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(57) **Abrégé/Abstract:**

A structural adhesive composition that is suitable for high-strength bonding of metals and aerospace structural materials. In one embodiment, the structural adhesive composition based on a two-part system, which is curable at or below 200°F (93 °C). The two-part system is composed of a resinous part (A) and a catalyst part (B), which may be stored separately at room temperature until they are ready to be used. The resinous part (A) includes at least two different multifunctional epoxy resins with different functionality selected from difunctional, trifunctional, and tetrafunctional epoxy resins, certain toughening components, and inorganic filler particles as a rheology/thixotropy modifying component. The toughening components include core-shell rubber particles with different particle sizes and at least one of an elastomeric polymer and a polyethersulfone polymer. The catalyst part (B) includes an aliphatic or cyclic amine compound as a curing agent and inorganic filler as a rheology/thixotropy modifying component. The weight ratio of part (A) to part (B) is within the range of 3:2 to 10:2. In another embodiment, the structural adhesive composition is based on a one-part system which includes the components of the resinous part (A) in the two-part system mixed with a latent amine curing agent. The one-part system may further include an imidazole and/or an aliphatic amine. The one-part system is curable within the temperature range of 140-300°F (60-150°C). The paste adhesive disclosed herein has film-like properties and is particularly useful in rapid-assembly aerospace structure bonding applications.



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(54) Title: STRUCTURAL ADHESIVE AND BONDING APPLICATION THEREOF

(57) Abstract: A structural adhesive composition that is suitable for high-strength bonding of metals and aerospace structural materials. In one embodiment, the structural adhesive composition based on a two-part system, which is curable at or below 200°F (93 °C). The two-part system is composed of a resinous part (A) and a catalyst part (B), which may be stored separately at room temperature until they are ready to be used. The resinous part (A) includes at least two different multifunctional epoxy resins with different functionality selected from difunctional, trifunctional, and tetrafunctional epoxy resins, certain toughening components, and inorganic filler particles as a rheology/thixotropy modifying component. The toughening components include core-shell rubber particles with different particle sizes and at least one of an elastomeric polymer and a polyethersulfone polymer. The catalyst part (B) includes an aliphatic or cyclic amine compound as a curing agent and inorganic filler as a rheology/thixotropy modifying component. The weight ratio of part (A) to part (B) is within the range of 3:2 to 10:2. In another embodiment, the structural adhesive composition is based on a one-part system which includes the components of the resinous part (A) in the two-part system mixed with a latent amine curing agent. The one-part system may further include an imidazole and/or an aliphatic amine. The one-part system is curable within the temperature range of 140-300°F (60-150°C). The paste adhesive disclosed herein has film-like properties and is particularly useful in rapid-assembly aerospace structure bonding applications.



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STRUCTURAL ADHESIVE AND BONDING APPLICATION THEREOF

BACKGROUND

[0001] Structural adhesives have been conventionally used for structural bonding in the manufacturing of structural parts that demand stringent mechanical requirements such as automobile and aircraft body parts. Generally, heat-curable epoxy adhesives are used as structural adhesives. Such heat-curable epoxy adhesives often require relatively high-temperature curing, e.g. 120-180°C (248-356°F). High-temperature curing often requires large autoclaves, higher production run time and may cause exothermic concerns. On the other hand, there are conventional adhesives that are curable at lower temperature, e.g. ambient temperature; however, they lack the toughness and bonding strength properties required for structural bonding in the manufacturing of aerospace structural parts. The structural adhesives for aerospace application must have the durability to withstand the harsh environmental conditions.

[0002] For structural bonding operations such as rapid assembly of aircraft parts, it is desirable to have an adhesive that enables low temperature or room-temperature curing flexibility, out-of-autoclave (OOA) processing, and is capable of forming strong bond to both composite and metal surfaces with excellent long-term durability under aerospace environmental conditions.

SUMMARY

[0003] The present disclosure provides a structural adhesive composition that is suitable for high-strength bonding of metals and aerospace structural materials. In one embodiment, the structural adhesive composition based on a two-part system, which is curable at or below 200°F (93°C), including room temperature (20-25°C or 68-77°F). The two-part system is composed of a resinous part (A) and a catalyst part (B), which may be stored separately at room temperature until they are ready to be used. Mixing of part (A) and part (B) is required before application. The resinous part (A) includes at least two different multifunctional epoxy resins with different functionality selected from difunctional, trifunctional, and tetrafunctional epoxy resins, certain toughening components, and inorganic filler particles as

a rheology/thixotropy modifying component. The toughening components include core-shell rubber particles with different particle sizes and at least one of an elastomeric polymer and a polyethersulfone polymer. The catalyst part (B) includes one or more aliphatic or cyclic amine compounds as curing agents and inorganic filler particles as a rheology/thixotropy modifying component. The weight ratio of part (A) to part (B) is within the range of 3:2 to 10:2.

[0004] In another embodiment, the structural adhesive composition is based on a one-part system which includes the components of the resinous part (A) in the two-part system and a latent amine curing agent. The one-part system may further include an imidazole and/or an aliphatic amine to control the curing kinetics such that further lowering of the curing temperature is possible. The one-part system is curable within the temperature range of 140-300°F (60-150°C).

DETAILED DESCRIPTION

[0005] For the two-part system, a curable paste adhesive is formed by mixing the resinous Part (A) with the catalyst Part (B) prior to applying the adhesive to a surface. The mixed paste adhesive can be cured at a low temperature of less than or equal to 93°C (200°F), including ambient temperature (20-25°C or 68-77°F). Low temperature curing enables adhesive bonding of substrates without the use of an autoclave, i.e. out-of-autoclave (OOA). As such, adhesive bonding and curing may be carried out by applying low contact pressure of about 1-3 psi (pounds per square inch) on the bonded substrates with or without external heating. Upon curing within the range of 65°C-93°C (150°F-200°F), the paste adhesive yields a structural adhesive with a glass transition temperature (T_g) of greater than 95°C (203°F). In certain embodiments, upon curing at 93°C (200°F), the cured adhesive has a T_g of greater than 120°C (248°F), e.g. 120°C-130°C (248°F-266°F).

[0006] The resinous part (A) includes at least two different multifunctional epoxy resins with different functionality and selected from difunctional, trifunctional, and tetrafunctional epoxy resins, certain toughening components, and inorganic filler particles as a rheology/thixotropy modifying component. The toughening components include a first type of core-shell rubber (CSR) particles having smaller particle sizes of less than 100 nm, and a second type of core-shell rubber particles having larger particle sizes of greater than 100 nm. The toughening components further include at least one of an elastomeric polymer with a functional group capable of reacting with the multifunctional epoxy resins during curing and a polyethersulfone (PES) polymer. In one embodiment, both elastomeric polymer and

polyethersulfone are present in the resinous part (A). The catalyst part (B) includes one or more amine curing agents to react with the epoxy resins and inorganic filler particles as a rheology/thixotropy modifying component. The amine curing agents are aliphatic or cyclic amine compounds. The weight ratio of the resinous part (A) to the catalyst part (B) is within the range of 3:2 to 10:2. In a preferred embodiment, the weight ratio of the resinous part (A) to the catalyst part (B) is 2:1.

[0007] The resinous part (A) has a storage viscosity in the range of 500-1000 Poise at room temperature (20-25°C or 68-77°F) and a density (specific gravity) in the range of 1.0-1.2 g/cc, and the catalyst part (B) has a storage viscosity in the range of 150-300 Poise at room temperature 20-25°C (68-77°F) and a density in the range of 0.9-1.1 g/cc. The two parts have a long shelf-life and may be stored in separate containers at room temperature for up to one year. When the parts (A) and (B) are mixed, the resultant product is a paste adhesive that is curable at or below 200°F (93°C) and has a viscosity of 200-600 Poise, preferably 300-500 Poise, at room temperature 20-25°C (68-77°F), thereby allowing the adhesive to be easily applied onto a surface by conventional methods such as bead or film application. From here onwards, the terms “room temperature” and “ambient temperature” will be used interchangeably to refer to the temperature range of 20-25°C (68-77°F).

[0008] For the one-part system, the resultant adhesive after mixing its components is a curable paste adhesive that is ready for application and is curable within the temperature range of 140-300°F (60-150°C), or 160-200°F (71-93°C), however, it does not have a long shelf-life at ambient temperature, normally about 15 days. As such, freezing would be required to extend its shelf-life. The one-part adhesive has a viscosity in the range of 400-1000 Poise, preferably 300-500 Poise, at room temperature.

Epoxy Resins

[0009] The multifunctional epoxy resins to be used in the resinous part (A) are those polyepoxides containing an average of two to four epoxy groups (oxirane rings) per molecule with the epoxy groups being the terminal groups. A difunctional epoxy resin is an epoxy resin that contains an average of two epoxy groups per molecule, a trifunctional epoxy resin is an epoxy resin that contains an average of three epoxy groups per molecule, and a tetrafunctional epoxy resin contains an average of four epoxy groups per molecule. The difunctional epoxy resins may have an average epoxy equivalent weight (EEW) in the range of 150-700 g/eq. An epoxy equivalent weight is the molecular weight of the epoxy molecule divided by the number of epoxy groups in the molecule. Thus, for example, a difunctional epoxy having a molecular weight of 400 would have an epoxy equivalent

weight of 200. The trifunctional epoxy resins may have an average EEW in the range of 90-180 g/eq. The tetrafunctional epoxy resins may have an average EEW in the range of 100-200 g/eq.

[0010] In a preferred embodiment, at least one of the multifunctional epoxy resins is a cycloaliphatic epoxy. In some embodiments, a mixture of all three types of multifunctional epoxy resins (difunctional, trifunctional, and tetrafunctional epoxy resins) is present in the resinous part (A) to control the cross-linking density of the cured epoxy resin mixture and to optimize T_g and toughness of the final cured adhesive. In other embodiments, the resin mixture includes a non-cycloaliphatic difunctional epoxy, either a trifunctional epoxy or a tetrafunctional epoxy, and a cycloaliphatic epoxy with epoxy functionality of greater than one (i.e. a cycloaliphatic multifunctional epoxy). Difunctional resin is making up the majority of the resin mixture (more than 50 wt.% of the resin mixture) in all cases. When all three multifunctional epoxy resins are used, the following proportions are preferred, based on the total weight of the resin mixture: more than 50 wt.% difunctional epoxy resin, less than 10 wt.% tetrafunctional epoxy resin, and trifunctional epoxy resin making up the balance.

[0011] In general, the multifunctional resins suitable for the resinous part (A) may be saturated, unsaturated, cyclic or acyclic, aliphatic, alicyclic, aromatic or heterocyclic polyepoxides. Examples of suitable polyepoxides include polyglycidyl ethers, which are prepared by reaction of epichlorohydrin or epibromohydrin with a polyphenol in the presence of alkali. Suitable polyphenols therefore are, for example, resorcinol, pyrocatechol, hydroquinone, bisphenol A (bis(4-hydroxyphenyl)-2,2-propane), bisphenol F (bis(4-hydroxyphenyl)methane), bisphenol S, bis(4-hydroxyphenyl)-1,1-isobutane, fluorene 4,4'-dihydroxybenzophenone, bis(4-hydroxyphenyl)-1,1-ethane, bisphenol Z (4,4'-Cyclohexylidenebisphenol), and 1,5-hydroxynaphthalene. Also suitable are the polyglycidyl ethers of polyalcohols, aminophenols or aromatic diamines.

[0012] Other types of polyepoxides which may be used are glycidyl polyester resins prepared by reacting an epihalohydrin with an aromatic or aliphatic polycarboxylic acid. Another type of polyepoxide resin is a glycidyl amine which is prepared by reacting a polyamine with an epichlorohydrin. Other suitable multifunctional epoxy resins include multifunctional epoxy novolac resins with two to four epoxy groups. The epoxy novolac resins that are useful include epoxy cresol novolacs and epoxy phenol novolacs. Additional suitable multifunctional epoxy resins include aliphatic multifunctional epoxy such as polyglycidyl ether type epoxy, and sorbitol glycidyl ether.

[0013] Liquid multifunctional epoxy resins or a combination of solid and liquid multifunctional epoxy resins may be used to form the resin mixture. Particularly suitable are

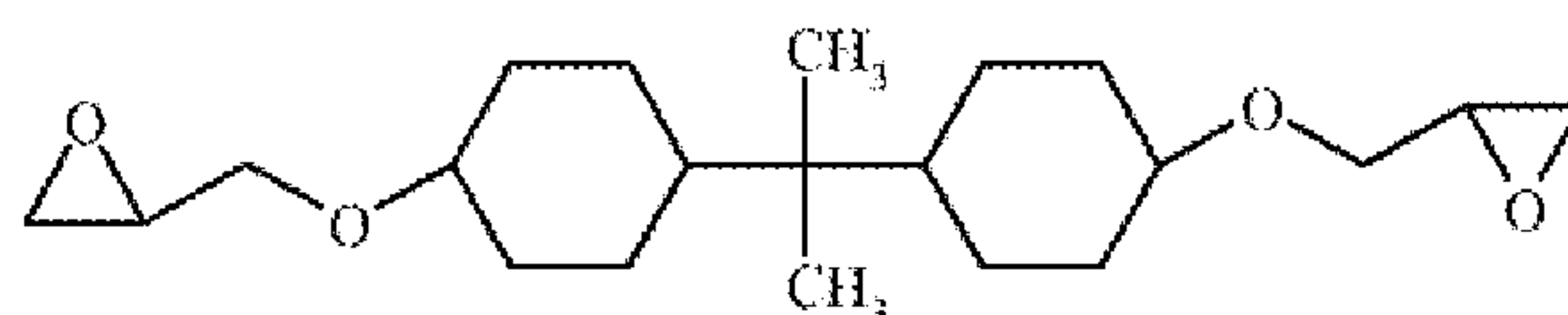
liquid epoxy resins having relatively low molecular weight derived by reaction of bisphenol A or bisphenol F and epichlorohydrin. The bisphenol-based epoxy resins that are liquid at room temperature generally have an epoxy equivalent weight of from about 150 to about 350 g/eq. The epoxy resins that are solid at room temperature are obtainable from polyphenols and epichlorohydrin and have epoxy equivalent weights of greater than 400 g/eq. The solid epoxy resins differ from the liquid epoxy resins in that they are solid at room temperature and have a melting point of from 45°C to 130°C.

[0014] Examples of difunctional epoxy resins include diglycidyl ethers of bisphenol A-based materials (e.g. Epon™ 828 (liquid epoxy resin) from Hexion, DER 331, D.E.R. 661 (solid epoxy resin) supplied by Dow Chemical Co., Tactix 123, and Araldite® 184 supplied by Huntsman Advanced Materials).

[0015] Examples of trifunctional epoxy resins include triglycidyl ether of aminophenol, e.g. Araldite® MY 0510, MY 0500, MY 0600, MY 0610 supplied by Huntsman Advanced Materials.

[0016] Examples of tetrafunctional epoxy resins include tetraglycidyl ether of methylene dianiline (e.g. Araldite® MY 9655 supplied by Huntsman Advanced Materials), tetraglycidyl diaminodiphenyl methane (e.g., Araldite® MY-721, MY-720, 725, MY 9663, 9634, 9655 supplied by Huntsman Advanced Materials), EJ-190 from JSI Co., Ltd., and ERISYS GE-60 from CVC Chemical, Inc.

[0017] Suitable cycloaliphatic epoxies comprise compounds that contain at least one cycloaliphatic group and at least two oxirane rings per molecule. Specific examples include diepoxide of cycloaliphatic alcohol, hydrogenated Bisphenol A (Epalloy™ 5000, 5001 supplied by CVC Thermoset Specialties) represented by the following structure:



[0018] Other examples of cycloaliphatic epoxies include: EPONEX cycloaliphatic epoxy resins (e.g. EPONEX Resin 1510) supplied by Momentive Specialty Chemicals; cycloaliphatic Epotec® epoxy resins (e.g. YDH 184, YDH 3000) supplied by Aditya Birla Chemicals; ERL-4221 (3,4-epoxycyclohexylmethyl-3',4'-epoxycyclohexane carboxylate) from Dow Chemicals; and Araldite® CY 179 MA supplied by Huntsman Advanced Materials.

Toughening agents

[0019] Two different types of core-shell rubber (CSR) particles are incorporated in the resinous part (A) to create a bi-modal particle size distribution with different toughening morphology domains. These CSR particles act as toughening agents which allow for the toughening of the adhesive upon curing. The smaller particles may have an average particle size of less than or equal to 100 nm, preferably 50-90 nm, and the larger particles may have an average size of greater than 100 nm, preferably 150-300 nm. The weight ratio of smaller CSR particles to larger CSR particle may be in the range of 3:1 to 5:1. The CSR particles, in total, may be present in the resinous part (A) in an amount of 5% - 30% by weight based on the total weight of part (A). By having different particle sizes, one can control the balance of the key properties such as shear strength, peel strength, and resin fracture toughness.

[0020] 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 could also be covalently crosslinked through the use of 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.

[0021] The core-shell rubber particles may be pre-dispersed in a liquid resin matrix system such as those available from Kaneka Texas Corporation under the trademarks Kane Ace MX. It is preferred that the core-shell rubber particles are pre-dispersed in one of difunctional, trifunctional and tetrafunctional epoxy resins to be used in the resinous part (A). As examples, suitable resin matrix systems containing CSR particles 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).

[0022] In addition to CSR particles, thermoplastic and/or elastomeric toughening agents are added to the epoxy resin mixture to further increase the toughness of the finally cured adhesive. Particularly preferred are elastomeric polymers with functional groups capable of reacting with the multifunctional epoxy resins during curing, and a polyether sulfone (PES) polymer having an average molecular weight in the range of 8,000-14,000.

[0023] Elastomeric polymers with epoxy functional groups are particularly suitable. Specific examples include epoxy-elastomer adduct formed by reacting epoxy resin with carboxyl-terminated butyl nitrile elastomer or amine-terminated butadiene acrylonitrile (ATBN) elastomer. A specific example is Epon 58005, which is an elastomer-modified epoxy-functional adduct formed from the reaction of the diglycidyl ether of bisphenol A and a carboxyl-terminated butadiene-acrylonitrile elastomer. Additional elastomer modified epoxy resins include Epon 58006, Epon 58042, Epon 58120, Epon 58091 from Hexion Specialty Chemicals, Inc.

[0024] Other suitable elastomeric polymers include carboxyl-terminated butadiene nitrile polymer (CTBN) and amine-terminated butadiene acrylonitrile (ATBN) elastomer, or similar reactive liquid polymer chemicals. Moreover, CTBN and/or ATBN may also added to either part (A) or part (B) of the two-part system or to the one-part system to further improve the toughness and resiliency of the adhesive.

[0025] The polyether sulfone (PES) polymer includes polyethersulfone-polyetherethersulfone (PES-PEES) copolymer having T_g above 190°C, e.g., KM 170 and KM 180, which have T_g of about 200°C, available from Cytec Industries Inc.

[0026] Other suitable toughening agents include phenoxy resins, which are long chain linear poly hydroxy ethers with different molecular weights such as phenol,4,4'-(1-methylethylidene) bispolymer with (chloromethyl) oxirane. Commercial examples include Phenoxy PKHP-200 and PKHB-100 available from InChem Corp.

Inorganic fillers

[0027] A significant challenge for a resin-based adhesive composition is to maintain the adhesive's rheology performance between the time it is manufactured and the time it is applied. The inorganic fillers act as a thixotropy or rheology modifying component in the two-part or the one-part system. Suitable inorganic fillers are those in particulate form and include silica, alumina, calcium oxide, talc, and kaolin. Fumed silica with surface area in the range of 90-380 m²/g has been found to be suitable for either the two-part system or the one-part system. For the two-part system, the weight percentage of inorganic filler in the resinous part (A) is within the range of 1-6 wt.% based on the total weight of part (A). For the catalyst part (B), the weight percentage of inorganic filler is within the range of 3-10 wt.% based on the total weight of part (B). For the one-part system, the weight percentage of inorganic filler is within the range of 0.5-2.5 wt.%.

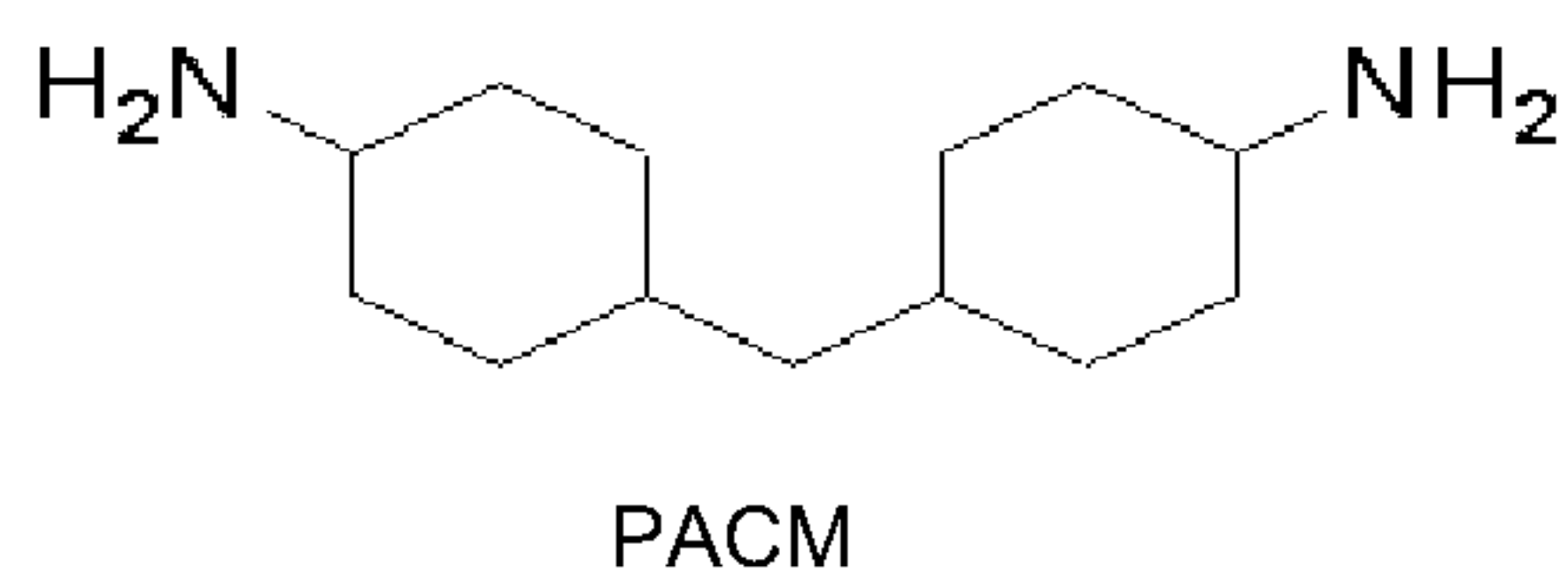
[0028] In one embodiment of the two-part system, the inorganic filler in the resinous part (A) is hydrophobic fumed silica, such as CAB-O-SIL TS-720 available from Cabot Corporation, and the inorganic filler in the catalyst part (B) is hydrophilic fumed silica, such as CAB-O-SIL M-5 available from Cabot Corporation. In one embodiment of the one-part system, the inorganic filler is hydrophobic fumed silica, such as CAB-O-SIL TS-720. Other examples of fumed silica- based rheology modifiers include Aerosil R202, and VPR 2935 supplied by Evonik Degussa Corp. The presence of fumed silica helps maintain the desired viscosity for the adhesive and also improves the sagging resistance of the adhesive during application and curing. Sagging or slump resistance is desirable when the adhesive is applied on vertical or high-angle surfaces.

Amine Curing Agents for Two-Part System

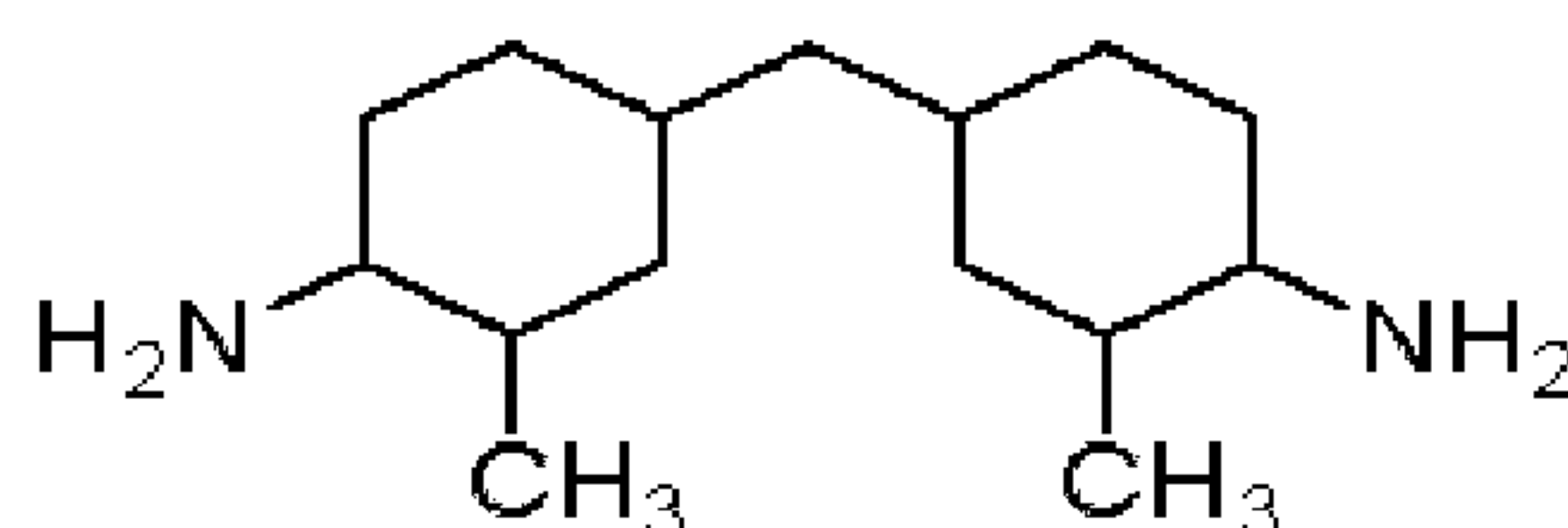
[0029] One or more amine curing agents may be used in the catalyst part (B) of the two-part system. The amine curing agents for the catalyst part (B) are aliphatic or cyclic amine compounds capable of reacting with the multifunctional epoxy resins in part (A) to form highly cross-linked resin matrix. In a preferred embodiment, the amine compounds are selected from the group consisting of cycloaliphatic amines, polyethylene polyamines, amine-

terminated piperazines, imidazoles, and combinations thereof. The total weight percentage of the amine curing agent(s) is within the range of 80-95 wt.% based on the total weight of part (B).

[0030] Suitable cycloaliphatic amines include dicyclohexylamines such as bis-(paminocyclohexyl)methane (PACM) having the following structure:



and dimethyl PACM having the following structure:

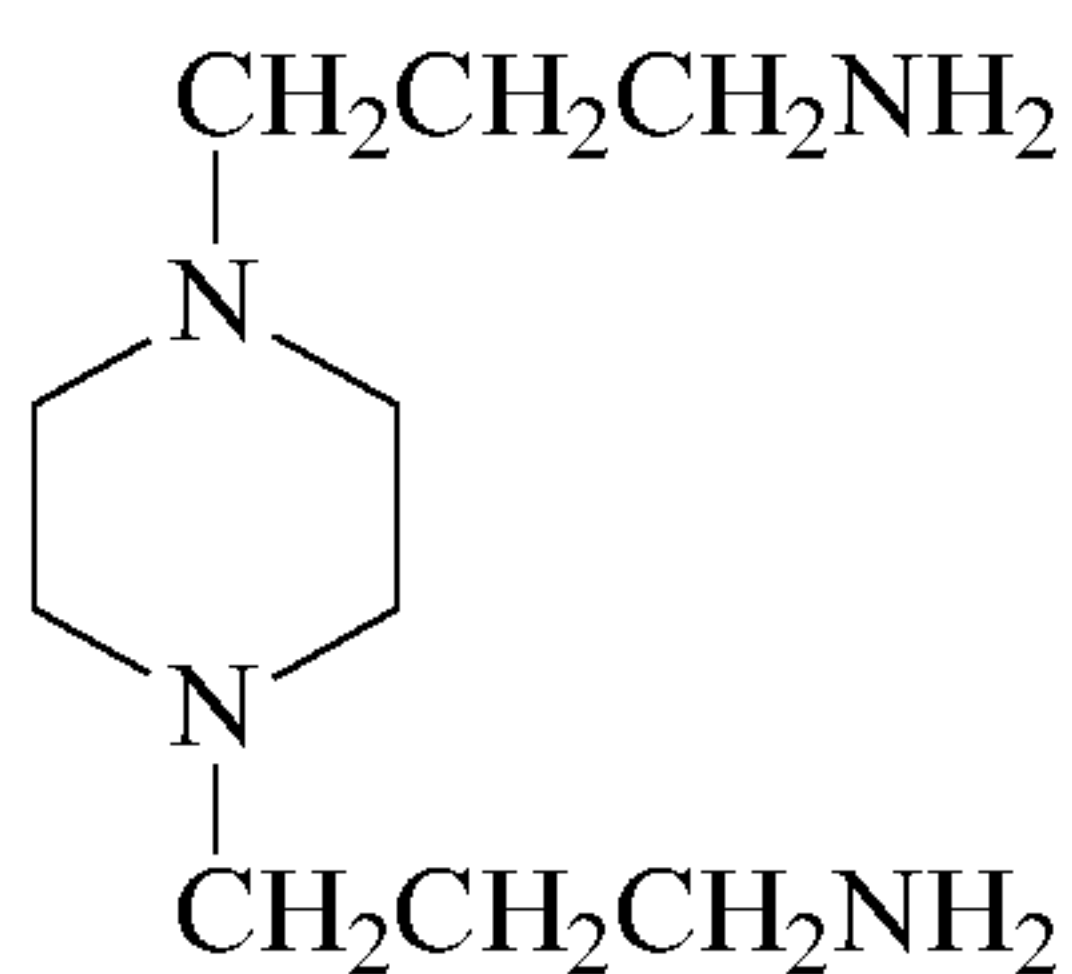


[0031] Suitable polyethylene polyamines include tetraethylene pentamine (linear C-8 pentamine) having the following chemical structure:

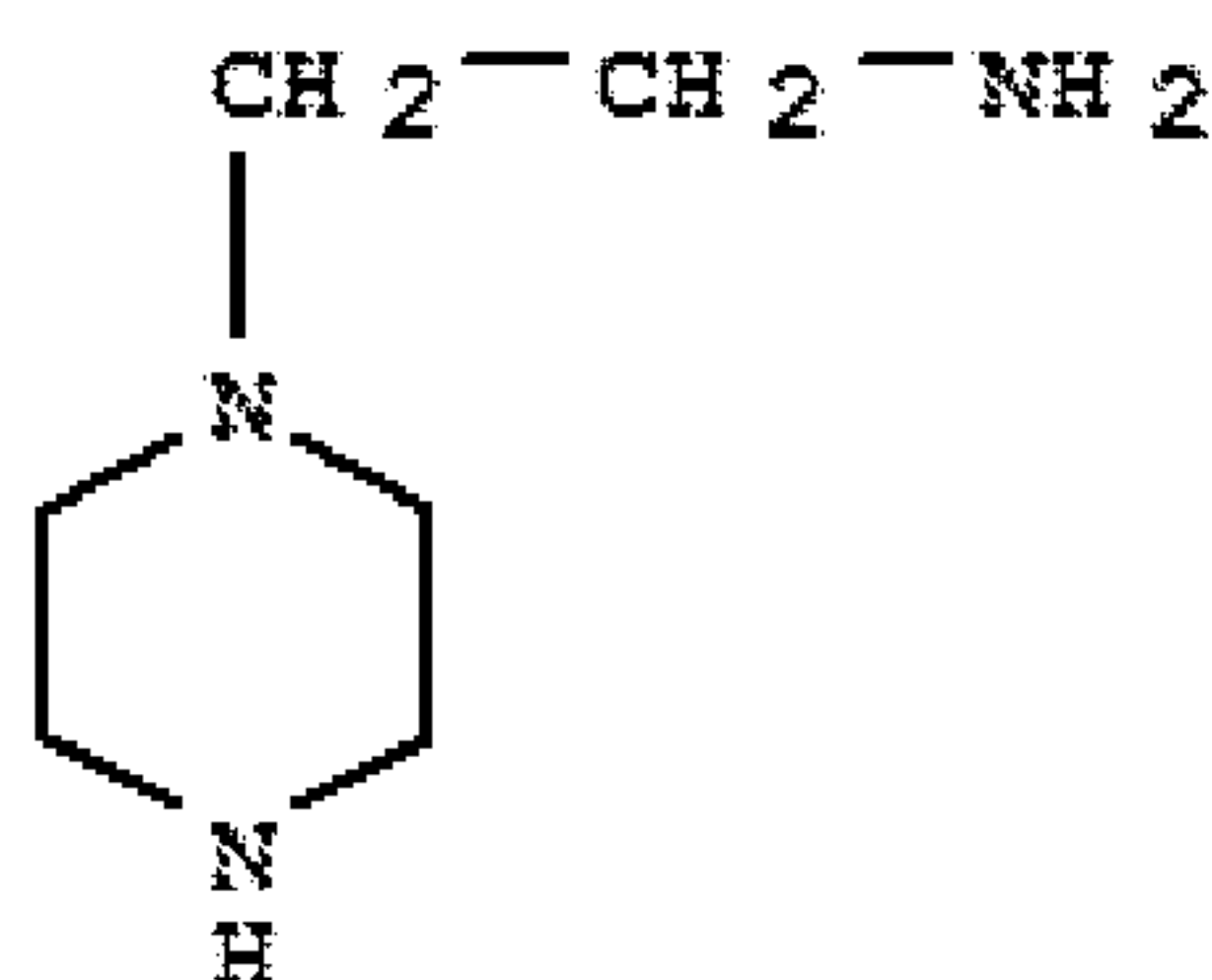


[0032] Other suitable examples of polyethylene polyamines include diethylenetriamine (linear C-4 diamine), triethylenetetramine (linear C-6 triamine), and pentaethylenhexamine (linear C-10 hexamine).

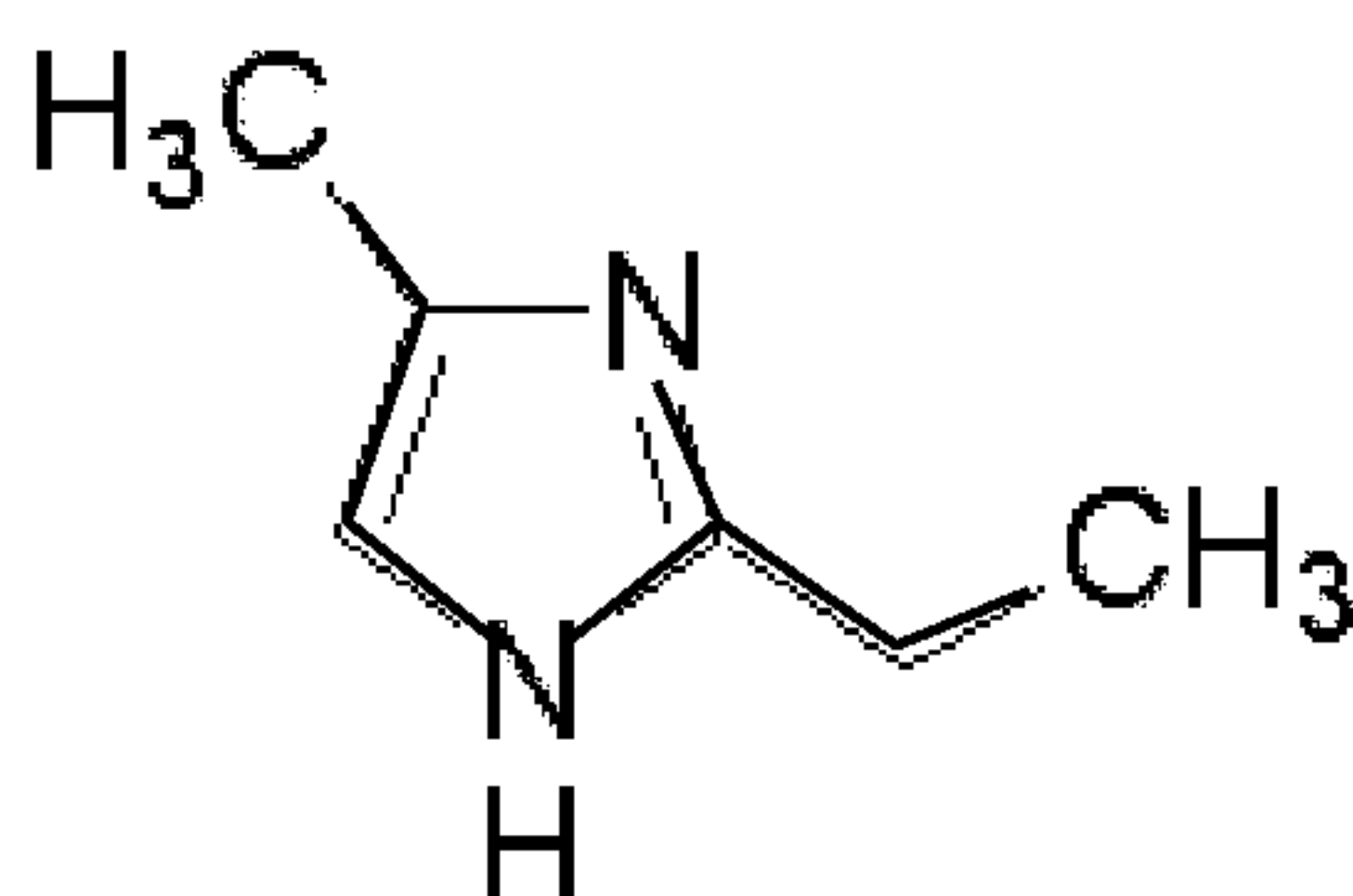
[0033] An example of a suitable amine-terminated piperazine is 1,4 Bisaminopropyl piperazine having the following structure:



[0034] Another example is aminoethyl piperazine having the following structure:



[0035] Suitable imidazoles include 2-ethyl-4-methyl imidazole having the following structure:



[0036] This type of imidazole is commercially available as Imicure EMI-2,4 from Air Products.

[0037] Additional examples of amine curing agents include tris-(dimethylaminomethyl) phenol (available as Ancamine K54 from Air Products), and diethylene glycol, di(3-aminopropyl) ether (available as Ancamine 1922A).

Amine curing agents for one-part system

[0038] The curing agents for the one-part system include latent amine-based curing agents, which may be used in combination with at least one of an imidazole and an aliphatic amine. The inclusion of imidazole and/or aliphatic amine further decreases the curing temperature of the adhesive composition. Latent amine-based curing agents that can be activated at a temperature greater than 160°F (71°C) are suitable for the one-part system. Examples of suitable latent amine-based curing agents include dicyandiamide (DICY), guanamine, guanidine, aminoguanidine, and derivatives thereof. A particularly suitable latent amine-based curing agent is dicyandiamide. The latent amine-based curing agent may be present in an amount within the range of 2-6 wt%.

[0039] A curing accelerator may be used in conjunction with the latent amine-based curing agent to promote the curing reaction between the epoxy resins and the amine-based curing agent. Suitable curing accelerators may include alkyl and aryl substituted ureas

(including aromatic or alicyclic dimethyl urea); bisureas based on toluenediamine or methylene dianiline. An example of bisurea is 2,4-toluene bis(dimethyl urea) (commercially available as Omicure U-24 or CA 150 from CVC Chemicals). Another example is 4,4'-methylene bis(phenyl dimethyl urea) (commercially available as Omicure U-52 or CA 152 from CVC Chemicals), which is a suitable accelerator for dicyandiamide. The curing accelerator may be present in an amount within the range of 1-6 wt%. In one embodiment, dicyandiamide is used in combination with a substituted bisurea as a curing accelerator.

[0040] Suitable imidazoles include 2-ethyl-4-methyl imidazole, e.g. Imicure® EMI-24, as described above for the two-part system.

[0041] Suitable aliphatic amines are those with amine value (mg KOH/g) in the range of 180-300, and equivalent weight (H) in the range of 35-90. Examples of suitable aliphatic amines include Ancamine 2014AS (modified aliphatic amine), and Ancamine 2037S available from Air Products. Other examples of aliphatic amines are Aradur™ 956-4, 943, 42 from Huntsman, and EPICURE™ 3202, 3223, 3234 from Momentive Specialty Chemicals.

[0042] In one embodiment of the one-part adhesive, a matrix encapsulated amine, such as Intelimer® 7004 (2-ethyl-4-methyl-imidazole covalently attached to Intelimer® polymer) and Intelimer® 7024 (Intelimer® polymer encapsulated 2-ethyl-4-methyl-imidazole) from Air Products, is used as a latent curing agent. These materials are composed of imidazole-based catalyst encapsulated within Intelimer® polymer via matrix encapsulation. Intelimer® polymers are crystalline polyacrylate polymers in which the crystallinity results from the side chains which are attached to the polymer backbone. These crystalline polymers have a very sharp, well defined melting point. Encapsulation may be done by physical blending or deliberate covalent attachment (i.e. covalently modified polymer). By this encapsulation arrangement, the activity of the amine catalyst is blocked by a polymer network until thermal activation, e.g. curing. The inclusion of these matrix encapsulated amines in the adhesive increases the stability of the adhesive at ambient temperature.

Additional Additives

[0043] Additives such as coloring dyes or pigments may be added to the two-part system (either part A or part B) and to the one-part system to adjust the color of the adhesive.

Adhesive bonding application

[0044] The two-part and the one-part adhesives of the present disclosure are suitable for bonding various aerospace structural materials to form a laminate structure, including metal to metal, metal to composite material, composite material to composite material. Composite materials include fiber-reinforced resin composites, such as prepregs or prepreg layup used for making aircraft composite structures. The term “prepreg” as used herein refers to sheet or lamina of fibers that has been impregnated with a matrix resin. The matrix resin may be present in an uncured or partially cured state. The term “prepreg layup” as used herein refers to a plurality of prepreg layers that are placed adjacent one another in a stack. The prepreg layers within the layup may be positioned in a selected orientation with respect to one another. For example, prepreg layups may comprise prepreg layers having unidirectional fiber architectures, with the fibers oriented at 0°, 90°, a selected angle θ , and combinations thereof, with respect to the largest dimension of the layup, such as the length. It should be further understood that, in certain embodiments, prepregs may have any combination of fiber architectures, such as unidirectional and multi-dimensional.

[0045] After mixing, the two-part adhesive composition yields a paste adhesive that can be applied by conventional dispensing means such as bead or film application onto one or more surfaces to be bonded. For structural bonding of metals and aerospace composite materials, the adhesive may be applied at a thickness of 10-80 mils (0.254 mm – 2.032 mm). The surfaces are then brought together to form a laminate with an adhesive film in between the substrates. Subsequently, the resultant laminate may be cured at or below 93°C (or 200°F), including ambient temperature. Such low-temperature curing method enables out-of-autoclave (OOA) curing of the laminate. The cured adhesive of the two-part system is a structural adhesive with enhanced mechanical properties: a lap shear strength of 33-37 MPa at 20°C-25°C and 24-27 MPa at 82°C, 15-18 MPa at 121°C according to ASTM D3165, a peel strength of 250-350 Nm/m (or 50-75 lbs/in) at 20°C-25°C according to ASTM D3167. Furthermore, when the two-part adhesive is used for bonding fiber-reinforced resin composite substrates, it exhibits a fracture toughness (or interlaminar toughness, G_{Ic}) of greater than 650 J/m², for example, 651- 1500 J/m², according to ASTM 5528. The T_g and lap shear strength remain substantially unchanged (more than 90% retention) after aging exposure to air containing relative humidity of 100% at 71°C for 14 days or at 49°C for 30 days.

[0046] For the one-part adhesive, the cured adhesive film has the following properties: a glass transition temperature (T_g) of greater than 100°C (212°F) upon curing in the temperature range of 65-93°C (150°F-200°F), a lap shear strength of 28-40 MPa at 20°C-25°C

and 25-28 MPa at 82°C, 17-21 MPa at 121°C according to ASTM D3165 testing, a peel strength of 150-250 Nm/m (or 30-50 lbs/in) at 20°C-25°C according to ASTM D3167.

[0047] ASTM D3165 refers to a Standard Test Method for Strength Properties of Adhesives in Shear by Tension Loading of Single-Lap-Joint Laminated Assemblies. Lap Shear determines the shear strength of adhesives for bonding materials when tested on a single-lap-joint specimen.

[0048] ASTM D3167 refers to a Standard Test Method for Floating Roller Peel Resistance of Adhesives. This test method covers the determination of the relative peel resistance of adhesive bonds between one rigid adherend and one flexible adherend when tested under specified conditions of preparation and testing. Adhesion is measured by peeling the flexible adherend from the rigid substrate. The peel force is a measure of fracture energy.

[0049] ASTM D5528 refers to a Standard Test Method for Mode I Interlaminar Fracture Toughness of Fiber-Reinforced Polymer Matrix Composites.

[0050] The paste adhesive disclosed herein has film-like properties which enable automated dispensing of the adhesive – this is particularly useful in rapid-assembly, aerospace structure bonding applications. Furthermore, the advantages of the disclosed two-part adhesive include:

- Low temperature curing paste with structural adhesive film-like properties
- High strength/high toughness and excellent hot/wet properties for metal and composite bonding
- Flexible low temperature curing schedule
- Stable properties
- Long pot life/Long assembly time
- No Bagging, OOA Structural Bonding
- Thixotropic, slump-resistant, and easy to use
- Automation placement capability
- Room temperature storage for up to 1 year (1 year shelf life)
- Lower Manufacturing cost

EXAMPLES

[0051] The following examples are provided for the purposes of illustrating the various embodiments, but are not intended to limit the scope of the present disclosure.

Example 1*Two-Part System*

[0052] For the two-part adhesive system, Tables 1A and 1B show exemplary formulations for the resinous part (A). A-1 to A-7 represent the more preferred formulations, and A-8 and A-9 are comparative formulations. Table 2 shows exemplary formulations for the catalyst part (B). To form a paste adhesive, any one of A-1 to A-9 may be mixed with any one of B-1 to B-7. Unless indicated otherwise, the amounts in the tables are expressed in parts.

TABLE 1A –Resinous Part (A)

<i>Components</i>	Part A-1	Part A-2	Part A-3	Part A-4
Diglycidylether of Bisphenol A				
Liquid Bisphenol A diglycidyl ether with ~25 wt.% CSR particles (particle size=70-90 nm)	56	60.2	46	46
Triglycidyl ether of aminophenol	15	11.3	29	29
Diepoxide of cycloaliphatic alcohol, hydrogenated Bisphenol A (low viscosity cycloaliphatic diepoxide)	7	7.5		
Tetraglycidyl ether of methylene dianiline	3.5	3.8		
Sorbitol polyglycol ether (Aliphatic Multifunctional epoxy)				
PES-PEES thermoplastic polymer				4.6
Core-Shell Rubber (CSR) particles (ave. particle size 200 nm)	4.2	4.5	10.3	5.8
Low MW adduct of epichlorohydrin & bisphenol A	7	7.5	9.6	9.6
Elastomer-modified epoxy functional adduct	3.5	3.8	3	3
Hydrophobic fumed silica	3.8	1.5	2.4	2.4
Total	100	100.1	100.3	100.4

TABLE 1B –Resinous Part (A)

<i>Components</i>	Part A-5	Part A-6	Part A-7	Part A-8 (comparative)	Part A-9 (comparative)
Diglycidylether of Bisphenol A				60.2	
Liquid Bisphenol A diglycidyl ether with ~25 wt.% CSR particles (particle size=70-90nm)	57	57.6	57		63
Triglycidyl ether of aminophenol	18	18		11.3	11.8
Diepoxide of cycloaliphatic alcohol, hydrogenated Bisphenol A (low viscosity cycloaliphatic diepoxide)				7.5	7.9
Tetraglycidyl ether of methylene dianiline	3.6	3.6	3.6	3.8	3.9
Sorbitol polyglycol ether (Aliphatic multifunctional epoxy)			18		
PES-PEES thermoplastic polymer	4.3	0	4.3		
Core-Shell Rubber (CSR) particles (ave. particle size 200 nm)	4.3	7.2	4.3	4.5	0
Low MW adduct of epichlorohydrin & bisphenol A	7.1	3.6	7.1	7.5	7.9
Elastomer-modified epoxy functional adduct	3.6	5	3.6	3.8	3.9
Hydrophobic fumed silica	0.8	1.4	0.8	1.4	1.6
Total	98.7	96.4	98.7	100	100

TABLE 2 - Catalyst Part (B)

Components	Part B-1	Part B-2	Part B-3	Part B-4	Part B-5	Part B-6	Part B-7
Dimethyl PACM	92		40				
PACM		90	55				
Tetraethylene pentamine				60	50		
1,4-Bisaminopropyl piperazine				34			
Aminoethyl piperazine (AEP)					44		
Diethylene glycol, di(3-aminopropyl) ether						84	90
Tris(dimethylamino-methyl) phenol							5
Phenol, 4,4'-(1-methylethylidene) bispolymer with (chloromethyl) oxirane (toughener)						10	
Untreated fumed silica	8	10	5	6	6	6	5
Total	100	100	100	100	100	100	100

[0053] The resinous part and the catalyst part based on the above formulations were prepared separately by weighting and adding the required components at different steps to a double planetary mixer with heating and cooling capability. The epoxy and CSR components of the resinous part were mixed first under high heat (between 150°F and 200°F) to get a homogeneous, resinous mixture. The mixture was cool down to 150°F and Epon 58005 was added to the mixture. Epon 58005 was pre-heated at 120°F prior to adding to the mixture to facilitate handling. The mixture was cooled to 90°F and fumed silica was then added. Mixing continued while applying vacuum to de-air the mixture. The resulting resinous base was then removed from the mixer when the temperature was below 80°F. For the catalyst part, the amine curing agent(s) and fumed silica were added to the mixer and mixed at room temperature until the silica was uniformly dispersed.

Example 2

[0054] A two-part adhesive based on Part A-1 and Part B-1 (disclosed in Example 1), and a two-part adhesive based on Part A-2 and Part B-3 (disclosed in Example 1), have the properties shown in Table 3. The mixed density (i.e. specific gravity) was determined after mixing the resinous part with the catalyst part at room temperature, and after curing at 93°C (200°F).

TABLE 3 - Properties of Two-Part Adhesive

		Part A-1 & Part B-1	Part A-2 & Part B-3
Mix ratio	By weight	2:1	2:1
Viscosity at 24°C (Poise)	Part A	810	850
	Part B	200	200
	Mixed viscosity	400	420
Vertical slump at 24°C (mm)	9.525 mm thickness bead (3/8 inch thick beads)	3.6	3
Density (g/cc)	Part A	1.1	1.1
	Part B	0.99	1.0
	Mixed density before curing	1.05	1.05
	Mixed density after curing	1.05	1.05

Example 3

Bonding Performance

[0055] Metal bonding performance and composite bonding performance of various two-part adhesives based on the formulations disclosed in Example 1 were measured. Al-2024-T3 aluminum sheets from Alcoa Inc. were used as the substrates for metal-metal bonding. The aluminum metal was first wiped with a solvent, followed by alkaline degreasing, FPL etching (chrome sulphuric etch), and phosphoric acid anodization (PAA) per ASTM 3933. Solvent based primer BR[®]127 from Cytec Industries Inc. was sprayed on the aluminum metal to a thickness of 0.00015 inches. The primer was air dried for 15 minutes and then cured at 121°C (250 °F) for 60 minutes. Two aluminum sheets were bonded to each other by applying the paste adhesive between the sheets. The glue line thickness is controlled with glass beads at about 10 mils (254 microns). All bonded samples were cured in a hot press at temperatures between 71°C (160°F) and 93°C (200°F) for the stated length of time. Contact pressure from 0.021 to 0.035 MPa (3 to 5 psi) was applied throughout curing. The metal-metal adhesion

strength (Wide Area Lap Shear - WALs) and toughness (floating roller peel –FRP, or Climbing drum peel - CDP) properties of the paste adhesive were tested at different temperatures. The testing results are reported as the mean average of five specimens for each test group. Glass transition temperature (T_g onset) of the cured paste adhesive was determined using a thermal mechanical analyzer (TMA 2940) from TA Instruments.

[0056] Composite bonding was carried out using fiber-reinforced prepregs as test substrates. The prepregs used were pre-cured Torayca[®] T800H/3900-2 prepreg tape from Toray Composites, Inc. Either a dry polyester peel ply or resin-rich peel ply was used as surface treatment on the composite substrates. Curing was carried out under out-of-autoclave (OOA) conditions.

For bonding performance testing, the following test methods were used:

- a) Wide Area Lap Shear (WALS) – ASTM D3165
- b) Floating Roller Peel (FR Peel) – ASTM D3167
- c) Double Cantilever Beam (DCB, G_{IC}) for composite bonding – ASTM D5528

[0057] Table 4 shows the metal bonding properties of a paste adhesive formed by mixing Part A-2 and Part B-1 at mix ratio (A:B) of 2:1 by weight.

TABLE 4

Press Curing Cycles	200°F- 2 hrs	200°F- 1.5 hrs	180°F- 4 hrs	160°F- 6 hrs	160°F- 4 hrs
	WALS	WALS	WALS	WALS	WALS
WALS @RT, psi	5072	5125	5237	4961	4889
WALS @180°F/ 82°C, psi	3896	3757	3963	3605	3505
WALS @250°F/ 121°C, psi	1188	1081	1426	1391	579
FR Peel @RT, pli	56	58	72	73	58
T_g (Dry, °C)	114	108	105	99	94

[0058] Table 5 shows the composite-composite bonding properties of a paste adhesive formed by mixing Part A-1 and Part B-1 at mix ratio (A:B) of 2:1 by weight.

TABLE 5

Composite bonding properties		200°F – 2hrs	180°F -4hrs
Lap Shear (WALS, psi)			
	75°F / 25°C	5105	
	180°F / 82°C	3759	
	250°F / 121°C	2560	
G _{1C} Fracture Toughness (in-lb/in ²)			
	75°F / 25°C	5.8	7

[0059] Table 6 shows the metal-metal bonding properties of a paste adhesive formed by mixing Part A-2 and Part B-3 at mix ratio (A:B) of 2:1 by weight.

TABLE 6

Curing Cycles	160°F-4 hrs	200°F- 2 hrs	220°F- 1 hr
Property	WALS	WALS	WALS
WALS @RT, psi	4893	5228	4905
WALS @180°F/82°C, psi	3658	3955	3724
WALS @250°F/121°C, psi	896	1555	2064
FR Peel @RT, pli	74	67	55
T _g (Dry,TMA), °C	94	101	102

[0060] Table 7 shows the metal-metal bonding properties of a paste adhesive formed by mixing Part A-1 and either Part B-4 or Part B-5 at mix ratios indicated (by weight).

TABLE 7

	Part A-1/Part B-4	Part A-1/Part B-4	Part A-1/Part B-4	Part A-1/Part B-5
Curing Cycles	150°F- 1 hr	RT -7 Days	150°F- 1 hr	150°F- 1 hr
Property	WALS	WALS	WALS	WALS
WALS @RT, psi	4850	3883	4230	4782
WALS @180°F, psi	3000	2100	2532	2964
WALS @250°F, psi	1500	1500	1740	1954
FR Peel @RT, pli	50	10	33	43
Mix Ratio (A/B)	4 to1	4 to1	5 to1	5 to1
T _g (Dry, °C)	93	65	95	97

[0061] The room-temperature curable, two-part adhesive based on Part A-1 combined with Part B-4 (A:B weight ratio of 4:1) was tested for composite bonding. The results show a G_{Ic} value of 4.5 in-lb/in² (788 J/m²) and cohesive failure mode.

Comparative examples

[0062] For comparison, each of Part A-8 and Part A-9 disclosed in Table 1B was mixed with Part B-1 formulation disclosed in Table 2 to form a paste adhesive. The resultant adhesives were then tested for metal-metal bonding properties as described above. The results are shown in Table 8.

TABLE 8

Metal Bonding Property	Part A-8/Part B-1	Part A-9/Part B-1
Curing Cycles	200°F- 2 hrs	180°F- 4 hrs
	WALS	WALS
WALS @RT, psi	4858	5269
WALS @180°F, psi	3980	3791
WALS @250°F, psi	2803	1920
FR Peel @RT, pli	10	50
T _g (Dry, °C)	128	121

[0063] Table 8 shows that the floating roller peel strength at room temperature of the comparative adhesives is lower than that of the more preferred adhesives at the same curing temperature.

Example 4*Effect of Bond Line Thickness on Paste Adhesive Bonding Performance*

[0064] The effect of bond line thickness on the metal-metal bonding performance of the paste adhesive was measured using bonded aluminum specimens, wherein the adhesive bonding was done using a two-part adhesive composed of Part A-1 and Part B-1 formulations disclosed in Example 1, at mix ratio of 2:1. Curing was carried out under OOA curing at 93°C for 2 hours. Results for WALs and FRP testing with varying bond line thicknesses are shown in Table 9. The paste adhesive showed decreases in both lap shear and peel strength with increasing bond line thickness. However, the peel strength was much more tolerant to bond line thickness variation. At high bond line thickness (40-80 mils), the paste adhesive exhibited fairly high peel strength and mainly cohesive failure mode. At high bond line thickness, it also retained more than 50% of its original wide area lap shear strength. The good tolerance of the paste adhesive to bond line thickness variation reflects its intrinsically high toughness. The tolerance to the high glue line thickness makes it very attractive for structural bonding applications where non-uniform or high bond line thickness occurs.

TABLE 9

Cure Cycle 93°C, 2 hrs	WALS 25°C (psi)	WALS 82°C (psi)	WALS 121°C (psi)	FRP 25°C (pli)	FRP 82°C (pli)	FRP 121°C (pli)
0.254 mm (10 mils)	5202	3741	2668	55	67	50
0.508 mm (20 mils)	4304	2797	1797	48	102	54
1.016 mm (40 mils)	2872	2865	1305	43	63	59
2.032 mm (80 mils)	2667	2842	1521	-	-	-

Example 5*Effect of Humidity Exposure on Adhesive Bonding Performance*

[0065] To ensure the durability of composite-to-composite or composite-to-metal bonded structures, a tough, moisture-resistant, flow-controlled epoxy-based adhesive is required. Toughened adhesives must have good durability performance under hot/wet conditions and other environmental exposure conditions. The effect of post-bond humidity on the paste

adhesive was evaluated by exposing individually cut, wide area lap shear specimens to air at 71°C and 100% relative humidity (RH) for 14 days, or exposing them at 49°C and 100% RH for 30 days. Table 10 shows the results for bonded metal specimens, which were formed using a two-part adhesive composed of Part A-1 and Part B-1, mix ratio 2:1. As shown in Table 10, the paste adhesive demonstrates excellent retention of shear strength after post-bond humidity exposures. The failure modes for the hot/wet exposed specimens were mainly cohesive or thin cohesive reflecting the good humidity resistance of the material.

TABLE 10

Metal Bonding WALS (psi) @Test Temperature	Dry	Wet -14 day @160°F-100% RH	Exposed -30 day @120°F-100% RH
180°F	3627	3418	3757

[0066] The composite bonding performance of the same two-part adhesive (Part A-1/Part B-1, mix ratio 2:1) was determined using WALS and double cantilever beam (G_{IC}) test as described in Example 3. Curing was carried out at 200°F for 2 hours. The results after aging exposure to humidity are shown in Table 11.

TABLE 11

Composite Bonding WALS (psi) @Test Temperature	Dry	Wet -14 day @160°F-100% RH	Exposed -30 day @120°F-100% RH
180°F	3356	3345	3449
160°F	3759	3977	3790

Example 6

One-Part System

[0067] Table 12 shows exemplary one-part adhesive formulations 1A-1E. All amounts are expressed in parts.

TABLE 12

<i>Components</i>	1A	1B	1C	1D	1E
~25 wt.% CSR particles (particle size=70-90 nm) dispersed in liquid Bisphenol A diglycidyl ether	55	57	50	52	53
Triglycidyl ether of aminophenol	10	11	9.3	9.7	16.5
Low viscosity cycloaliphatic diepoxide	6.9	7.1	6.2	6.5	-
Tetraglycidyl ether of methylene dianiline	3.4	3.6	3.1	3.1	3.3
Core-Shell Rubber (CSR) particles (ave. particle size 200 nm)	4.1	4.3	3.7	3.9	4
PES-PEES thermoplastic polymer	-	-	-	-	4
Low MW adduct of epichlorohydrin & bisphenol A	6.9	7.1	6.2	6.5	6.6
Elastomer-modified epoxy functional adduct	3.5	3.5	3.1	3.2	3.3
Dicyandiamide	4.2	4.2	3.7	3.7	4
Bisurea	4.8	-	1.2	1.2	4
Hydrophobic fumed silica	1.3	1.3	1.3	1.3	2
2-ethyl-4-methyl-imidazole	0	2.8	0	0	-
Intelimer encapsulated 2-ethyl-4-methyl-imidazole	0	0	12	0	-
Modified aliphatic. amine	0	0	0	6.5	-
Total	100.1	101.9	99.8	97.6	100.7

[0068] The metal bonding properties of Formulations 1A-1E were measured as described in Example 3. The results are shown in Table 13.

TABLE 13

Metal Bonding Property	1A	1B	1C	1D	1E
Curing Cycles	200°F-2 hrs	200°F-2 hrs	200°F-2 hrs	200°F-2 hrs	200F-1.5 hrs
WALS @RT, psi	4285	4150	2905	3137	4129
WALS @180°F, psi	3857	3810	3111	2581	3560
WALS @250°F, psi	2617	2655	1850	1210	2882
FR Peel @RT, pli	36	31	45	21	28
T _g (Dry,TMA) -°C	114	116	108	78	113

[0069] The composite bonding properties of Formulation 1A were measured as described in Example 3. For WALS measurement, polyester peel ply was used for surface treatment prior to bonding, and for G_{1c} measurement, the composite surface was treated by plasma prior to bonding. The results are shown in Table 14.

TABLE 14

Composite bonding property		Composite Surface treatment	200°F/2 hrs
WALS, psi	75°F	Polyester peel ply	6112
	180°F	Polyester peel ply	4173
	250°F	Polyester peel ply	3120
G _{1c} (in-lb/in ²)		Air plasma treated surface	4.1

[0070] Ranges disclosed herein are inclusive and independently combinable (e.g., ranges of “up to approximately 25 wt%, or, more specifically, approximately 5 wt% to approximately 20 wt%”, is inclusive of the endpoints and all intermediate values of the ranges of “approximately 5 wt% to approximately 25 wt%,” etc).

[0071] While various embodiments are described herein, it will be appreciated from the specification that various combinations of elements, variations of embodiments disclosed herein may be made by those skilled in the art, and are within the scope of the present disclosure. In addition, many modifications may be made to adapt a particular situation or material to the teachings of the embodiments disclosed herein without departing from

essential scope thereof. Therefore, it is intended that the claimed invention not be limited to the particular embodiments disclosed herein, but that the claimed invention will include all embodiments falling within the scope of the appended claims.

What is claimed is:

1. A structural adhesive curable at or below 200°F (93°C), said structural adhesive being formed from mixing a resinous part (A) with a catalyst part (B),

the resinous part (A) comprising:

at least two different multifunctional epoxy resins with different epoxy functionality selected from di-functional, tri-functional, and tetra-functional epoxy resins;

smaller core-shell rubber particles having particle sizes less than 100 nm and larger core-shell rubber particles having particle sizes greater than 100nm, the weight ratio of smaller core-shell rubber particles to larger core-shell rubber particles being in the range of 3:1 to 5:1;

at least one of an elastomeric polymer with a functional group capable of reacting with the multifunctional epoxy resins and a polyethersulfone polymer having an average molecular weight in the range of 8,000-14,000;

inorganic filler particles in an effective amount to control rheology of the resinous part;

the catalyst part (B) comprising:

at least one amine curing agent selected from a group consisting of: cycloaliphatic amines, amine-terminated piperazine, polyethylene polyamine, imidazoles, and combinations thereof; and

inorganic filler particles present in an effective amount to control rheology of the catalyst part,

wherein the weight ratio of part (A) to part (B) is within the range of 3:2 to 10:2, and

wherein, upon curing in the temperature range of 65-93°C (150-200°F), the structural adhesive has a glass transition temperature (T_g) of greater than 95°C (203°F), a lap shear strength of 33-37 MPa at 20°C-25°C and 24-27 MPa at 82°C, 15-18 MPa at 121°C according to ASTM D3165, a peel strength of 250-350 Nm/m at 20°C-25°C according to ASTM D3167.

2. The structural adhesive of claim 1, wherein the weight ratio of part (A) to part (B) is 2:1.
3. The structural adhesive of claim 1 or 2, wherein the amine curing agent is dicyclohexylamine.
4. The structural adhesive of any one of the preceding claims, wherein tetraethylene pentamine (TEPA) and amine-terminated piperazine are used as amine curing agents.
5. The structural adhesive of any one of the preceding claims, wherein the inorganic filler particles in the resinous part (A) are hydrophobic silica particles having surface area in the range of 90-380 m²/g, and the inorganic filler particles in the catalyst part (B) are hydrophilic silica particles having surface area in the range of 90-380 m²/g.
6. The structural adhesive of any one of the preceding claims, wherein the resinous part (A) comprises a combination of non-cycloaliphatic difunctional epoxy resin, trifunctional epoxy resin, tetrafunctional epoxy resin, and cycloaliphatic multifunctional epoxy resin.
7. The structural adhesive of any one of the preceding claims, wherein at least one multifunctional epoxy resin is a cycloaliphatic epoxy.
8. The structural adhesive of claim 1, wherein the polyethersulfone polymer is a polyethersulfone-polyetherethersulfone (PES-PEES) copolymer.
9. The structural adhesive of any one of the preceding claims, wherein the elastomeric polymer is selected from the group consisting of carboxyl-terminated butadiene nitrile (CTBN), amine-terminated butadiene acrylonitrile (ATBN), epoxy-elastomer adduct formed by reacting epoxy resin with carboxyl-terminated butyl nitrile elastomer or ATBN elastomer.
10. The structural adhesive of any one of the preceding claims, wherein the smaller core-shell rubber particles have particle sizes within the range of 50-90 nm and the larger core-shell rubber particles have particle sizes within the range of 150-300 nm.
11. The structural adhesive of any one of the preceding claims has a glass transition temperature (T_g) of greater than 120°C upon curing at 93°C.

12. A laminate structure comprising a first substrate bonded to a second substrate and a cured structural adhesive film between the first and second substrates,

wherein the structural adhesive film has a thickness of 10-80 mils, a glass transition temperature (T_g) of greater than 95°C (203°F) upon curing in the temperature range of 65-93°C (150-200°F), a lap shear strength of 33-37 MPa at 20-25°C and 24-27 MPa at 82°C, 15-18 MPa at 121°C according to ASTM D3165 testing, a peel strength of 250-350 Nm/m (or 50-75 lbs/in) at 20-25°C according to ASTM D3167, and

wherein the structural adhesive film is formed from a composition comprising:

at least two different multifunctional epoxy resins with different epoxy functionality selected from di-functional, tri-functional, and tetra-functional epoxy resins;

smaller core-shell rubber particles having particle sizes less than 100 nm and larger core-shell rubber particles having particle sizes greater than 100nm, the weight ratio of smaller core-shell rubber particles to larger core-shell rubber particles being in the range of 3:1 to 5:1;

at least one of an elastomeric polymer with a functional group capable of reacting with the multifunctional epoxy resins and a polyethersulfone polymer having an average molecular weight in the range of 8,000-14,000;

an amine curing agent selected from a group consisting of: cycloaliphatic amines, amine-terminated piperazine, polyethylene polyamine, imidazoles, and combinations thereof; and

inorganic filler particles.

13. The laminate structure of claim 12, wherein the first and second substrates are metal substrates.

14. The laminate structure of claim 13, wherein the first and second substrates are made of aluminum or aluminum alloy.

15. The laminate structure of claim 12, wherein the first substrate is a metal substrate and the second substrate is a fiber-reinforced resin composite.

16. The laminate structure of claim 12, wherein the first and second substrates are fiber-reinforced resin composite substrates comprising reinforcing fibers and a resin matrix, and the adhesive film exhibits a fracture toughness of greater than 650 J/m^2 (3.5 in-lb/in^2) according to ASTM D5528.
17. The laminate structure of any one of claims 12-16, wherein the adhesive film exhibits a fracture toughness in the range of $651\text{-}1500 \text{ J/m}^2$ (3.5 to 8.1 in-lb/in^2).
18. The laminate structure of any one of claims 12-17, wherein the T_g and lap shear strength remain substantially unchanged after aging exposure to air containing relative humidity of 100% at 71°C for 14 days or at 49°C for 30 days.
19. A laminate structure comprising a first substrate bonded to a second substrate and a cured adhesive film formed there between, the adhesive film being formed from an adhesive composition comprising:
- at least two different multifunctional epoxy resins selected from difunctional, tri-functional, and tetrafunctional epoxy resins;
 - smaller core-shell rubber particles having particle sizes less than 100 nm and a larger core-shell rubber particles having particle sizes greater than 100nm, the weight ratio of the smaller particles to the larger particles being in the range of 3:1 to 5:1;
 - at least one of an elastomeric polymer with an epoxy functional group and a polyethersulfone polymer having an average molecular weight in the range of 8,000-14,000;
 - inorganic filler particles; and
 - a latent amine-based curing agent,
- wherein the cured adhesive film has the following properties: a glass transition temperature (T_g) of greater than 100°C (212°F) upon curing in the temperature range of 65°C - 93°C (150°F - 200°F), a lap shear strength of 28-40 MPa at $20\text{-}25^\circ\text{C}$ and 25-28 MPa at 82°C , 17-21 MPa at 121°C according to ASTM D3165, a peel strength of 150-250 Nm/m (30-50 lbs/in) at 20°C - 25°C according to ASTM D3167.

20. The laminate structure of claim 19, wherein the adhesive composition further comprises at least one of an imidazole and an aliphatic amine.
21. The laminate structure of claim 19 or 20, wherein at least one of the multifunctional epoxy resins is a cycloaliphatic multifunctional epoxy resin.
22. The laminate structure of any one of claims 19-21, wherein the adhesive composition further comprises an imidazole-based catalyst encapsulated within a crystalline polymer network.
23. The laminate structure of any one of claims 19-21, wherein the adhesive composition further comprises an aliphatic amine having an amine value (mg KOH/g) in the range of 180-300, and an equivalent weight (H) in the range of 35-90.
24. A structural adhesive curable at or below 200°F (93°C), said structural adhesive comprising two separate parts,

a resinous part (A) comprising:

a non-cycloaliphatic difunctional epoxy resin; at least one of trifunctional and tetrafunctional epoxy resins; a cycloaliphatic epoxy resin with epoxy functionality of more than one;

smaller core-shell rubber particles having particle sizes less than 100 nm and larger core-shell rubber particles having particle sizes greater than 100nm, the weight ratio of smaller core-shell rubber particles to larger core-shell rubber particles being in the range of 3:1 to 5:1;

at least one of an elastomeric polymer with an epoxy functional group and a polyethersulfone polymer having an average molecular weight in the range of 8,000-14,000;

inorganic filler particles in an effective amount to control rheology of the resinous part;

a catalyst part (B) comprising:

at least one amine curing agent selected from a group consisting of: cycloaliphatic amines, amine-terminated piperazines, polyethylene polyamines, imidazoles, and combinations thereof; and

inorganic filler particles present in an effective amount to control rheology of the catalyst part,

wherein the weight ratio of part (A) to part (B) is within the range of 3:2 to 10:2,

wherein the resinous part (A) has a storage viscosity in the range of 500-1000 Poise at 20-25°C (or 68-77°F) and a density in the range of 1.0-1.2 g/cc, and the catalyst part (B) has a storage viscosity in the range of 150-300 Poise at 20-25°C (68-77°F) and a density in the range of 0.9-1.1 g/cc,

wherein said structural adhesive has a mixed viscosity of 200-600 Poise at 20-25°C (68-77°F) after mixing part (A) and part (B), and

wherein, upon curing at 93°C, said adhesive has a glass transition temperature (T_g) of greater than 120°C (248°F).