

STRUCTURAL ADHESIVE COMPOSITIONS

FIELD OF THE INVENTION

[0001] The present invention relates to structural adhesive compositions and more particularly to 1K and 2K structural adhesive compositions.

BACKGROUND INFORMATION

[0002] Structural adhesives are utilized in a wide variety of applications to bond together two or more substrate materials. For example, structural adhesives may be used for binding together wind turbine blades or binding together automotive structural components.

[0003] The present invention is directed towards one-component (1K) and two-component (2K) adhesive compositions that provide sufficient bond strength, are easy to apply, and, where applicable, have sufficiently long pot lives for use in bonding together substrate materials.

SUMMARY OF THE INVENTION

[0004] One embodiment of the present invention discloses a composition comprising (a) a first component comprising (i) an epoxy-adduct formed as a reaction product of reactants comprising a first epoxy compound, a polyol, and an anhydride and/or a diacid; (b) rubber particles having a core/shell structure and/or graphenic carbon particles; and (c) a second component that chemically reacts with the first component at ambient or slightly thermal conditions.

[0005] Another embodiment of the present invention discloses a composition comprising (a) an epoxy-capped flexibilizer; and (b) a heat-activated latent curing agent; and optionally (c) rubber particles having a core/shell structure and/or graphenic carbon particles; (d) an epoxy/CTBN adduct; and/or (e) an epoxy/dimer acid adduct.

BRIEF DESCRIPTION OF FIGURES

[0006] Figure 1 is a perspective view of a Teflon template assembly for evaluating tensile properties of structural adhesives according to an exemplary embodiment of the present invention.

DETAILED DESCRIPTION

[0007] For purposes of the following detailed description, it is to be understood that the invention may assume various alternative variations and step sequences except where expressly specified to the contrary. Moreover, other than in any operating examples, or where otherwise indicated, all numbers expressing, for example, quantities of ingredients used in the specification and claims, are to be understood as being modified in all instances by the term “about”. Accordingly, unless indicated to the contrary, the numerical parameters set forth in the following specification and attached claims are approximations that may vary depending upon the desired properties to be obtained by the present invention. At the very least, and not as an attempt to limit the application of the doctrine of equivalents to the scope of the claims, each numerical parameter should at least be construed in light of the number of reported significant digits and by applying ordinary rounding techniques.

[0008] Notwithstanding that the numerical ranges and parameters setting forth the broad scope of the invention are approximations, the numerical values set forth in the specific examples are reported as precisely as possible. Any numerical value, however, inherently contains certain errors necessarily resulting from the standard variation found in their respective testing measurements.

[0009] Also, it should be understood that any numerical range recited herein is intended to include all sub-ranges subsumed therein. For example, a range of “1 to 10” is intended to include all sub-ranges between (and including) the recited minimum value of 1 and the recited maximum value of 10, that is, having a minimum value equal to or greater than 1 and a maximum value of equal to or less than 10.

[0010] In this application, the use of the singular includes the plural and plural encompasses singular, unless specifically stated otherwise. In addition, in this application, the use of “or” means “and/or” unless specifically stated otherwise, even though “and/or” may be explicitly used in certain instances.

[0011] As noted above, in general, the present invention discloses 1K (“One-Component”) and 2K (“Two-Component”) structural adhesive compositions that are used to

bond together two substrate materials for a wide variety of potential applications in which the bond between the substrate materials provides particular mechanical properties related to elongation, tensile strength, lap shear strength, T-peel strength, modulus, or impact peel strength. The structural adhesive is applied to either one or

both of the materials being bonded. The pieces are aligned and pressure and spacers may be added to control bond thickness. For 2K adhesives, the curing begins upon the mixing together of the components at ambient or slightly thermal temperatures. By contrast for 1K adhesives, the adhesive is cured using an external source such as an oven (or other thermal means) or through the use of actinic radiation (UV light, etc.).

[0012] Suitable substrate materials that may be bonded by the structural adhesive compositions include, but are not limited to, materials such as, metals or metal alloys, natural materials such as wood, polymeric materials such as hard plastics, or composite materials. The structural adhesives of the present invention are particularly suitable for use in various automotive applications and for use in wind turbine technology.

[0013] As noted above, the structural adhesive compositions of the present invention are suitable for use in bonding the two half shells of wind turbine blades. In this application, for a 2K adhesive, the mixed adhesive composition is applied along the edges of one or both of the half shells of the wind turbine blades. The half shells are then pressed together and the 2K adhesive is allowed to cure for a number of hours at ambient or slightly thermal conditions. A thermal blanket (at about 70°C) may be applied to the half shells to aid in the curing process. By contrast, for 1K adhesives, as opposed to a system in which the components substantially cure upon mixing, an oven or actinic radiation source is used to complete the curing process.

[0014] The half shells, or other components of wind turbine blades, may be formed from metals such as aluminum, metal alloys such as steel, woods such as wood, polymeric materials such as hard plastics, or composite materials such as fiber reinforced plastics. In one embodiment, the half shells are formed from fiberglass composites or carbon fiber composites.

[0015] The 2K structural adhesives of the present invention are formed from two chemical components, namely, a first component and a second component which are mixed just prior to application. The first component (i.e., an epoxy component), in certain embodiments, comprises an epoxy-adduct and another epoxy compound, or second epoxy compound. The second component, in certain embodiments, comprises a curing component that reacts with the first component to form a bond that provides the substrates to which it is applied with desirable bonding characteristics. In certain

embodiments, the curing component is an amine compound, although other curing components such as sulfide curing components may alternatively be utilized.

[0016] The equivalent ratio of amine to epoxy in the adhesive composition may vary from about 0.5:1 to about 1.5:1, such as from 1.0:1 to 1.25:1. In certain embodiments, the equivalent ratio of amine to epoxy is slightly above 1:1. As described herein, the equivalents of epoxy used in calculating the equivalent ratio of epoxy are based on the epoxy equivalent weight of the first component, and the equivalents of amine used in calculating the equivalent ratio of amine are based on the amine hydrogen equivalent weight (AHEW) of the second component.

[0017] In one embodiment, the epoxy-adduct is formed as the reaction product of reactants comprising a first epoxy compound, a polyol, and an anhydride.

[0018] In another embodiment, the epoxy-adduct is formed as the reaction product of reactants comprising a first epoxy compound, a polyol, and a diacid.

[0019] In still another embodiment, the epoxy-adduct is formed as the reaction product of reactants comprising a first epoxy compound, a polyol, an anhydride, and a diacid.

[0020] In these embodiments, the epoxy-adduct comprises from 3 to 50 weight percent such as from 3 to 25 weight percent of the first component, while the second epoxy compound comprises from 50 to 97 weight percent such as from 75 to 97 weight percent of the first component.

[0021] Useful first epoxy compounds that can be used to form the epoxy-adduct include polyepoxides. Suitable polyepoxides include polyglycidyl ethers of Bisphenol A, such as Epon[®] 828 and 1001 epoxy resins, and Bisphenol F diepoxides, such as Epon[®] 862, which are commercially available from Hexion Specialty Chemicals, Inc. Other useful polyepoxides include polyglycidyl ethers of polyhydric alcohols, polyglycidyl esters of polycarboxylic acids, polyepoxides that are derived from the epoxidation of an olefinically unsaturated alicyclic compound, polyepoxides containing oxyalkylene groups in the epoxy molecule, and epoxy novolac resins. Still other non-limiting first epoxy compounds include epoxidized Bisphenol A novolacs, epoxidized phenolic novolacs, epoxidized cresylic novolac, and triglycidyl *p*-aminophenol bismaleimide.

[0022] Useful polyols that may be used to form the epoxy-adduct include diols, triols, tetraols and higher functional polyols. The polyols can be based on a polyether chain derived from ethylene glycol, propylene glycol, butylenes glycol,

hexylene glycol and the like and mixtures thereof. The polyol can also be based on a polyester chain derived from ring opening polymerization of caprolactone. Suitable polyols may also include polyether polyol, polyurethane polyol, polyurea polyol, acrylic polyol, polyester polyol, polybutadiene polyol, hydrogenated polybutadiene polyol, polycarbonate polyols, polysiloxane polyol, and combinations thereof. Polyamines corresponding to polyols can also be used, and in this case, amides instead of carboxylic esters will be formed with acids and anhydrides.

[0023] Suitable diols that may be utilized to form the epoxy-adduct are diols having a hydroxyl equivalent weight of between 30 and 1000. Exemplary diols having a hydroxyl equivalent weight from 30 to 1000 include diols sold under the trade name Terathane[®], including Terathane[®] 250, available from Invista. Other exemplary diols having a hydroxyl equivalent weight from 30 to 1000 include ethylene glycol and its polyether diols, propylene glycol and its polyether diols, butylenes glycol and its polyether diols, hexylene glycols and its polyether diols, polyester diols synthesized by ring opening polymerization of caprolactone, and urethane diols synthesized by reaction of cyclic carbonates with diamines. Combination of these diols and polyether diols derived from combination various diols described above could also be used. Dimer diols may also be used including those sold under trade names Pripol[®] and Solvermol[™] available from Cognis Corporation.

[0024] Polytetrahydrofuran-based polyols sold under the trade name Terathane[®], including Terathane[®] 650, available from Invista, may be used. In addition, polyols based on dimer diols sold under the trade names Pripol[®] and Empol[®], available from Cognis Corporation, or bio-based polyols, such as the tetrafunctional polyol Agrol 4.0, available from BioBased Technologies, may also be utilized.

[0025] Useful anhydride compounds to functionalize the polyol with acid groups include hexahydrophthalic anhydride and its derivatives (e.g. methyl hexahydrophthalic anhydride); phthalic anhydride and its derivatives (e.g. methyl phthalic anhydride); maleic anhydride; succinic anhydride; trimellitic anhydride; pyromellitic dianhydride (PMDA); 3,3', 4,4'-oxydiphthalic dianhydride (ODPA); 3,3', 4,4'-benzophenone tetracarboxylic dianhydride (BTDA); and 4,4'-diphthalic (hexamfluoroisopropylidene) anhydride (6FDA). Useful diacid compounds to functionalize the polyol with acid groups include phthalic acid and its derivatives

(e.g. methyl phthalic acid), hexahydrophthalic acid and its derivatives (e.g. methyl hexahydrophthalic acid), maleic acid, succinic acid, adipic acid, etc. Any diacid and anhydride can be used; however, anhydrides are preferred.

[0026] In one embodiment, the polyol comprises a diol, the anhydride and/or diacid comprises a monoanhydride or a diacid, and the first epoxy compound comprises a diepoxy compound, wherein the mole ratio of diol, monoanhydride (or diacid), and diepoxy compounds in the epoxy-adduct may vary from 0.5:0.8:1.0 to 0.5:1.0:6.0.

[0027] In another embodiment, the polyol comprises a diol, the anhydride and/or diacid comprises a monoanhydride or a diacid, and the first epoxy compound comprises a diepoxy compound, wherein the mole ratio of diol, monoanhydride (or a diacid), and diepoxy compounds in the epoxy-adduct may vary from 0.5:0.8:0.6 to 0.5:1.0:6.0.

[0028] In another embodiment, the second epoxy compound of the first component is a diepoxide compound that has an epoxy equivalent weight of between about 150 and about 1000. Suitable diepoxides having an epoxy equivalent weight of between about 150 and about 1000 include polyglycidyl ethers of Bisphenol A, such as Epon[®] 828 and 1001 epoxy resins, and Bisphenol F diepoxides, such as Epon[®] 862, which are commercially available from Hexion Specialty Chemicals, Inc.

[0029] In another embodiment, the second epoxy compound of the first component is a diepoxide compound or a higher functional epoxides (collectively, a "polyepoxide"), including polyglycidyl ethers of polyhydric alcohols, polyglycidyl esters of polycarboxylic acids, polyepoxides that are derived from the epoxidation of an olefinically unsaturated alicyclic compound, polyepoxides containing oxyalkylene groups in the epoxy molecule, and epoxy novolac resins.

[0030] Still other non-limiting second epoxy compounds include epoxidized Bisphenol A novolacs, epoxidized phenolic novolacs, epoxidized cresylic novolac, and triglycidyl *p*-aminophenol bismaleimide.

[0031] In another embodiment, the second epoxy compound of the first component comprises an epoxy-dimer acid adduct. The epoxy-dimer acid adduct may be formed as the reaction product of reactants comprising a diepoxide compound (such as a Bisphenol A epoxy compound) and a dimer acid (such as a C₃₆ dimer acid).

[0032] In another embodiment, the second epoxy compound of the first component comprises a carboxyl-terminated butadiene-acrylonitrile copolymer modified epoxy compound.

[0033] Useful amine compounds that may be used include primary amines, secondary amines, tertiary amines, and combinations thereof. Useful amine compounds that can be used include diamines, triamines, tetramines, and higher functional polyamines.

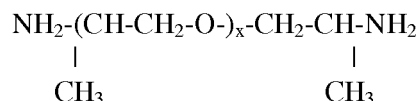
[0034] Suitable primary amines include alkyl diamines such as 1,2-diaminoethane, 1,3-diaminopropane, 1,4-diaminobutane, neopentyl diamine, 1,8-diaminooctane, 1,10-diaminodecane, 1,12-diaminododecane and the like; 1,5-diamino-3-oxapentane, diethylene-triamine, triethylenetetramine, tetraethylenepentamine and the like; cycloaliphatic diamines such as 1,2-bis(aminomethyl)cyclohexane, 1,3-bis(aminomethyl)cyclohexane, 1,4-bis(aminomethyl)cyclohexane, bis(aminomethyl)norbornane and the like; aromatic alkyl diamines such as 1,3-bis(aminomethyl)benzene (*m*-xylene diamine) and 1,4-bis(aminomethyl)benzene (*p*-xylenediamine) and their reaction products with epichlorohydrin such as Gaskamine 328 and the like; amine-terminated polyethyleneglycol such as Huntsman Corporation Jeffamine ED series and amine-terminated polypropylene glycol such as Huntsman Corporation Jeffamine D series; and amine-terminated polytetrahydrofuran such as Huntsman Jeffamine EDR series. Primary amines having a functionality higher than 2 include, for example, the Jeffamine T series, available from Huntsman Corporation, which are amine-terminated propoxylated trimethylolpropane or glycerol and aminated propoxylated pentaerythritols.

[0035] Still other amines that may be utilized include isophorone diamine, methenediamine, 4,8-diamino-tricyclo[5.2.1.0]decane and N-aminoethylpiperazine.

[0036] In certain embodiments, the amine compounds comprise triethylenetetramine (TETA), isophorone diamine, 1,3 bis(aminomethyl)cyclohexane, and polypropylene oxide-based polyetheramines.

[0037] In certain embodiments, the polypropylene oxide-based polyetheramines comprise the Jeffamine series products available from Huntsman Chemical of Houston, Texas. Jeffamine series products are polyetheramines characterized by repeating oxypropylene units in their respective structures.

[0038] One exemplary class of Jeffamine products, the so-called “Jeffamine D” series products, are amine terminated PPGs (propylene glycols) with the following representative structure (Formula (I)):



(I)

wherein x is 2 to 70.

[0039] In certain embodiments, Jeffamine D-230 is one D series product that is used. Jeffamine D-230 has an average molecular weight of about 230 (wherein x is 2.5) and an amine hydrogen equivalent weight (AHEW) of about 60. Other exemplary Jeffamine D series products that may be used according to Formula (I) include those wherein x is from 2.5 to 68.

[0040] Another series of polypropylene oxide-based polyetheramines that are used are predominantly tetrafunctional, primary amines with a number average molecular weight from 200 to 2000, and more preferably from 600 to 700, and having an AHEW of greater than 60, and more preferably from 70 to 90. Jeffamine XTJ-616 is one such polypropylene oxide-based polyetheramines that may be utilized in the present invention. Jeffamine XTJ-616 has a number average molecular weight of about 660 and an AHEW of 83.

[0041] Higher AHEW amine compounds, such as Jeffamine XTJ-616 and Jeffamine D-230, may be particularly useful in 2K adhesive composition wherein a longer pot life is desired. Conventional tetramines, such as triethylenetetramine, with lower AHEWS have substantially shorter pot lives by comparison. This present invention thus provides a way to manipulate pot life with tetrafunctional amines such as Jeffamine XTJ-616.

[0042] In still another embodiment, reinforcement fillers may be added to the adhesive composition as a part of the first component or as a part of the second component, or both.

[0043] Useful reinforcement fillers that may be introduced to the adhesive composition to provide improved mechanical properties include fibrous materials

such as fiberglass, fibrous titanium dioxide, whisker type calcium carbonate (aragonite), and carbon fiber (which includes graphite and carbon nanotubes). In addition, fiber glass ground to 5 microns or wider and to 50 microns or longer may also provide additional tensile strength. More preferably, fiber glass ground to 5 microns or wider and to 100-300 microns in length is utilized. Preferably, such reinforcement fillers, if utilized, comprise from 0.5 to 25 weight percent of the adhesive composition.

[0044] In still another embodiment, fillers, thixotropes, colorants, tints and other materials may be added to the first or second component of the adhesive composition.

[0045] Useful thixotropes that may be used include untreated fumed silica and treated fumed silica, Castor wax, clay, and organo clay. In addition, fibers such as synthetic fibers like Aramid[®] fiber and Kevlar[®] fiber, acrylic fibers, and engineered cellulose fiber may also be utilized.

[0046] Useful colorants or tints may include red iron pigment, titanium dioxide, calcium carbonate, and phthalocyanine blue.

[0047] Useful fillers that may be used in conjunction with thixotropes may include inorganic fillers such as inorganic clay or silica.

[0048] In still another embodiment, if needed, a catalyst may be introduced to the adhesive composition, preferably as a part of the second component, to promote the reaction of the epoxide groups of first component and amine groups of the second component.

[0049] Useful catalysts that may be introduced to the adhesive composition include Ancamide[®] products available from Air Products and products marketed as "Accelerators" available from the Huntsman Corporation. One exemplary catalyst is piperazine-base Accelerator 399 (AHEW: 145) available from the Huntsman Corporation. When utilized, such catalysts comprise between 0 and about 10 percent by weight of the total adhesive composition.

[0050] In addition, a catalytic effect may be expected from the reaction product of epichlorohydrin from the first component and the amine compound from the second component in an equivalent ratio of 1:1. An example of such a product is Tetrad[®] and Tetrad[®]C available from Mitsubishi Gas Chemical Corporation.

[0051] In certain embodiments, rubber particles having a core/shell structure may be included in the 2K structural adhesive formulation.

[0052] Suitable core-shell rubber particles are comprised of butadiene rubber; however, other synthetic rubbers could be employed; such as styrene-butadiene and acrylonitrile-butadiene and the like. The type of synthetic rubber and the rubber concentration should not be limited as long as the particle size falls under the specified range as illustrated below.

[0053] In certain embodiments, the average particle size of the rubber particles may be from about 0.02 to 500 microns (20 nm to 500,000 nm).

[0054] In certain embodiments, the core/shell rubber particles are included in an epoxy carrier resin for introduction to the 2K adhesive composition. Suitable finely dispersed core-shell rubber particles in an average particle size ranging from 50 nm to 250 nm are master-batched in epoxy resin such as aromatic epoxides, phenolic novolac epoxy resin, bisphenol A and bisphenol F diepoxide and aliphatic epoxides, which include cyclo-aliphatic epoxides at concentration ranging from 20 to 40 weight percent. Suitable epoxy resins may also include a mixture of epoxy resins.

[0055] Exemplary non-limiting commercial core/shell rubber particle products using poly(butadiene) rubber particles having an average particle size of 100 nm that may be utilized in the 2K adhesive composition includes Kane Ace MX 136 (a core-shell poly(butadiene) rubber dispersion (25%) in bisphenol F), Kane Ace MX 153 (a core-shell poly(butadiene) rubber dispersion (33%) in Epon[®] 828), Kane Ace MX 257 (a core-shell poly(butadiene) rubber dispersion (37%) in bisphenol A), and Kane Ace MX 267 (a core-shell poly(butadiene) rubber dispersion (37%) in bisphenol F), each available from Kaneka Texas Corporation.

[0056] Exemplary non-limiting commercial core/shell rubber particle products using styrene-butadiene rubber particles having an average particle size of 100 nm that may be utilized in the 2K adhesive composition includes Kane Ace MX 113 (a core-shell styrene-butadiene rubber dispersion (33%) in low viscosity bisphenol A), Kane Ace MX 125 (a core-shell styrene-butadiene rubber dispersion (25%) in bisphenol A), Kane Ace MX 215 (a core-shell styrene-butadiene rubber dispersion (25%) in DEN-438 phenolic novolac epoxy), and Kane Ace MX 416 (a core-shell styrene-butadiene rubber dispersion (25%) in MY-721 multi-functional epoxy), Kane Ace MX 451 (a core-shell styrene-butadiene rubber dispersion (25%) in MY-0510 multi-functional epoxy), Kane Ace MX 551 (a core-shell styrene-butadiene rubber dispersion (25%) in Synasia 21 Cyclo-aliphatic Epoxy), Kane Ace MX 715 (a core-

shell styrene-butadiene rubber dispersion (25%) in polypropylene glycol (MW 400)), each available from Kaneka Texas Corporation.

[0057] In certain embodiments, the amount of core/shell rubber particles included in the 2K adhesive formulation is from 0.1 to 10 weight percent, such as from 0.5 to 5 weight percent, based on the total weight of the 2K coating composition.

[0058] In still other embodiments, graphenic carbon particles may be included in the 2K structural adhesive formulation.

[0059] Graphene, as defined herein, is an allotrope of carbon, whose structure is one-atom-thick planar sheets of sp^2 -bonded carbon atoms that are densely packed in a honeycomb crystal lattice. Graphene is stable, chemically inert and mechanically robust under ambient conditions. As used herein, the term “graphenic carbon particles” means carbon particles having structures comprising one or more layers of one-atom-thick planar sheets of sp^2 -bonded carbon atoms that are densely packed in a honeycomb crystal lattice. As such, the term “graphenic carbon particles” includes one layer thick sheets (i.e. graphene) and multilayer thick sheets. The average number of stacked layers may be less than 100, for example, less than 50. In certain embodiments, the average number of stacked layers is 30 or less. The graphenic carbon particles may be substantially flat, however, at least a portion of the planar sheets may be substantially curved, curled or buckled. The particles typically do not have a spheroidal or equiaxed morphology.

[0060] In certain embodiments, the graphenic carbon particles utilized in the present invention have a thickness, measured in a direction perpendicular to the carbon atom layers, of no more than 10 nanometers, such as no more than 5 nanometers, or, in certain embodiments, no more than 3 or 1 nanometers. In certain embodiments, the graphenic carbon particles may be from 1 atom layer to 10, 20 or 30 atom layers thick, or more. The graphenic carbon particles may be provided in the form of ultrathin flakes, platelets or sheets having relatively high aspect ratios of greater than 3:1, such as greater than 10:1.

[0061] In certain embodiments, graphenic carbon particles are roll-milled in an epoxy carrier resin, such as Epon[®] 828, for introduction to the 2K adhesive composition. In one exemplary embodiment, a master-batch of graphenic carbon particles/added epoxy resin is formed by milling the graphenic carbon particles into the epoxy resin at 10 weight percent or higher concentration. A dispersing method

includes typical pigment grind mills such as three-roll mill, Eiger mill, Netsch/Premier mill and the like.

[0062] One exemplary graphenic carbon particle material that may be used in the 2K adhesive formulation is XG Sciences Graphene Grade C, which has a surface area of 750 m²/g, an average thickness about 2 nano-meters, and an average diameter less than 2 microns.

[0063] In certain embodiments, the amount of graphenic carbon particles included in the 2K adhesive formulation is sufficient to provide increased tensile modulus while maintaining a glass transition temperature as compared with formulations not including the graphenic carbon particles.

[0064] In certain embodiments, the amount of graphenic carbon particles included in the 2K adhesive formulation is from about 0.5 to 25 weight percent based on the total weight of the 2K coating composition.

[0065] As also noted above, in certain embodiments, the 1K structural adhesives of the present invention comprise: (a) an epoxy-capped flexibilizer; and (b) a heat-activated latent curing agent. In certain other embodiments, the 1K structural adhesives may further comprise one or more of the following components: (c) an epoxy/CTBN (carboxy-terminated butadiene acrylonitrile polymer) adduct; (d) an epoxy/dimer acid adduct; (e) rubber particles having a core/shell structure; and (f) graphenic carbon particles. Each component (a)-(e) is described further below.

[0066] In certain embodiments, the (a) epoxy-capped flexibilizer is formed as the reaction product of reactants comprising a first epoxy compound, a polyol, and an anhydride and/or a diacid (i.e. an anhydride, a diacid, or both an anhydride and a diacid may be part of the reaction product).

[0067] Useful epoxy compounds that can be used include polyepoxides. Suitable polyepoxides include polyglycidyl ethers of Bisphenol A, such as Epon[®] 828 and 1001 epoxy resins, and Bisphenol F diepoxides, such as Epon[®] 862, which are commercially available from Hexion Specialty Chemicals, Inc. Other useful polyepoxides include polyglycidyl ethers of polyhydric alcohols, polyglycidyl esters of polycarboxylic acids, polyepoxides that are derived from the epoxidation of an olefinically unsaturated alicyclic compound, polyepoxides containing oxyalkylene groups in the epoxy molecule, and epoxy novolac resins. Still other non-limiting first epoxy compounds include epoxidized Bisphenol A novolacs, epoxidized phenolic novolacs, epoxidized cresylic novolac, and triglycidyl *p*-aminophenol bismaleimide.

[0068] Useful polyols that may be used include diols, triols, tetraols and higher functional polyols. The polyols can be based on a polyether chain derived from ethylene glycol, propylene glycol, butylenes glycol, hexylene glycol and the like and mixtures thereof. The polyol can also be based on a polyester chain derived from ring opening polymerization of caprolactone. Suitable polyols may also include polyether polyol, polyurethane polyol, polyurea polyol, acrylic polyol, polyester polyol, polybutadiene polyol, hydrogenated polybutadiene polyol, polycarbonate polyols, polysiloxane polyol, and combinations thereof. Polyamines corresponding to polyols can also be used, and in this case, amides instead of carboxylic esters will be formed with acids and anhydrides.

[0069] Suitable diols that may be utilized are diols having a hydroxyl equivalent weight of between 30 and 1000. Exemplary diols having a hydroxyl equivalent weight from 30 to 1000 include diols sold under the trade name Terathane®, including Terathane® 250, available from Invista. Other exemplary diols having a hydroxyl equivalent weight from 30 to 1000 include ethylene glycol and its polyether diols, propylene glycol and its polyether diols, butylenes glycol and its polyether diols, hexylene glycols and its polyether diols, polyester diols synthesized by ring opening polymerization of caprolactone, and urethane diols synthesized by reaction of cyclic carbonates with diamines. Combination of these diols and polyether diols derived from combination various diols described above could also be used. Dimer diols may also be used including those sold under trade names Pripol® and Solvermol™ available from Cognis Corporation.

[0070] Polytetrahydrofuran-based polyols sold under the trade name Terathane®, including Terathane® 650, available from Invista, may be used. In addition, polyols based on dimer diols sold under the trade names Pripol® and Empol®, available from Cognis Corporation, or bio-based polyols, such as the tetrafunctional polyol Agrol 4.0, available from BioBased Technologies, may also be utilized.

[0071] Useful anhydride compounds to functionalize the polyol with acid groups include hexahydrophthalic anhydride and its derivatives (e.g. methyl hexahydrophthalic anhydride); phthalic anhydride and its derivatives (e.g. methyl phthalic anhydride); maleic anhydride; succinic anhydride; trimellitic anhydride; pyromellitic dianhydride (PMDA); 3,3', 4,4'-oxydiphthalic dianhydride (ODPA); 3,3', 4,4'-benzophenone tetracarboxylic dianhydride (BTDA); and 4,4'-diphthalic

(hexamfluoroisopropylidene) anhydride (6FDA). Useful diacid compounds to functionalize the polyol with acid groups include phthalic acid and its derivatives (e.g. methyl phthalic acid), hexahydrophthalic acid and its derivatives (e.g. methyl hexahydrophthalic acid), maleic acid, succinic acid, adipic acid, etc. Any diacid and anhydride can be used; however, anhydrides are preferred.

[0072] In one embodiment, the polyol comprises a diol, the anhydride and/or diacid comprises a monoanhydride or a diacid, and the first epoxy compound comprises a diepoxy compound, wherein the mole ratio of diol, monoanhydride (or diacid), and diepoxy compounds in the epoxy-capped flexibilizer may vary from 0.5:0.8:1.0 to 0.5:1.0:6.0.

[0073] In another embodiment, the polyol comprises a diol, the anhydride and/or diacid comprises a monoanhydride or a diacid, and the first epoxy compound comprises a diepoxy compound, wherein the mole ratio of diol, monoanhydride (or a diacid), and diepoxy compounds in the epoxy-capped flexibilizer may vary from 0.5:0.8:0.6 to 0.5:1.0:6.0.

[0074] In certain embodiments, the (a) epoxy-capped flexibilizer comprises the reaction product of reactants comprising an epoxy compound, an anhydride and/or a diacid, and a caprolactone. In certain other embodiments, a diamine and/or a higher functional amine may also be included in the reaction product in addition to the epoxy compound, caprolactone, and the anhydride and/or a diacid.

[0075] Suitable epoxy compounds that may be used to form the epoxy-capped flexibilizer include epoxy-functional polymers that can be saturated or unsaturated, cyclic or acyclic, aliphatic, alicyclic, aromatic or heterocyclic. The epoxy-functional polymers can have pendant or terminal hydroxyl groups, if desired. They can contain substituents such as halogen, hydroxyl, and ether groups. A useful class of these materials includes polyepoxides comprising epoxy polyethers obtained by reacting an epihalohydrin (such as epichlorohydrin or epibromohydrin) with a di- or polyhydric alcohol in the presence of an alkali. Suitable polyhydric alcohols include polyphenols such as resorcinol; catechol; hydroquinone; bis(4-hydroxyphenyl)-2,2-propane, i.e., bisphenol A; bis(4-hydroxyphenyl)-1,1-isobutane; 4,4-dihydroxybenzophenone; bis(4-hydroxyphenyl)-1,1-ethane; bis(2-hydroxyphenyl)-methane and 1,5-hydroxynaphthalene.

[0076] Frequently used polyepoxides include polyglycidyl ethers of Bisphenol A, such as Epon[®] 828 epoxy resin which is commercially available from Hexion

Specialty Chemicals, Inc and having a number average molecular weight of about 400 and an epoxy equivalent weight of about 185-192. Other useful polyepoxides include polyglycidyl ethers of other polyhydric alcohols, polyglycidyl esters of polycarboxylic acids, polyepoxides that are derived from the epoxidation of an olefinically unsaturated alicyclic compound, polyepoxides containing oxyalkylene groups in the epoxy molecule, epoxy novolac resins, and polyepoxides that are partially defunctionalized by carboxylic acids, alcohol, water, phenols, mercaptans or other active hydrogen-containing compounds to give hydroxyl-containing polymers.

[0077] Useful anhydride compounds that may be utilized include hexahydrophthalic anhydride and its derivatives (e.g. methyl hexahydrophthalic anhydride); phthalic anhydride and its derivatives (e.g. methyl phthalic anhydride); maleic anhydride; succinic anhydride; trimellitic anhydride; pyromellitic dianhydride (PMDA); 3,3', 4,4'-oxydiphthalic dianhydride (ODPA); 3,3', 4,4'-benzophenone tetracarboxylic dianhydride (BTDA); and 4,4'-diphthalic (hexamfluoroisopropylidene) anhydride (6FDA). Useful diacid compounds to functionalize the polyol with acid groups include phthalic acid and its derivatives (e.g. methyl phthalic acid), hexahydrophthalic acid and its derivatives (e.g. methyl hexahydrophthalic acid), maleic acid, succinic acid, adipic acid, etc. Any diacid and anhydride can be used; however, anhydrides are preferred.

[0078] Useful caprolactones that can be used include caprolactone monomer, methyl, ethyl, and propyl substituted caprolactone monomer, and polyester diols derived from caprolactone monomer. Exemplary polyester diols having a molecular weight from about 400 to 8000 include diols sold under the trade name CAPA[®], including CAPA[®] 2085, available from Perstorp.

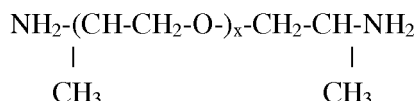
[0079] Useful diamine or higher functional amine compounds that can be used to form the epoxy-capped flexibilizer include primary amines, secondary amines, tertiary amines, and combinations thereof. Useful amine compounds that can be used include diamines, triamines, tetramines, and higher functional polyamines.

[0080] Suitable primary diamines or higher functional amines that may be used include alkyl diamines such as 1,2-diaminoethane, 1,3-diaminopropane, 1,4-diaminobutane, neopentyl diamine, 1,8-diaminooctane, 1,10-diaminodecane, 1,12-diaminododecane and the like; 1,5-diamino-3-oxapentane, diethylene-triamine, triethylenetetramine, tetraethylenepentamine and the like; cycloaliphatic diamines such as 1,2-bis(aminomethyl)cyclohexane, 1,3-bis(aminomethyl)cyclohexane, 1,4-

bis(aminomethyl) cyclohexane, bis(aminomethyl)norbornane and the like; aromatic alkyl diamines such as 1,3-bis(aminomethyl)benzene (*m*-xylene diamine) and 1,4-bis(aminomethyl)benzene (*p*-xylenediamine) and their reaction products with epichlorohydrin such as Gaskamine 328 and the like; amine-terminated polyethyleneglycol such as Huntsman Corporation Jeffamine ED series and amine-terminated polypropylene glycol such as Huntsman Corporation Jeffamine D series; and amine-terminated polytetrahydrofuran such as Huntsman Jeffamine EDR series. Primary amines having a functionality higher than 2 include, for example, the Jeffamine T series, available from Huntsman Corporation, which are amine-terminated propoxylated trimethylolpropane or glycerol and aminated propoxylated pentaerythritols.

[0081] In certain embodiments, the polypropylene oxide-based polyetheramines comprise the Jeffamine series products available from Huntsman Chemical of Houston, Texas. Jeffamine series products are polyetheramines characterized by repeating oxypropylene units in their respective structures.

[0082] One exemplary class of Jeffamine products, the so-called “Jeffamine D” series products, are amine terminated PPGs (propylene glycols) with the following representative structure (Formula (I)):



(I)

wherein x is 2 to 70.

[0083] In one embodiment, the caprolactone comprises a caprolactone monomer, the anhydride and/or diacid comprises a monoanhydride or a diacid, and the first epoxy compound comprises a diepoxy compound, wherein the mole ratio of caprolactone monomer, monoanhydride (or diacid), and diepoxy compounds in the epoxy-capped flexibilizer may vary from 0.5:0.8:1.0 to 0.5:1.0:6.0.

[0084] In one embodiment, the caprolactone comprises a caprolactone monomer, the anhydride and/or diacid comprises a monoanhydride or a diacid, and the first epoxy compound comprises a diepoxy compound, wherein the mole ratio of caprolactone monomer, monoanhydride (or diacid), and diepoxy compounds in the epoxy-capped flexibilizer may vary from 0.5:0.8:0.6 to 0.5:1.0:6.0.

[0085] In one embodiment, the caprolactone comprises a caprolactone monomer, the anhydride and/or diacid comprises a monoanhydride or a diacid, the diamine or higher functional amine comprises a diamine, and the first epoxy compound comprises a diepoxy compound, wherein the mole ratio of caprolactone monomer, monoanhydride (or diacid), diamine and diepoxy compounds in the epoxy-capped flexibilizer may vary from 2:1: 2:2 to 3:1:3:3.

[0086] In certain embodiments, the (a) epoxy-capped flexibilizer comprises the reaction product of reactants comprising an epoxy compound and a primary or secondary polyether amine.

[0087] Suitable epoxy compounds that may be used to form the epoxy-capped flexibilizer include epoxy-functional polymers that can be saturated or unsaturated, cyclic or acyclic, aliphatic, alicyclic, aromatic or heterocyclic. The epoxy-functional polymers can have pendant or terminal hydroxyl groups, if desired. They can contain substituents such as halogen, hydroxyl, and ether groups. A useful class of these materials includes polyepoxides comprising epoxy polyethers obtained by reacting an epihalohydrin (such as epichlorohydrin or epibromohydrin) with a di- or polyhydric alcohol in the presence of an alkali. Suitable polyhydric alcohols include polyphenols such as resorcinol; catechol; hydroquinone; bis(4-hydroxyphenyl)-2,2-propane, i.e., bisphenol A; bis(4-hydroxyphenyl)-1,1-isobutane; 4,4-dihydroxybenzophenone; bis(4-hydroxyphenyl)-1,1-ethane; bis(2-hydroxyphenyl)-methane and 1,5-hydroxynaphthalene.

[0088] Frequently used polyepoxides include polyglycidyl ethers of Bisphenol A, such as Epon[®] 828 epoxy resin which is commercially available from Hexion Specialty Chemicals, Inc and having a number average molecular weight of about 400 and an epoxy equivalent weight of about 185-192. Other useful polyepoxides include polyglycidyl ethers of other polyhydric alcohols, polyglycidyl esters of polycarboxylic acids, polyepoxides that are derived from the epoxidation of an olefinically unsaturated alicyclic compound, polyepoxides containing oxyalkylene groups in the epoxy molecule, epoxy novolac resins, and polyepoxides that are partially defunctionalized by carboxylic acids, alcohol, water, phenols, mercaptans or other active hydrogen-containing compounds to give hydroxyl-containing polymers.

[0089] Useful primary and secondary polyether amine compounds that can be used to form the epoxy-capped flexibilizer include amine-terminated polyethyleneglycol such as Huntsman Corporation Jeffamine ED series and amine-

terminated polypropylene glycol such as Huntsman Corporation Jeffamine D series; and amine-terminated polytetrahydrofuran such as Huntsman Jeffamine EDR series. Primary amines having a functionality higher than 2 include, for example, the Jeffamine T series, available from Huntsman Corporation, which are amine-terminated propoxylated trimethylolpropane or glycerol and aminated propoxylated pentaerythritols.

[0090] In one embodiment, the epoxy compound comprises a diepoxide, and the primary or secondary polyether amine comprises a difunctional amine, wherein the mole ratio of diepoxide to difunctional amine varies from 2:0.2 to 2:1.

[0091] In certain embodiments, the 1K structural adhesive may include from 2 to 40 weight percent, such as from 10 to 20 weight percent, of (a) the epoxy-capped flexibilizer, based on the total weight of the 1K structural adhesive composition, of any of the forms of described above.

[0092] In still other related embodiments, the (a) the epoxy-capped flexibilizer may comprise a mixture of any two or more of the epoxy-capped flexibilizers described above, wherein the total weight percent of the mixture of the two or more of the epoxy-capped flexibilizers comprises from 2 to 40 weight percent, such as from 10 to 20 weight percent, based on the total weight of the 1K structural adhesive composition.

[0093] In certain embodiments, the heat-activated latent curing agent that may be used include guanidines, substituted guanidines, substituted ureas, melamine resins, guanamine derivatives, cyclic tertiary amines, aromatic amines and/or mixtures thereof. The hardeners may be involved stoichiometrically in the hardening reaction; they may, however, also be catalytically active. Examples of substituted guanidines are methylguanidine, dimethylguanidine, trimethylguanidine, tetra-methylguanidine, methylisobiguanidine, dimethylisobiguanidine, tetramethylisobiguanidine, hexamethylisobiguanidine, heptamethylisobiguanidine and, more especially, cyanoguanidine (dicyandiamide). Representatives of suitable guanamine derivatives which may be mentioned are alkylated benzoguanamine resins, benzoguanamine resins or methoxymethylethoxymethylbenzoguanamine. In addition, catalytically-active substituted ureas may also be used. Suitable catalytically-active substituted ureas include p-chlorophenyl-N,N-dimethylurea, 3-phenyl-1,1-dimethylurea (fenuron) or 3,4-dichlorophenyl-N,N-dimethylurea.

[0094] In certain other embodiments, the heat-activated latent curing agent also or alternatively comprises dicyandiamide and 3,4-dichlorophenyl-N,N-dimethylurea (also known as Diuron).

[0095] In certain embodiments, the 1K structural adhesive may include from 3 to 25 weight percent, such as from 5 to 10 weight percent, of (b) the heat-activated latent curing agent, based on the total weight of the 1K structural adhesive composition.

[0096] As noted above, in certain embodiments, the 1K structural adhesive composition may include (c) an epoxy/CTBN adduct. In certain embodiments, CTBN liquid polymers undergo addition esterification reactions with epoxy resins, allowing them to serve as elastomeric modifiers to enhance impact strength, peel strength, and crack resistance.

[0097] Suitable epoxy compounds that may be used to form the epoxy/CTBN adduct include epoxy-functional polymers that can be saturated or unsaturated, cyclic or acyclic, aliphatic, alicyclic, aromatic or heterocyclic. The epoxy-functional polymers can have pendant or terminal hydroxyl groups, if desired. They can contain substituents such as halogen, hydroxyl, and ether groups. A useful class of these materials includes polyepoxides comprising epoxy polyethers obtained by reacting an epihalohydrin (such as epichlorohydrin or epibromohydrin) with a di- or polyhydric alcohol in the presence of an alkali. Suitable polyhydric alcohols include polyphenols such as resorcinol; catechol; hydroquinone; bis(4-hydroxyphenyl)-2,2-propane, i.e., bisphenol A; bis(4-hydroxyphenyl)-1,1-isobutane; 4,4-dihydroxybenzophenone; bis(4-hydroxyphenyl)-1,1-ethane; bis(2-hydroxyphenyl)-methane and 1,5-hydroxynaphthalene.

[0098] Frequently used polyepoxides include polyglycidyl ethers of Bisphenol A, such as Epon[®] 828 epoxy resin which is commercially available from Hexion Specialty Chemicals, Inc and having a number average molecular weight of about 400 and an epoxy equivalent weight of about 185-192. Other useful polyepoxides include polyglycidyl ethers of other polyhydric alcohols, polyglycidyl esters of polycarboxylic acids, polyepoxides that are derived from the epoxidation of an olefinically unsaturated alicyclic compound, polyepoxides containing oxyalkylene groups in the epoxy molecule, epoxy novolac resins, and polyepoxides that are partially defunctionalized by carboxylic acids, alcohol, water, phenols, mercaptans or other active hydrogen-containing compounds to give hydroxyl-containing polymers.

[0099] In certain embodiments, at least a portion, often at least 5 percent by weight, of the polyepoxide has been reacted with a carboxy-terminated butadiene acrylonitrile polymer. In certain of these embodiments, the carboxy-terminated butadiene acrylonitrile polymers have an acrylonitrile content of 10 to 26 percent by weight. Suitable CTBN compounds having an acrylonitrile content of 10 to 26 percent by weight that may be used include Hypro 1300X8, Hypro 1300X9, Hypro 1300X13, Hypro 1300X18, and Hypro 1300X31, each available from Emerald Specialty Polymers, LLC of Akron, Ohio

[00100] In certain other embodiments, the polyepoxide may be reacted with a mixture of different carboxy-terminated butadiene acrylonitrile polymers.

[00101] In certain embodiments, the functionality of the CTBN utilized is from 1.6 to 2.4, and the epoxy compound is reacted with the CTBN material in a stoichiometric amount to form the epoxy/CTBN adduct.

[00102] In certain embodiments, the epoxy/CTBN adduct comprises from about 1 to 20 weight percent, such as from 5 to 10 weight percent, of the total weight of the 1K structural adhesive composition.

[00103] As noted above, in certain embodiments, the 1K structural adhesive composition may include (d) an epoxy/dimer acid adduct. In certain embodiments, the epoxy/dimer acid adduct may be formed by reacting an epoxy compound with a dimer acid.

[00104] Suitable epoxy compounds that may be used to form the epoxy/dimer acid adduct include epoxy-functional polymers that can be saturated or unsaturated, cyclic or acyclic, aliphatic, alicyclic, aromatic or heterocyclic. The epoxy-functional polymers can have pendant or terminal hydroxyl groups, if desired. They can contain substituents such as halogen, hydroxyl, and ether groups. A useful class of these materials includes polyepoxides comprising epoxy polyethers obtained by reacting an epihalohydrin (such as epichlorohydrin or epibromohydrin) with a di- or polyhydric alcohol in the presence of an alkali. Suitable polyhydric alcohols include polyphenols such as resorcinol; catechol; hydroquinone; bis(4-hydroxyphenyl)-2,2-propane, i.e., bisphenol A; bis(4-hydroxyphenyl)-1,1-isobutane; 4,4-dihydroxybenzophenone; bis(4-hydroxyphenyl)-1,1-ethane; bis(2-hydroxyphenyl)-methane and 1,5-hydroxynaphthalene.

[00105] Frequently used polyepoxides include polyglycidyl ethers of Bisphenol A, such as Epon[®] 828 epoxy resin which is commercially available from Hexion

Specialty Chemicals, Inc and having a number average molecular weight of about 400 and an epoxy equivalent weight of about 185-192. Other useful polyepoxides include polyglycidyl ethers of other polyhydric alcohols, polyglycidyl esters of polycarboxylic acids, polyepoxides that are derived from the epoxidation of an olefinically unsaturated alicyclic compound, polyepoxides containing oxyalkylene groups in the epoxy molecule, epoxy novolac resins, and polyepoxides that are partially defunctionalized by carboxylic acids, alcohol, water, phenols, mercaptans or other active hydrogen-containing compounds to give hydroxyl-containing polymers.

[00106] As defined herein, dimer acids, or dimerized fatty acids, are dicarboxylic acids prepared by dimerizing unsaturated fatty acids obtained from tall oil, usually on clay catalysts. Dimer acids usually predominantly contain a dimer of stearic acid known as C36 dimer acid. A suitable dimer acid for use in forming the epoxy/dimer acid adduct of the present invention may be obtained from Croda, Inc. or from Cognis.

[00107] In certain embodiments, the epoxy compounds and dimer acids are reacted in stoichiometric amounts to form the epoxy/dimer acid adduct.

[00108] In certain embodiments, the epoxy/dimer acid adduct comprises from about 1 to 15 weight percent, such as from 2 to 7 weight percent, of the total weight of the 1K structural adhesive composition.

[00109] As noted above, in certain embodiments, the 1K structural adhesive composition may also include (e) rubber particles having a core/shell structure. Suitable core shell rubber particles for use in the 1K structural adhesives are the same as those described above with respect to the 2K adhesive formulations and therefore not repeated herein.

[00110] In certain embodiments, the 1K structural adhesive may include from 0 to 75 weight percent, such as from 5 to 60 weight percent, of (e) the rubber particles having a core/shell structure, based on the total weight of the 1K structural adhesive composition.

[00111] As noted above, in certain embodiments, the 1K structural adhesive composition may also include (f) graphenic carbon particles. Suitable graphenic carbon particles for use in the 1K structural adhesives are the same as those described above with respect to the 2K adhesive formulations and therefore not repeated herein.

[00112] In certain embodiments, the 1K structural adhesive may include from 0 to 40 weight percent, such as from 0.5 to 25 weight percent, of (f) the graphenic carbon particles, based on the total weight of the 1K structural adhesive composition.

[00113] In still other embodiments, the 1K structural adhesive formulation may also include epoxy compounds or resins that are not incorporated into or reacted as a part of any of the components (a)-(f) above, including epoxy-functional polymers that can be saturated or unsaturated, cyclic or acyclic, aliphatic, alicyclic, aromatic or heterocyclic. The epoxy-functional polymers can have pendant or terminal hydroxyl groups, if desired. They can contain substituents such as halogen, hydroxyl, and ether groups. A useful class of these materials includes polyepoxides comprising epoxy polyethers obtained by reacting an epihalohydrin (such as epichlorohydrin or epibromohydrin) with a di- or polyhydric alcohol in the presence of an alkali. Suitable polyhydric alcohols include polyphenols such as resorcinol; catechol; hydroquinone; bis(4-hydroxyphenyl)-2,2-propane, i.e., bisphenol A; bis(4-hydroxyphenyl)-1,1-isobutane; 4,4-dihydroxybenzophenone; bis(4-hydroxyphenyl)-1,1-ethane; bis(2-hydroxyphenyl)-methane and 1,5-hydroxynaphthalene.

[00114] Frequently used polyepoxides include polyglycidyl ethers of Bisphenol A, such as Epon[®] 828 epoxy resin which is commercially available from Hexion Specialty Chemicals, Inc and having a number average molecular weight of about 400 and an epoxy equivalent weight of about 185-192. Other useful polyepoxides include polyglycidyl ethers of other polyhydric alcohols, polyglycidyl esters of polycarboxylic acids, polyepoxides that are derived from the epoxidation of an olefinically unsaturated alicyclic compound, polyepoxides containing oxyalkylene groups in the epoxy molecule, epoxy novolac resins, and polyepoxides that are partially defunctionalized by carboxylic acids, alcohol, water, phenols, mercaptans or other active hydrogen-containing compounds to give hydroxyl-containing polymers.

[00115] In still another embodiment, reinforcement fillers may be added to the adhesive composition. Useful reinforcement fillers that may be introduced to the adhesive composition to provide improved mechanical properties include fibrous materials such as fiberglass, fibrous titanium dioxide, whisker type calcium carbonate (aragonite), and carbon fiber (which includes graphite and carbon nanotubes). In addition, fiber glass ground to 5 microns or wider and to 50 microns or longer may also provide additional tensile strength. More preferably, fiber glass ground to 5 microns or wider and to 100-300 microns in length is utilized. Preferably, such

reinforcement fillers, if utilized, comprise from 0.5 to 25 weight percent of the 1k adhesive composition.

[00116] In still another embodiment, fillers, thixotropes, colorants, tints and other materials may be added to the 1K adhesive composition.

[00117] Useful thixotropes that may be used include untreated fumed silica and treated fumed silica, Castor wax, clay, and organo clay. In addition, fibers such as synthetic fibers like Aramid[®] fiber and Kevlar[®] fiber, acrylic fibers, and engineered cellulose fiber may also be utilized.

[00118] Useful colorants or tints may include red iron pigment, titanium dioxide, calcium carbonate, and phthalocyanine blue.

[00119] Useful fillers that may be used in conjunction with thixotropes may include inorganic fillers such as inorganic clay or silica.

[00120] Exemplary other materials that may be utilized include, for example, calcium oxide and carbon black.

[00121] Illustrating the invention are the following examples that are not to be considered as limiting the invention to their details. All parts and percentages in the examples, as well as throughout the specification, are by weight unless otherwise indicated.

EXAMPLES

Example 1 - 2K Adhesive Compositions

Part A - Synthesis of Polyether- Polyester Modified Epoxy Resin

[00122] To a four-neck flask fitted with condenser, thermometer, stirrer, and nitrogen inlet, add 304.6 grams of hexahydrophthalic anhydride and 248.1 grams of Terathane[®] 250. Heat the mixture to 100°C with stirring under nitrogen atmosphere and hold the reaction mixture at 100°C for 155 minutes. Cool the reaction mixture to 60°C and then add 1431.6 grams of Epon[®] 828 and 15.0 grams of triphenyl phosphine. Heat the reaction mixture to 110°C and hold at this temperature for 150 minutes. Then, cool the mixture to room temperature. The resultant compound has 99.89% solids, an acid value of 0.2, and an epoxy equivalent weight of 380.7. The resultant compound is the epoxy adduct of the first component of the 2K adhesive material listed in Part 1 of Table 1 below.

Part B- Evaluation of 2K Adhesives with and without Epoxy-adduct; Evaluation of 2K Adhesives with Varying Amine Hydroxyl Equivalent Weights

[00123] The following examples compare 2K adhesive compositions without an epoxy-adduct (Example 1) to those with an epoxy-adduct (Examples 2-4). The formulations for the first component (Part 1) and second component (Part 2) of the 2K adhesive compositions are shown in Table 1.

Table 1

Formula	Ex. 1	Ex. 2	Ex. 3	Ex. 4
Part 1				
Epon [®] 828 ¹	46	41	40.5	43
Epon [®] 828/Terathane 250/HHPA ²	-	12	12	6
Microglass 9132 ³	6	2	-	4
Hakuenka CCR-S ⁴	-	-	-	1.5
Wacker HDK H17 ⁵	3.5	3.25	3.5	3
Tint AYD ST 8454 ⁶	0.02	0.02	0.02	0.01
Part 2				
Jeffamine D-230 ⁷	11.5	12	12	11.6
Jeffamine XTJ-616 ⁸	5	5	-	2.5
Triethylenetetramine (TETA) ⁹	-	-	2.3	-
IPDA ¹⁰	-	-	-	1.35
Accelerator 399 ¹¹	2.2	2.2	2.2	0.5
Microglass 9132 ³	1.5	6	8	4
Hakuenka CCR-S ⁴	1	1.5	6	2
Wacker HDK H17 ⁵	2.75	2.5	2	2.5
Tint AYD PC 9298 ¹²	0.01	0.01	0.01	0.01
Results				
Amine/Epoxy Ratio	1.030	1.032	1.033	1.036

Lap Shear Strength (MPa)	24.5	26.7	25.5	31.4
Elongation (%)	3.5	3.4	3.7	3.5
Tensile Strength (MPa)	65	61	68	55
Modulus (MPa)	3185	3127	3473	2931
(data range)	(3025-3300)	(2974-3274)	(3233-3671)	(2733-3218)

Fatigue Test (8MPa Stress)

cycles to fail	173532	>432000	337062	329371
cycles to fail	219062	>432000	>432000	>432000
Average	196297	>432000	337062	329371

1. Bisphenol A/Epichlorohydrin resin available from Huntsman Advance Materials
2. Synthesis example from Example 1, Part A
3. Silane treated chopped fiberglass from Fibertec
4. Precipitated Calcium Carbonate available from Shiraishi Kogyo Kaisha
5. Hydrophobic Fumed Silica available from Wacker Chemie AG
6. ORG Yellow Tint Base available from Elementis Specialties
7. Polyoxyalkyleneamine available from Huntsman
8. Polyoxyalkyleneamine available from Huntsman
9. Triethylenetetramine available from Dow Chemical Co.
10. Isophorone Diamine available from Evonik AG
11. Mix of Alkanolamine/piperazine derivative available from Huntsman
12. Phthalo Blue Pigment Dispersion available from Elementis Specialties

Test Methods

[00124] In each of the Examples, the raw materials listed in Table 1 were mixed using a Speedmixer DAC 600 FVZ (commercially available from FlackTek, Inc.). Ingredients 1 and 2 were mixed for 2 minutes at 2350 revolutions per minute (“RPM”) in Part 1. Then, items 3 to 6 were added and mixed for one minute at 2350 RPM. Items 7 to 11 were mixed for 1 minute in Part 2 and then the rest of the ingredients were added and mixed for one minute in Part 2. During the mixing process, the mixture was examined with a spatula and given additional mix time, if necessary, to ensure uniformity. The final step of the mixing process involved mixing the mixture with an air motor prop in a vacuum sealed apparatus for 5 minutes at 28 to 30 inches of vacuum pressure. After the final mixing step with the air motor prop, the adhesive compositions were ready for testing.

[00125] Part 1 and Part 2 were targeted for 2:1 volume mix ratio. In some instances, appropriate weight ratios were determined to test properties. Amine to epoxy ratio were kept slightly over one for all the examples to insure complete reaction of epoxy as shown in the result section of Table 1. Appropriate weight ratio of Part 1 and Part 2 were weighed and mixed in the DAC mixer for one minute at 2350 RPM and immediately mixed under vacuum as described in previous paragraph. The mixed sample was then subjected to the following tests:

[00126] **Lap-Shear Testing:** 25mm X 100mm Coupons were cut from 6-ply unidirectional glass/epoxy laminates supplied by MFG, Inc. with peel ply removed. Coupons were scribed at one end at 12.5mm. Adhesive was applied evenly on one of the coupons within the scribed area for each bond assembly. Uniformity of bond thickness is insured by adding 1.0 ± 0.5 mm glass spacer beads. Spacer beads were sprinkled evenly over the material, covering no more than 5% of the total bond area. The other test coupon was placed on the bond area and spring loaded clips, such as Binder Clips from Office Max or Mini Spring Clamp from Home Depot, were attached, one to each side of the bond, to hold the assembly together during bake. Care was given to align parallel edges. Excess adhesive that was squeezed out was removed with a spatula before baking. Bond assemblies were given an open time of 15 to 30 minutes and baked at 70 degrees Celsius for six hours, and after cooling, remaining excess was sanded. Bonds were conditioned at room temperature for at least 24 hours. Bonds were inserted in wedge action grips and pulled apart at a rate of 10 mm per minute using an Instron model 5567 in tensile mode. Lap Shear strength was calculated by Instron's Blue Hill software package.

[00127] **Free film mechanical properties:** The same adhesive mix was used to prepare void free dog-bone shaped free film by skiving material with care to avoid any air pockets. Figure 1 is an example of a Teflon template to make five dog-bone cavities. The template was glued to a solid Teflon piece with double-side adhesive tape prior to skiving adhesive in the cavity. This assembly was given an open air time of 15 to 30 minutes and then baked at 70°C for 6 hours. It was conditioned at least 24 hours and then the dog-bone shaped free film was popped out of the template. Actual thickness and width were recorded into Instron 5567 software. Then, the dog-bone was inserted into the wedge action grip and pulled at a rate of 50 mm per minute. Percent elongation, tensile strength, and modulus were determined with Instron's Blue Hill software package. Alternatively, ISO 527-1 & 2 method and die configuration

was used wherever indicated in the tables to prepare the dog-bone (dumb-bell) shaped free film.

[00128] Load controlled lap-shear fatigue test was done using the same laminate and coupon construction as described in the previous paragraph. An automated system utilizing Instron, servo-controlled, hydraulically actuated, closed loop test equipment, and a personal computer with software designed by Westmoreland Mechanical Testing and Research, Inc. provided the means for machine control. Each specimen was inserted in wedge action grips along with frictionally retained shims with thickness equal to that of the fiberglass substrates and bond-line to ensure axial loading. The test was run at room temperature with an R-ratio of 0.1 at 5 Hz sinusoidal waveform and load application of 8 MPa. Testing was continued until 432,000 cycles or failure.

Part C - Evaluation of Pot Life with 2K Adhesives Having Varying Amine Hydroxy Equivalent Weights:

[00129] Table 2 shows pot life comparison between propylene oxide-based polyether tetramine, Jeffamine XTJ-616, and ethylene oxide-based triethylenetetramine in similar formulas, wherein the amine/epoxy ratio was maintained between 1.03 and 1.05. The formulations and results are shown in Table 2:

Table 2

Pot life Comparison

Formula	Ex. 5	Ex. 6
Part 1		
Epon [®] 828 ¹	44	43.5
Epon [®] 828/Terathane 250/HHPA ²	6	6
Microglass 9132 ³	2	1
Wacker HDK H17 ⁵	3.5	3
Tint AYD ST 8454 ⁶	0.01	0.01

Part 2

Jeffamine D-230⁷	12	12
Jeffamine XTJ-616⁸	5	
Triethylenetetramine (TETA)⁹	-	2.3
Accelerator 399¹¹	0.5	0.5
Microglass 9132³	5	7
Hakuenka CCR-S⁴	3	6.64
Wacker HDK H17⁵	2.25	2.36
Tint AYD PC 9298¹²	0.01	0.01

Amine/Epoxy Ratio (2:1 volume mix)	1.033	1.0464
Pot Life, minutes	174	63
Peak Temperature (°C)	73	150
Minutes to reach Peak	239	83

[00130] In this experiment, both formulas (Examples 5 and 6) utilized the same amount of Accelerator 399 which also has significant influence on pot-life. If Accelerator 399 was absent, the pot life was found to be significantly higher.

[00131] Pot-life was defined as the interval from time when Part 1 (the epoxy component) and Part 2 (the amine component) were mixed to the time when internal temperature of adhesive reaches 50°C in 415 ml. of mass. Part 1 and Part 2 were mixed in a 2 to 1 volume ratio using a static mixer; P C COX pneumatic dual applicator dispensed mixed adhesive into a paper cup marked with 415 ml. level line and initial time was noted. The cup was immediately placed in 25°C water bath with a thermo-couple inserted to the center location of the mixed adhesive mass. PC based data logger was employed to record temperature every minute to determine Pot-life time taken to reach 50°C, the peak temperature, and the time to reach the peak temperature.

Part D - Evaluation of 2K Adhesives With and Without Reinforcement Filler

[00132] In this experiment, the effect of the addition of fiberglass as a reinforcement filler was compared in a sample formulation as described in Table 3:

[00133] Examples 7 and 8 in Table 3 are a comparative study without and with Microglass 9132 (fiberglass strands with an average of 220 micron length). Results indicate significant increase in modulus when Microglass 9132 is present.

Table 3**Effects of Fiberglass on Modulus Properties**

Formula	Ex. 7	Ex. 8
Part 1		
Epon[®] 828¹	41	41
Epon[®] 828/Terathane 250/HHPA²	12	12
Microglass 9132³	-	6
Wacker HDK H17⁵	3.25	2
Tint AYD ST 8454⁶	0.02	0.02
Part 2		
Jeffamine D-230⁷	12	12
Jeffamine XTJ-616⁸	5	5
Accelerator 399¹¹	2.2	2.2
Microglass 9132³	-	6
Hakuenka CCR-S⁴	1.5	1.5
Wacker HDK H17⁵	2.5	2.5
Tint AYD PC 9298¹²	0.01	0.01
<u>Amine/Epoxy Ratio</u>	1.032	1.032
<u>Lap Shear Strength (MPa)</u>	27.7	24.4

Elongation (%)	4.8	3.5
Tensile Strength (MPa)	66	61
Modulus (MPa)	2444	3211
(data range)	(2246-2673)	(3160-3269)

Part E - Evaluation of 2K Adhesives with Graphenic Carbon Particles;

Evaluation of 2K Adhesive Systems with Rubber Particles Having a Core-Shell Structure

The following examples compare 2K adhesive compositions with graphenic carbon particles (Example 2) or with rubber particles having a core-shell structure (Example 3). The formulations for the first component (Part 1) and second component (Part 2) of the 2K adhesive compositions are shown in Table 4.

In the example utilizing graphenic carbon particles, twenty grams of xGnP® Graphene Nanoplatelets (Grade C surface area 750 m²/g (available from XG Sciences Corporation)) was added to pre-weighed Epon® 828 (180 grams available from Hexion Specialty Chemicals Corporation) and the mixture was hand-mixed with spatula inside a laboratory glove box. The mixture was then poured into a three-roll mill (manufactured by Kent Industrial U.S.A. Inc) and ground 6 times. The graphene ground Epon® 828 was poured out from the mill and introduced to the mixture as in Example 2 below.

Table 4

Formula	Ex. 1	Ex. 2	Ex. 3
Part 1			
Epon® 828¹	41.05	-	38
Epon® 828/Terathane 650/HHPA¹³	13	13	5
10% Graphenic carbon particles in Epon® 828¹⁴	-	45.61	-
Kane Ace MX-153¹⁵	-	-	9

Part 2

Jeffamine D-230⁵	10.35	10.35	10.35
Jeffamine D-400¹⁶	4.46	4.46	4.46
Jeffamine XTJ-616⁸	2.92	2.92	2.92
IPDA¹⁰	2.92	2.92	2.92
1,3-Bis(aminomethyl)cyclohexane¹⁷	1.04	1.04	1.04
Triethylenetetramine (TETA)⁹	0.1	0.1	0.1
Accelerator 399¹¹	0.08	0.08	0.08
Tint AYD PC 9298¹²	0.01	0.01	0.01

Results

Amine/Epoxy Ratio	1.078	1.081	1.085
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Adhesive mechanical properties measured according to ISO527-1 & 2

Elongation (%)	5.8	4.8	4.5
Tensile Strength (MPa)	55.1	53.6	50.3
Modulus (MPa)	2663	4041	2616
(data range)	(2548-2861)	(3571-4505)	(2443-2958)

13. Epon[®] 828/Terathane 650/Hexahydrophthalic anhydride adduct; EEW 412

14. Available from XG Sciences, Graphenic carbon particles dispersion (10%) in Epon[®] 828

15. Core-shell poly(butadiene) rubber dispersion (33%) in Epon[®] 828 available from Kaneka Texas Corporation

16. Polyoxyalkeleneamine available from Huntsman

17. 1,3 bis(aminomethyl)cyclohexane (1,3-BAC) available from Mitsubishi Gas Chemical

Example 2 - 1K Adhesive Compositions**Part A - Synthesis of Polyether- Polyester Modified Epoxy Resin**

[00134] To a four-neck flask fitted with condenser, thermometer, stirrer, and nitrogen inlet, add 321.3 grams of hexahydrophthalic anhydride and 677.7 grams of Terathane[®] 650. The mixture was heated to 100°C with stirring under nitrogen atmosphere and the reaction was checked for an exotherm. After the exotherm subsided, the temperature was set at 150°C and held until the anhydride peak at 1785

and 1855 CM-1 disappeared. The reaction mixture was then cooled to 120°C, wherein 1646.0 grams of EPON 828 and 15.0 grams of triphenyl phosphine were added. The reaction mixture was held at 120°C until the acid value was below 2.2, resulting in a polyether-polyester modified epoxy resin having an epoxy equivalent weight of 412.

Part B - Synthesis of Polycaprolactone Diol Modified Epoxy Resin

[00135] To a suitable flask equipped with a reflux condenser and stirrer, add 211.9 grams of hexahydrophthalic anhydride and 570.6 grams of polycaprolactone CAPA 2085. The mixture was heated to 100°C while stirring and held until the acid value was below 125 and the IR anhydride peaks at 1785 to 1855 CM-1 disappeared. The reaction mixture was then cooled to ambient temperature and 221 grams of this derivative was added into another flask equipped with a reflux condenser and stirrer. 310.6 grams of Epon[®] 828 (bisphenol A epichlorohydrin) and 3.00 grams of triphenylphosphine was added to the derivative, and the mixture was heated to 110°C while stirring. The heating mantle was removed when the exotherm temperature peaked at about 145°C to allow temperature to drop. The reaction temperature was then maintained at about 110°C until the acid value of the mixture was below 2. The reaction mixture was then cooled to ambient temperature and stored. The polycaprolactone diol modified epoxy resin that resulted had a Molecular Weight by Number Average (M_n) of 2042 and an Epoxy Equivalent Weight (EEW) of 435.

Part C - Synthesis of Amide-Polyether-Polyester Modified Epoxy Resin

[00136] 323.5 grams of Jeffamine D400 and 167.6 grams of E-caprolactone was added to a suitable flask equipped with a reflux condenser and stirrer. The mixture was heated to 150°C while stirring until the MEQ amine value was below 0.75 MEQ/gm. The mixture was then cooled to 60°C, wherein 226.5 grams of hexahydrophthalic anhydride was added to the mixture while stirring. The mixture was then heated to 100°C and held until the acid value was below 103. The mixture was then cooled to 60°C, wherein 1061.8 grams of Epon[®] 828 and 3.7 grams of Triphenylphosphine were added. The mixture was then heated to 110°C while stirring and held at that temperature until the acid value was below 2. The mixture

was then cooled to ambient temperature and stored. The resultant amide-polyether-polyester modified epoxy resin had a Molecular Weight by Number Average of 1664 and an epoxy equivalent weight (EEW) was 408.6.

Part D - Synthesis of Epoxy/Dimer Acid Adduct

[00137] Empol[®] 1022 Dimer acid (26.95 grams, available from Emory), Epon[®] 828 (32.96 grams available from Hexion) and triphenylphosphine (0.06 gram available from BASF) were added in a round-bottom flask, which was equipped with a mechanical stirrer, a reflux condenser. A thermometer and an addition funnel were attached. Nitrogen gas was briefly introduced into the flask. The flask was heated to 105°C and the reaction continued until the acid value reached the desired range between 85 to 88 mg KOH per gram. An additional amount of Epon[®] 828 (40.03 grams) was added to the flask through a funnel at 105°C and nitrogen gas was briefly introduced inside the flask. The flask was heated to 116°C. A mild exothermic reaction took place and the reaction temperature rose to 177°C. The flask temperature was returned to and kept under 168°C by cooling. The reaction continued until the acid value became less than 1, wherein the flask was cooled to room temperature. This synthesis made a 43.6% epoxy/dimer acid adduct dispersed in an epoxy resin having an Epoxy Equivalent Weight (EEW) of 338.6.

Part E - Synthesis of Epoxy/CTBN Adduct

[00138] HYCAR 1300X8 carboxylic acid-terminated butadiene – acrylonitrile rubber (40 grams, available from Emerald Performance Materials Corporation) and Epon[®] 828 (60 grams) were added to a round-bottom flask, equipped with a mechanical stirrer, a thermometer and a reflux condenser. The flask was warmed to 115°C under a nitrogen atmosphere. The mixture was then heated to 165°C and stirred at that temperature until the acid value became less than 0.1, wherein the flask was cooled to room temperature. This synthesis made a 43.9% epoxy/CTBN adduct dispersed in an epoxy resin having an Epoxy Equivalent Weight (EEW) of 357.

Part F - Synthesis of Polyetheramine Modified Epoxy Resin

[00139] 187 grams of Epon[®] 828 was added to a pint metal can and heated in a 95°C oven for 30 minutes. The can was removed from the oven and was fitted with an air-motor driven mechanical stirrer with cowls blade for high shear mixing. 38.33 grams of Jeffamine D-400 was gradually added to the can under high speed mixing, and the mixture was stirred for for three hours. During this period, the temperature of the mixture, initially at about 120°C (as measured by a thermocouple), was gradually decreased. After three hours, the can was cooled to room temperature. This synthesis made a polyetheramine modified epoxy resin.

Part G - Evaluation of 1K Adhesives

Test Methods

[00140] All the mechanical properties were tested on 1 mm thick Hot dip galvanized (HDG) substrate as supplied by Hövelmann & Lueg GmbH, Germany. Curing conditions for all the testing was 177°C (350°F) for 30 minutes.

[00141] An extension to the ISO 11343 method for wedge impact, "Adhesives - Determination of dynamic resistance to cleavage of high strength adhesive bonds under impact conditions-- Wedge impact method" was used as described in Ford test method BU121-01. Three bond specimens were prepared for each testing condition

[00142] **Wedge Impact Bond Preparation:** Cut 90mm X 20mm coupons. Place Teflon[™] tape around the coupons (both the upper and lower coupons) 30.0 ± 0.2 mm from one end. Then apply the adhesive to the top 30 mm. The bond-line thickness is maintained with 0.25mm (10 mil) glass beads. Remove adhesive squeeze out from the specimen edges with a spatula. Clamp specimens together to maintain flushness of coupon ends and sides. Bond assemblies are cured at 350°F (177°C) for 30 minutes. Then remove any excess adhesive from the edges by sanding and ensuring a flat and parallel impact end allowing hammer to impact the entire specimen simultaneously. Mark coupons 40.0 ± 0.2 mm from the bonded end as a locator for consistent placement on wedge. Place specimen on wedge, aligning mark on specimen with tip of wedge such that it is at the same place on the wedge each time. Do not prebend the specimens; however, allow the unbonded portion of the

specimens to conform to the shape of the wedge as the specimens are placed on the wedge. An Instron Dynatup Model 8200 Impact Test frame in conjunction with an integrated software package provided the means for load application and data acquisition respectively. The test frame was set-up with the objective of obtaining a minimum impact energy of 150 joules (110.634 lbf*ft) and an impact speed of at least 2 meters/second (6.562 ft./sec).

[00143] Bonds were conditioned at room temperature for at least 24 hours. Bonds were pulled apart using an Instron model 5567 in tensile mode.

[00144] Lap-Shear Testing: 25mm X 100mm Coupons were cut and scribed at one end at 12.5mm. Adhesive was applied evenly on one of the coupons within the scribed area for each bond assembly. Uniformity of bond thickness is insured by adding 0.25mm (10 mil) glass spacer beads. Spacer beads should be sprinkled evenly over the material, covering no more than 5% of the total bond area. The other test coupon is placed on the bond area and spring loaded clips, such as Binder Clips from Office Max or Mini Spring Clamp from Home Depot, are attached, one to each side of the bond, to hold the assembly together during bake. Excess squeeze out is removed with a spatula before baking. Bond assemblies were cured as specified, and after cooling, remaining excess was sanded. Bonds were conditioned at room temperature for at least 24 hours. Bonds were pulled apart using an Instron model 5567 in tensile mode.

[00145] T-peel: Cut metal substrate in pairs of 25mm x 87.5mm in dimension. Make a 90° bend at 12.5mm from one end on a vise so that paired pieces make T-shape configuration:  when bonded together. Apply a thin layer of adhesive on the three inch portion of bonding side of one piece. Apply 0.25mm diameter glass spacer beads evenly over the total bond area making sure to cover 5% of total bond area. Place two pieces together forming a T-shaped configuration known as T-PEEL assembly. Place 3 medium binder clips on the T-PEEL assembly to hold it together. Remove excess squeeze out of adhesive with a spatula prior to baking the assemblies in a preconditioned oven at a given temperature specified. Allow samples to cool, then remove binder clips, and sand any remaining excess squeeze out. Pull samples on INSTRON 5567 at rate of 127mm per minute. T-Peel assemblies in Instron jaws are conditioned in an environmental chamber for at least 30 minutes and tested within the chamber in case of -30°C testing. Instron 5567 calculates results in pounds per linear inch or Newton per mm through internal computer program.

**Evaluation of 1K Adhesive Compositions With Various Epoxy-Capped
Flexibilizers and Rubber Particles Having a Core/Shell Structure**

[00146] The following examples compare 1K adhesive compositions in accordance with certain embodiments of the present invention. The formulations are shown in Table 5 and the mechanical performance of the 1K adhesive compositions is shown in Tables 6-9, respectively.

Table 5

	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5
Epon 828/Dimer Acid¹⁸	4	12	4	4	4
Epon 828/CTBN¹⁹	12	16	12	12	12
Kane Ace MX-153²⁰	37.5	21	37.5	37.5	37.5
Epon 828¹	-	6.5	-	-	-
Epon 828/Terathane 650/HHPA²¹	10	10	-	-	-
Epon 828/Jeffamine D-400²²	-	-	10	-	-
Epon 828/Caprolactone/HHPA²³	-	-	-	10	-
Epon 828/Caprolactone/Jeffamine D-400/HHPA²⁴	-	-	-	-	10
Dicyandiamide²⁵	5.1	5.1	5.1	5.1	5.1
Diuron²⁶	0.35	0.35	0.35	0.35	0.35
Raven 410 Carbon Black²⁷	0.06	0.06	0.06	0.06	0.06
Calcium Oxide²⁸	3.1	3.1	3.1	3.1	3.1
Wacker HDK H17²⁹	2.75	3.25	2.5	2.75	2.5

18. Synthesis example from Example 2, Part D above.

19. Synthesis example from Example 2, Part E above.

20. Core/shell poly(butadiene) rubber dispersion (33%) in Epon[®] 828 available from Kaneka Texas Corporation.

21. Synthesis example from Example 2, Part A above.

22. Synthesis example from Example 2, Part F above.

23. Synthesis example from Example 2, Part B above.

24. Synthesis example from Example 2, Part C above.

25. Heat activated latent curing agent available from ALZ Chem.

26. Catalytically-active substituted urea available from ALZ Chem

27. Carbon black available from Phelps Dodge – Columbian Chemicals

28. Calcium oxide available from Mississippi Lime, Co.

29. Hydrophobic Fumed Silica available from Wacker Chemie AG

Table 6**Adhesive mechanical properties measured according to ISO527-1 & 2**

	Temp.	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5
Elongation (%) Pull Rate – 1 mm/min.	Room Temp (RT)	10.3	6.0	-	-	-
Tensile Strength (MPa) Pull Rate – 1 mm/min.	RT	42	38	-	-	-
Modulus (MPa) Pull Rate – 1 mm/min.	RT	2559	2421	-	-	-

Table 7

Lap Shear Strength (MPa)	Temp.	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5
Bond area – 25 x 10 x 0.2 mm	-40°C	31.4	28.4	29.1	28.4	29.6
GM - SAEJ1523	RT	25.3	24.5	23.5	24.9	25.8
Pull Rate – 10 mm/min.	+80°C	22.2	20.3	21.9	20.7	21.6

Table 8

T-Peel Strength (N/mm)	Temp.	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5
Bond area – 25 x 75 x 0.2 mm	-40°C	17.6	13.8	17.2	16.2	15.1
GM – ASTM D1876	RT	15.3	9.3	10.5	10.6	16.4
Pull Rate – 127 mm/min.	+80°C	9.0	8.3	6.5	8.0	8.7

Table 9

Impact Peel Strength (N/mm)	Temp.	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5
Bond area – 25 x 30 x 0.2 mm	-40°C	5.8-9.8	3.4-9.4	-	-	-
ISO 11343 modified	RT	36.9-41.3	29.1-35.1	-	-	-
Ford BU-12-01 (2 m/s speed, 150 joules impact energy)	+80°C	31.3-36.9	33.5-42.9	-	-	-

[00147] Whereas particular embodiments of this invention have been described above for purposes of illustration, it will be evident to those skilled in the art that numerous variations of the details of the present invention may be made without departing from the invention as defined in the appended claims.

WE CLAIM:

1. A composition comprising:
 - (a) a first component comprising:
 - (1) an epoxy-adduct that is the reaction product of reactants comprising a first epoxy compound, a polyol, and an anhydride and/or a diacid; and
 - (2) a second epoxy compound;
 - (b) rubber particles having a core/shell structure; and
 - (c) a second component that chemically reacts with said first component.
2. The composition of Claim 1 further comprising (d) graphenic carbon particles.
3. A composition comprising:
 - (a) a first component comprising:
 - (1) an epoxy-adduct that is the reaction product of reactants comprising a first epoxy compound, a polyol, and an anhydride and/or a diacid; and
 - (2) a second epoxy compound;
 - (b) graphenic carbon particles; and
 - (c) a second component that chemically reacts with said first component.
4. A coated substrate comprising the composition of Claim 3.
5. A composition comprising:
 - (a) an epoxy-capped flexibilizer that is the reaction product of reactants comprising an epoxy compound, a polyol, and an anhydride and/or a diacid; and
 - (b) a heat-activated latent curing agent.
6. The composition of Claim 5 further comprising (c) rubber particles having a core/shell structure.
7. The composition of Claim 5 further comprising (c) graphenic carbon particles.

8. The composition of Claim 5 further comprising:
 - (c) rubber particles having a core/shell structure; and
 - (d) graphenic carbon particles.
9. The composition of Claim 5 further comprising (c) an epoxy/CTBN adduct.
10. The composition of Claim 5 further comprising (c) an epoxy/dimer acid adduct.
11. The composition of Claim 5 further comprising:
 - (c) an epoxy/CTBN adduct; and
 - (d) an epoxy/dimer acid adduct.
12. A composition comprising:
 - (a) an epoxy-capped flexibilizer that is the reaction product of reactants comprising an epoxy compound, an anhydride and/or a diacid, and a caprolactone; and
 - (b) a heat-activated latent curing agent.
13. The composition of Claim 12 further comprising (c) rubber particles having a core/shell structure.
14. The composition of Claim 12 further comprising (c) graphenic carbon particles.
15. The composition of Claim 12 further comprising:
 - (c) rubber particles having a core/shell structure; and
 - (d) graphenic carbon particles.
16. The composition of Claim 12 further comprising (c) an epoxy/CTBN adduct.
17. The composition of Claim 12 further comprising (c) an epoxy/dimer acid adduct.

18. The composition of Claim 12 further comprising:
- (c) an epoxy/CTBN adduct; and
 - (d) an epoxy/dimer acid adduct.
19. The composition of Claim 12, wherein said epoxy-capped flexibilizer comprises the reaction product of reactants comprising an epoxy compound, an anhydride and/or a diacid, a caprolactone; and a diamine or higher functional amine.
20. A composition comprising:
- (a) an epoxy-capped flexibilizer that is the reaction product of reactants comprising an epoxy compound and a primary or secondary polyether amine; and
 - (b) a heat-activated latent curing agent.
21. The composition of Claim 20 further comprising (c) rubber particles having a core/shell structure.
22. The composition of Claim 20 further comprising (c) graphenic carbon particles.
23. The composition of Claim 20 further comprising:
- (c) rubber particles having a core/shell structure; and
 - (d) graphenic carbon particles.
24. The composition of Claim 20 further comprising (c) an epoxy/CTBN adduct.
25. The composition of Claim 20 further comprising (c) an epoxy/dimer acid adduct.
26. The composition of Claim 20 further comprising:
- (c) an epoxy/CTBN adduct; and
 - (d) an epoxy/dimer acid adduct.