17
MX154	15	10	-	-
SS3614	-	-	23	22
TMPMP	30	25	33	
Karenz MT PE-1	-	-	-	28
E1	18	-	-	-
E2	-	20	-	-
E4	-	-	15	-
E5	-	-	-	10
CaCO ₃	-	5	8	9
TS720	2	-	4	2

Evaluation:

Curability of the one-part curable adhesive composition

Differential scanning calorimetry (DSC) was used to measure the onset temperature of the one-part polythiol-epoxy composition. With lower onset temperature, it indicated that the adhesive composition had higher curability. In the present invention, the adhesive composition having an onset temperature not higher than 90°C was indicated as “excellent”, 90-110°C as “good”, 110-130°C as “fair”, and higher than 130°C as “poor”.

The onset temperature of the polythiol-epoxy composition was measured by TA Q2000 differential scanning calorimeter manufactured by TA Instruments, with the measuring sequence as follow: Equilibrium at -20°C, then heat from -20°C to 250°C at the rate of 10 °C /min. mm, at 25°C.

Storage stability

The storage stability was measured by the time required to double the viscosity of the one-part polythiol-epoxy composition. The adhesive composition was stored in a mixer cap without a top at room temperature. If the time required to double the viscosity was 15 days or more, the storage stability of the adhesive composition was indicated as “excellent”, 6-15 days as “good”, 1-6 days as “fair”, and less than 1 day as “poor”, respectively.

The viscosity of the one-part polythiol-epoxy compositions was measured by Rheometer Anton Paar MCR301 at room temperature. The shear rate is 15s⁻¹, the gap is 0.2 mm, and the diameter of the test bar is 25 mm.

Short time curability of the polythiol-epoxy composition

The liquid one-part polythiol-epoxy composition was applied on a 2 um cold rolled steel (CRS) substrate with a thickness of 50 um, and then the CRS substrate was subjected to thermocompression bonding on a hot plate at 200°C for 10s under the pressure of 20 kg/cm². FT-IR measurement of the polythiol-epoxy composition was performed before and after the thermocompression bonding. The ratio of the height

of the characteristic peak (about 1608 cm^{-1}) of a benzene ring to the characteristic peak (about 915 cm^{-1}) of an epoxy group was defined as the change ratio and was used to calculate the percentage of reacted epoxy group and indicate the short time curability of the polythiol-epoxy adhesive composition. The adhesive compositions having the change ratio of 80% or more was indicated as "excellent", 65%-80% as "good", 50% to 65% as "fair", and 50% or less as "poor", respectively.

The test results of the curability, storage stability and short time curability of the one-part polythiol-epoxy compositions are shown in Table 4.

Table 4. Test results of the evaluation

Item	Adhesive Example							
	AE-1	AE-2	AE-3	AE-4	AE-5	AE-6	AE-7	AE-8
Onset temperature	excellent	excellent	excellent	excellent	excellent	good	good	good
Storage stability	excellent	excellent	good	excellent	excellent	excellent	excellent	excellent
Short time curability	excellent	excellent	excellent	excellent	excellent	excellent	excellent	excellent

Item	Adhesive Example					Comparative Adhesive Example			
	AE-9	AE-10	AE-11	AE-12	AE-13	CAE-1	CAE-2	CAE-3	CAE-4
Onset temperature	good	excellent	excellent	excellent	excellent	poor	poor	good	excellent
Storage stability	excellent	excellent	excellent	excellent	excellent	excellent	excellent	poor	poor
Short time curability	excellent	excellent	excellent	excellent	excellent	poor	poor	fair	excellent

As can be seen in the results in Table 5, all of the one-part polythiol-epoxy adhesive composition containing the latent curing accelerator produced by the latent curing accelerator composition according to the present invention exhibited much better results with respect to the property profile including DSC onset temperature, storage stability and/or short time curability than comparative examples (CAEs).

It is evident that the latent curing accelerator composition according to the present invention surprisingly achieved the stabilization of the non-latent curing accelerator component at room temperature and the release of the non-latent curing accelerator component at a relatively lower elevated temperature, and in turn contributes to a one-part polythiol-epoxy adhesive composition having such properties. In addition, the use of the latent curing accelerator composition further provided the one-part polythiol-epoxy adhesive composition with an excellent short time curability.

These and other modifications and variations of the present invention may be practiced by those of ordinary skill in the art, without departing from the spirit and scope of the present invention. In addition, it should be understood that aspects of the various embodiments may be interchanged both in whole or in component. Furthermore, those of ordinary skill in the art will appreciate that the foregoing description is by way of example only, and is not intended to limit the invention so further described in such appended claims.

What is claimed is:

1. A latent curing accelerator composition, comprising:
 - (a) an aromatic polyisocyanate,
 - (b) a chain extender,
 - (c) a chain stopper, and
 - (d) a non-latent curing accelerator having at least one tertiary amine group.
2. The latent curing accelerator composition according to claim 1, wherein the aromatic polyisocyanate is selected from the group consisting of aromatic diisocyanate, aromatic triisocyanate, aromatic tetraisocyanate, and the combination thereof, preferably aromatic diisocyanate.
3. The latent curing accelerator composition according to claim 1 or 2, wherein the aromatic polyisocyanate is present in an amount of 35% to 90%, preferably 40% to 80%, more preferably 50% to 75% by weight, based on the total weight of components (a) to (d) of the latent curing accelerator composition.
4. The latent curing accelerator composition according to any of claims 1 to 3, wherein the chain extender is selected from the group consisting of water, a polyamine having at least two primary amino groups, and the combination thereof.
5. The latent curing accelerator composition according to any of claims 1 to 4, wherein the polyamine having at least two primary amino groups further contains an additional acid group, preferably selected from the group consisting of lysine, arginine, glutamine, ornithine and the combination thereof.
6. The latent curing accelerator composition according to any of claims 1 to 5, wherein the chain extender is present in an amount of 0.5% to 35%,

preferably 1% to 30%, more preferably 2% to 25% by weight, based on the total weight of components (a) to (d) of the latent curing accelerator composition.

7. The latent curing accelerator composition according to any of claims 1 to 6, wherein the chain stopper is selected from the group consisting of monohydric alcohol, monohydric phenol, monohydric secondary amine, monohydric thiol, monohydric carboxylic acid, and the combination thereof, preferably monohydric alcohol, and more preferably ethanol.
8. The latent curing accelerator composition according to any of claims 1 to 7, wherein the chain stopper is present in an amount of 1% to 20%, preferably 3% to 18%, more preferably 4% to 15% by weight, based on the total weight of components (a) to (d) of the latent curing accelerator composition.
9. The latent curing accelerator composition according to any of claims 1 to 8, wherein the non-latent curing accelerator having at least one tertiary amine group is selected from the group consisting of trimethylamine, triethylamine, tetraethylmethylenediamine, benzyldimethylamine, N,N'-dimethylpiperazine, tetramethyl-1,3-diaminopropane, N,N,N',N'-tetramethyl-1,6-hexanediamine, pentamethyldiethylenetriamine, 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-methyl-N'-(2-dimethylamino)-ethylpiperazine, N-methylmorpholine, N-(N',N'-(dimethylamino)ethyl)morpholine, N-methyl-N'-(2-hydroxyethyl)morpholine, N,N-dimethylbenzylamine, dimethylaminomethylphenol, tris(dimethylaminomethyl)phenol, triethylenediamine, hexamethylenetetramine, 1,8-diazabicyclo (5,4,0)-undecene-7,

1,5-diazabicyclo (4,3,0)-nonene-5, imidazole, 1-methylimidazole, 1-vinylimidazole, 2-methylimidazole, 2-ethylimidazole, 2-ethyl-4-methylimidazole, 2-undecylimidazole, 2-heptadecylimidazole, 2-phenylimidazole, 2,4-dimethylimidazoline, 2-ethyl-4-methylimidazoline, and the combination thereof.

10. The latent curing accelerator composition according to any of claims 1 to 9, wherein the non-latent curing accelerator having at least one tertiary amine group is present in an amount of 1% to 50%, preferably 3% to 45%, more preferably 5% to 40% by weight, based on the total weight of components (a) to (d) of the latent curing accelerator composition.
11. A latent curing accelerator produced by the latent curing accelerator composition according to any of claims 1 to 10.
12. A method for preparing a latent curing accelerator, comprising:
 - (1) reacting an aromatic polyisocyanate with a chain stopper at 25 to 80 ° C for 1 to 8 hours, and obtaining a mixture;
 - (2) adding a chain extender to the mixture of step (1), and keeping the reaction at room temperature for 0.5 to 12 hours, and obtaining a mixture; and
 - (3) adding a non-latent curing accelerator having at least one tertiary amine group to the reaction mixture of step (2), and keeping the reaction under room temperature for 0.5 to 5 hours, and obtaining a latent curing accelerator.
13. A one-part curable adhesive composition, comprising:
 - (A) an epoxy resin,
 - (B) a compound having at least one group reactive towards the epoxy resin,
 - (C) the latent curing accelerator according to the present invention or prepared by the method according to the present invention,
 - (D) optionally an impact modifier and/or a toughener, and
 - (E) optionally a filler.

14. A method of bonding substrates together which comprises applying the one-part curable adhesive composition according to claim 13 to a first substrate, bringing a second substrate in contact with the adhesive composition applied to the first substrate, and subjecting the applied composition to conditions which allow the applied composition to be cured.
15. A cured product of the one-part curable adhesive composition according to claim 13 or prepared by the method of bonding substrates together according to claim 14.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2016/078036

A. CLASSIFICATION OF SUBJECT MATTER

C07C 231/12(2006.01)i; C07C 243/28(2006.01)i

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)

C07C231/-; C07C243/-

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)

CNPAT,WPI,EPODOC,CNKI:Henkel, cur+, accelerator?, isocyanate, amine, acid, extender, stopper, chain, phenol, alcohol

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2009277356 A1 (HENKEL CORP.) 12 November 2009 (2009-11-12) page 2 to page 5, page 11 to page 13, page 17 to page 18, table 3, claims 12-17	1-15
X	US 8481659 B2 (LOCTITE R&D LTD. ET AL.) 09 July 2013 (2013-07-09) page 3 to page 6	1-15
X	EP 2285773 A2 (HENKEL CORP.) 23 February 2011 (2011-02-23) 说明书第2-7页	1-15
A	EP 2285760 A2 (HENKEL CORP.) 23 February 2011 (2011-02-23) page 3 to page 5	1-15
A	CN 104395421 A (HENKEL US IP LLC. ET AL.) 04 March 2015 (2015-03-04) page 3 to page 8	1-15
A	CN 101405321 A (NAT. STARCH & CHEM. INVESTMENT HOLDING CORP.) 08 April 2009 (2009-04-08) page 4 to page 7	1-15

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

* Special categories of cited documents:

“A” document defining the general state of the art which is not considered to be of particular relevance

“E” earlier application or patent but published on or after the international filing date

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“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

“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

“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

“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

“&” document member of the same patent family

Date of the actual completion of the international search

02 December 2016

Date of mailing of the international search report

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Name and mailing address of the ISA/CN

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.

PCT/CN2016/078036

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