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(54) Titre : COMPOSITIONS DE REVETEMENT
(54) Title: COATING COMPOSITIONS

(57) Abrégé/Abstract:

The present invention is directed to compositions comprising a first component, a second component, and elastomeric particles. The first component comprises an epoxy-containing compound. The second component comprises a diamine comprising a cyclic ring and/or a polyamine comprising a cyclic ring. The diamine may chemically react with the epoxy-containing compound. Optionally, the cyclic ring of the diamine and/or the polyamine has at least one carbon positioned between the amino functional groups and the cyclic ring structure. Optionally, at least 50% by weight of the elastomeric particles comprise a styrene butadiene core based on total weight of the elastomeric particles. The present invention is also directed to methods of making the compositions, methods of coating a substrate, and coated substrates.

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The present invention is directed to compositions comprising a first component, a second component, and elastomeric particles. The first component comprises an epoxy-containing compound. The second component comprises a diamine comprising a cyclic ring and/or a polyamine comprising a cyclic ring. The diamine may chemically react with the epoxy-containing compound. Optionally, the cyclic ring of the diamine and/or the polyamine has at least one carbon positioned between the amino functional groups and the cyclic ring structure. Optionally, at least 50% by weight of the elastomeric particles comprise a styrene butadiene core based on total weight of the elastomeric particles. The present invention is also directed to methods of making the compositions, methods of coating a substrate, and coated substrates.

COATING COMPOSITIONS

CROSS-REFERENCE TO RELATED APPLICATION

[0001] This application claims the benefit of U.S. Provisional Patent Application Serial No. 62/890,816 filed August 23, 2019, the entire contents of which is incorporated herein by reference.

GOVERNMENT CONTRACT

[0002] This invention was made with Government support under Government Contract No. 201867-140932 entitled Consolidation of Adhesives and Sealants Phase II FY17 awarded by the CCDC Ground Vehicle Systems Center. The United States Government has certain rights in this invention.

FIELD OF THE INVENTION

[0003] The present invention relates to compositions, for example sealant, adhesive, and coating compositions, and to sealants, adhesives, and coatings.

BACKGROUND OF THE INVENTION

[0004] Coating compositions, including sealants and adhesives, are utilized in a wide variety of applications to treat a variety of substrates or to bond together two or more substrate materials.

SUMMARY OF THE INVENTION

[0005] Disclosed herein are compositions comprising: a first component comprising an epoxy-containing compound; a second component that chemically reacts with the epoxy-containing compound, the second component comprising a diamine comprising a cyclic ring and/or a polyamine comprising a cyclic ring, wherein the cyclic ring of the diamine and/or the polyamine has at least one carbon positioned between the amino functional groups and the cyclic ring structure; and elastomeric particles.

[0006] Also disclosed herein are compositions comprising: a first component comprising an epoxy-containing compound; a second component that chemically reacts with the

epoxy-containing compound, the second component comprising a diamine comprising a cyclic ring and/or a polyamine comprising a cyclic ring; and elastomeric particles, wherein at least 50% by weight of the elastomeric particles comprise a styrene butadiene core based on total weight of the elastomeric particles.

[0007] Also disclosed herein is an adhesive having a lap shear displacement of at least 2.5 mm at failure and a lap shear strength of at least 30.0 MPa, wherein the lap shear displacement and the lap shear strength are measured according to ASTM D1002-10 using 2024-T3 aluminum substrate of 1.6 mm thickness, as measured by an INSTRON 5567 machine in tensile mode with a pull rate of 1.3 mm per minute.

[0008] Also disclosed herein are substrates comprising a surface, at least a portion of which is coated with or embedded in one of the compositions disclosed herein.

[0009] Also disclosed herein are parts comprising a surface, at least a portion of which is coated with or embedded in one of the compositions disclosed herein.

[0010] Also disclosed herein are methods for forming a coating on a surface of a substrate comprising: mixing the first component and the second component of any of compositions disclosed herein; and applying the composition to the surface of the first substrate, wherein at least a portion of the substrate is coated with the composition following the applying.

[0011] Also disclosed herein are methods of forming an article comprising extruding the compositions of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

[0012] 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 such as those expressing values, amounts, percentages, ranges, subranges and fractions may be read as if prefaced by the word “about,” even if the term does not expressly appear. 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. Where a closed or open-ended numerical range is described herein, all numbers, values, amounts, percentages, subranges and fractions within or encompassed by the numerical range are to be considered as being specifically included in and belonging to the original disclosure of this application as if these numbers, values, amounts, percentages, subranges and fractions had been explicitly written out in their entirety.

[0013] 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.

[0014] As used herein, unless indicated otherwise, a plural term can encompass its singular counterpart and vice versa, unless indicated otherwise. For example, although reference is made herein to “an” epoxy and “a” curing agent, a combination (i.e., a plurality) of these components can be used.

[0015] 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.

[0016] As used herein, “including,” “containing” and like terms are understood in the context of this application to be synonymous with “comprising” and are therefore open-ended and do not exclude the presence of additional undescribed or unrecited elements, materials, ingredients or method steps. As used herein, “consisting of” is understood in the context of this application to exclude the presence of any unspecified element, ingredient or method step. As used herein, “consisting essentially of” is understood in the context of this application to include the specified elements, materials, ingredients or method steps “and those that do not materially affect the basic and novel characteristic(s)” of what is being described.

[0017] As used herein, the terms “on,” “onto,” “applied on,” “applied onto,” “formed on,” “deposited on,” “deposited onto,” mean formed, overlaid, deposited, or provided on but not necessarily in contact with the surface. For example, a coating composition “applied onto” a substrate does not preclude the presence of one or more other intervening coating layers of the same or different composition located between the coating composition and the substrate.

[0018] As used herein, “monoamine” refers to an organic compound having one amino functional group.

[0019] As used herein, “diamine” refers to an organic compound having two amino functional groups.

[0020] As used herein, “polyamine” refers to an organic compound having more than two amino functional groups.

[0021] As used herein, “amino functional group” refers to a functional group comprising a nitrogen atom attached by a single bond to a hydrogen atom(s), an alkyl group(s), and/or an aryl group(s).

[0022] As used herein, “epoxide functional group” refers to a functional group comprising a cyclic ether with a three-atom ring.

[0023] As used herein, “amine hydrogen” refers to the number of active hydrogens directly bonded to the nitrogen atom of an amine- or other nitrogen-containing functional group. “Active hydrogens” refer to hydrogens that can be displaced when the amine- or nitrogen-containing functional group reacts as a nucleophile with an appropriate electrophile and can be determined, for example, by the Zerewitinoff test.

[0024] As used herein, a “coating composition” refers to a composition, e.g., a solution, mixture, or a dispersion, that, in an at least partially dried or cured state, is capable of producing a film, layer, or the like on at least a portion of a substrate surface.

[0025] As used herein, a “seal” or a “sealant” or compositions thereof refers to a coating composition, e.g., a solution, mixture, or a dispersion, that, in an at least partially dried or cured state, has the ability to resist atmospheric conditions and particulate matter, such as moisture and temperature and at least partially block the transmission of materials, such as particulates, water, fuel, or other liquids and gasses.

[0026] As used herein, the term “structural adhesive” means an adhesive producing a load-bearing joint having both a lap shear strength of at least 20.0 MPa, measured according to ASTM D1002-10 using 2024-T3 aluminum substrate of 1.6 mm thickness, as measured by an INSTRON 5567 machine in tensile mode with a pull rate of 1.3 mm per minute.

[0027] As defined herein, a “2K” or “two-component” coating composition refers to a composition in which at least a portion of the reactive components readily react and at least partially cure when mixed without activation from an external energy source, such as at ambient

conditions. One of skill in the art understands that the two components of the coating composition are stored separately from each other and mixed just prior to application of the coating composition. As described in more detail below, the 2K coating compositions disclosed herein may be subjected to a curing process wherein (1) at least a portion of the first component and the second component chemically react when mixed at ambient conditions to at least partially cure the coating composition without activation from an external energy source, optionally followed by (2) the application of an external energy source to the coating composition to further cure the coating composition, such as a two-step curing process described herein. External energy sources that may be used to promote the curing reaction (i.e., the crosslinking of the epoxy component and the curing agent) include, for example, radiation (i.e., actinic radiation) and/or heat, such as by baking in an oven and/or forced hot air.

[0028] As further defined herein, ambient conditions generally refer to room temperature and humidity conditions or temperature and humidity conditions that are typically found in the area in which the coating composition is being applied to a substrate, e.g., at 10°C to 40°C and 5% to 80% relative humidity.

[0029] As used herein, “Mw” refers to the weight average molecular weight, for example the theoretical value as determined by Gel Permeation Chromatography using Waters 2695 separation module with a Waters 410 differential refractometer (RI detector) and polystyrene standards, tetrahydrofuran (THF) used as the eluent at a flow rate of 1 ml min⁻¹, and two PL Gel Mixed C columns used for separation.

[0030] As used herein, the term “accelerator” means a substance that increases the rate or decreases the activation energy of a chemical reaction. An accelerator may be either a “catalyst,” that is, without itself undergoing any permanent chemical change, or may be reactive, that is, capable of chemical reactions and includes any level of reaction from partial to complete reaction of a reactant.

[0031] As used herein, the terms “latent” or “blocked” or “encapsulated”, when used with respect to a curing agent or an accelerator, means a molecule or a compound that is activated by an external energy source prior to reacting (i.e., crosslinking) or having a catalytic effect, as the case may be. For example, an accelerator may be in the form of a solid at room temperature and have no catalytic effect until it is heated and melts or dissolves in the composition, or the latent accelerator may be reversibly reacted with a second compound that

prevents any catalytic effect until the reversible reaction is reversed by the application of heat and the second compound is removed, freeing the accelerator to catalyze reactions.

[0032] As used herein, the term “curing agent” means any reactive material that can be added to a composition to accelerate curing of the composition (e.g., curing of a polymer). The term “reactive” when used with respect to the curing agent means capable of chemical reactions and includes any level of reaction from partial to complete reaction of a reactant.

[0033] As used herein, the term “cure”, “cured” or similar terms, as used in connection with the composition described herein, means that at least a portion of the components that form the composition are cross-linked to form a coating, film, layer, or bond. Additionally, curing of the composition refers to subjecting said composition to curing conditions (e.g., elevated temperature, lowered activation energy through catalytic activity, etc.) leading to the reaction of the reactive functional groups of the components of the composition, and resulting in the crosslinking of the components of the composition and formation of an at least partially cured or gelled coating. As used herein, the term “at least partially cured” with respect to a coating refers to a coating formed by subjecting the composition to curing conditions such that a chemical reaction of at least a portion of the reactive groups of the components of the composition occurs to form a coating, film, layer, or bond. A coating composition may be considered to be “at least partially cured” if it has a lap shear strength of greater than 0.2 MPa measured according to ASTM D1002-10 by using an INSTRON 5567 machine in tensile mode with a pull rate of 1.3 mm per minute. As discussed in more detail below, the coating composition may also be subjected to a two-step curing process such that a substantially complete cure is attained and wherein further exposure to curing conditions results in no significant further improvement in the coating properties such as, for example, increased lap shear strength.

[0034] As used herein, unless indicated otherwise, the term “substantially free” means that a particular material is not purposefully added to a mixture or composition, respectively, and is only present as an impurity in a trace amount of less than 5% by weight based on a total weight of the mixture or composition, respectively. As used herein, unless indicated otherwise, the term “essentially free” means that a particular material is only present in an amount of less than 2% by weight based on a total weight of the mixture or composition, respectively. As used herein, unless indicated otherwise, the term “completely free” means that a mixture or

composition, respectively, does not comprise a particular material, i.e., the mixture or composition comprises 0% by weight of such material.

[0035] As used herein, the term “glass transition temperature” (“T_g”) refers to the temperature at which an amorphous material, such as a glass or a high molecular weight polymer, changes from a brittle vitreous state to a plastic or rubbery state or from a plastic or rubbery state to a brittle vitreous state. T_g values as used herein may be determined, for example, by the Fox Equation.

[0036] The present invention is directed to a composition comprising, or consisting essentially of, or consisting of, a first component, a second component, and elastomeric particles. The first component may comprise, or consist essentially of, or consist of, an epoxy-containing compound. The second component may comprise, or consist essentially of, or consist of, a diamine comprising a cyclic ring and/or a polyamine comprising a cyclic ring, wherein the cyclic ring of the diamine and/or the polyamine has at least one carbon positioned between the amino functional groups and the cyclic ring structure. The diamine and/or polyamine may chemically react with the epoxy-containing component.

[0037] The present invention also is directed to a composition comprising, or consisting essentially of, or consisting of, a first component, a second component, and elastomeric particles, wherein at least 50% by weight of the elastomeric particles comprise, or consist essentially of, or consist of, a styrene butadiene core based on total weight of the elastomeric particles. The first component may comprise, or consist essentially of, or consist of, an epoxy-containing compound. The second component may comprise, or consist essentially of, or consist of, a diamine comprising a cyclic ring and/or a polyamine comprising a cyclic ring. The diamine and/or polyamine may chemically react with the epoxy-containing component.

[0038] The first component of the composition may comprise an epoxy-containing compound. Suitable epoxy-containing compounds that may be used include monoepoxides, polyepoxides, or combinations thereof.

[0039] Suitable monoepoxides that may be used include glycidol, monoglycidyl ethers of alcohols and phenols, such as phenyl glycidyl ether, n-butyl glycidyl ether, cresyl glycidyl ether, isopropyl glycidyl ether, glycidyl versatate, for example, CARDURA E available from Shell Chemical Co., and glycidyl esters of monocarboxylic acids such as glycidyl neodecanoate, and mixtures of any of the foregoing.

[0040] Useful epoxy-containing compounds that can be used include polyepoxides (having an epoxy functionality greater than 1), epoxy adducts, or combinations thereof. Suitable polyepoxides include polyglycidyl ethers of Bisphenol A, such as Epon® 828 and 1001 epoxy resins, and Bisphenol F polyepoxides, 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 epoxy components include epoxidized Bisphenol A novolacs, epoxidized phenolic novolacs, epoxidized cresylic novolac, isosorbide diglycidyl ether, triglycidyl p-aminophenol, and triglycidyl p-aminophenol bismaleimide, triglycidyl isocyanurate, tetraglycidyl 4,4'-diaminodiphenylmethane, and tetraglycidyl 4,4'-diaminodiphenylsulphone. The epoxy-containing compound may also comprise a carboxyl-terminated butadiene-acrylonitrile copolymer modified epoxy-containing compound. The epoxy-containing compound may also comprise an epoxy-containing acrylic, such as glycidyl methacrylate.

[0041] The epoxy-containing compound may comprise an epoxy-adduct. The composition may comprise one or more epoxy-adducts. As used herein, the term "epoxy-adduct" refers to a reaction product comprising the residue of an epoxy and at least one other compound that does not include an epoxide functional group. For example, the epoxy-adduct may comprise the reaction product of reactants comprising an epoxy, a polyol, and an anhydride.

[0042] The epoxy used to form the epoxy-adduct may comprise any of the epoxy-containing compounds listed above that may be included in the composition.

[0043] The polyol used to form the epoxy-adduct may include diols, triols, tetraols and higher functional polyols. Combinations of such polyols may also be used. The polyols may be based on a polyether chain derived from ethylene glycol, propylene glycol, butylene glycol, hexylene glycol and the like as well as mixtures thereof. The polyol may also be based on a polyester chain derived from ring opening polymerization of caprolactone (referred to as polycaprolactone-based polyols hereinafter). Suitable polyols may also include polyether polyols, polyurethane polyols, polyurea polyols, acrylic polyols, polyester polyols, polybutadiene polyols, hydrogenated polybutadiene polyols, polycarbonate polyols, polysiloxane polyols, and

combinations thereof. Polyamines corresponding to polyols may also be used, and in this case, amides instead of carboxylic esters will be formed with the anhydrides.

[0044] The polyol may comprise a polycaprolactone-based polyol. The polycaprolactone-based polyols may comprise diols, triols or tetraols terminated with primary hydroxyl groups. Commercially available polycaprolactone-based polyols include those sold under the trade name Capa™ from Perstorp Group, such as, for example, Capa 2054, Capa 2077A, Capa 2085, Capa 2205, Capa 3031, Capa 3050, Capa 3091 and Capa 4101.

[0045] The polyol may comprise a polytetrahydrofuran-based polyol. The polytetrahydrofuran-based polyols may comprise diols, triols or tetraols terminated with primary hydroxyl groups. Commercially available polytetrahydrofuran-based polyols include those sold under the trade name Terathane®, such as Terathane® PTMEG 250 and Terathane® PTMEG 650 which are blends of linear diols in which the hydroxyl groups are separated by repeating tetramethylene ether groups, available from Invista. In addition, polyols based on dimer diols sold under the trade names Pripol®, Solvermol™ 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.

[0046] The anhydride that may be used to form the epoxy-adduct may comprise any suitable acid anhydride known in the art. For example, the anhydride may comprise 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 (hexafluoroisopropylidene) anhydride (6FDA).

[0047] The epoxy-adduct may comprise a diol, a monoanhydride, and a diepoxy compound, wherein the mole ratio of diol, monoanhydride, and diepoxy compounds in the epoxy-adduct may vary from 0.5:0.8:1.0 to 0.5:1.0:6.0.

[0048] The epoxy-adduct may comprise a triol, a monoanhydride, and a diepoxy compound, wherein the mole ratio of triol, monoanhydride, and diepoxy compounds in the epoxy-adduct may vary from 0.5:0.8:1.0 to 0.5:1.0:6.0.

[0049] The epoxy-adduct may comprise a tetraol, a monoanhydride, and a diepoxy compound, wherein the mole ratio of tetraol, monoanhydride, and diepoxy compounds in the epoxy-adduct may vary from 0.5:0.8:1.0 to 0.5:1.0:6.0.

[0050] Other suitable epoxy-containing compounds include epoxy-adducts such as epoxy polyesters formed as the reaction product of reactants comprising an epoxy-containing compound, a polyol and an anhydride, as described in U.S. Patent No. 8,796,361, col. 3, line 42 through col. 4, line 65, the cited portion of which is incorporated herein by reference.

[0051] In another example, the epoxy-containing compound of the composition may further include elastomeric particles. As used herein, “elastomeric particles” refers to particles comprised of one or more materials having at least one glass transition temperature (T_g) of greater than -150°C and less than 30°C , calculated, for example, using the Fox Equation. The elastomeric particles may be phase-separated from the epoxy in the epoxy-containing component. As used herein, the term “phase-separated” means forming a discrete domain within a matrix of the epoxy-containing compound.

[0052] The elastomeric particles may have a core/shell structure. Suitable core-shell elastomeric particles may be comprised of an acrylic shell and an elastomeric core. The core may comprise natural or synthetic rubbers, polybutadiene, styrene-butadiene, polyisoprene, chloroprene, acrylonitrile butadiene, butyl rubber, polysiloxane, polysulfide, ethylene-vinyl acetate, fluoroelastomer, polyolefin, hydrogenated styrene-butadiene, or combinations thereof. In examples, no more than 50% by weight of the elastomeric particles comprise a polybutadiene core and/or a polysiloxane core based on total weight of the elastomeric particles.

[0053] The elastomeric particles may optionally be included in an epoxy carrier resin for introduction into the coating composition. Suitable finely dispersed core-shell elastomeric particles in an average particle size ranging from 20 nm to 400 nm may be master-batched in epoxy resin such as aromatic epoxides, phenolic novolac epoxy resin, bisphenol A and/or bisphenol F diepoxide, and/or aliphatic epoxides, which include cyclo-aliphatic epoxides, at concentrations ranging from 1% to 80% core-shell elastomeric particles by weight based on the total weight of the elastomeric dispersion, such as from 5% to 50%, such as from 15% to 35%. Suitable epoxy resins may also include a mixture of epoxy resins. When utilized, the epoxy carrier resin may be an epoxy-containing component such that the weight of the epoxy-

containing component present in the coating composition includes the weight of the epoxy carrier resin.

[0054] Exemplary non-limiting commercial core-shell elastomeric particle products using poly(butadiene) rubber particles that may be utilized in the coating composition include core-shell poly(butadiene) rubber powder (commercially available as PARALOID™ EXL 2650A from Dow Chemical), a core-shell poly(butadiene) rubber dispersion (25% core-shell rubber by weight) in bisphenol F diglycidyl ether (commercially available as Kane Ace MX 136), a core-shell poly(butadiene) rubber dispersion (33% core-shell rubber by weight) in Epon® 828 (commercially available as Kane Ace MX 153), a core-shell poly(butadiene) rubber dispersion (33% core-shell rubber by weight) in Epiclone® EXA-835LV (commercially available as Kane Ace MX 139), a core-shell poly(butadiene) rubber dispersion (37% core-shell rubber by weight) in bisphenol A diglycidyl ether (commercially available as Kane Ace MX 257), and a core-shell poly(butadiene) rubber dispersion (37% core-shell rubber by weight) in Epon® 863 (commercially available as Kane Ace MX 267), each available from Kaneka Texas Corporation, and acrylic rubber dispersions.

[0055] Exemplary non-limiting commercial core-shell elastomeric particle products using styrene-butadiene rubber particles that may be utilized in the coating composition include a core-shell styrene-butadiene rubber powder (commercially available as CLEARSTRENGTH® XT100 from Arkema), core-shell styrene-butadiene rubber powder (commercially available as PARALOID™ EXL 2650J), a core-shell styrene-butadiene rubber dispersion (33% core-shell rubber by weight) in bisphenol A diglycidyl ether (commercially available as Fortegra™ 352 from Olin™), core-shell styrene-butadiene rubber dispersion (33% rubber by weight) in low viscosity bisphenol A diglycidyl ether (commercially available as Kane Ace MX 113), a core-shell styrene-butadiene rubber dispersion (25% core-shell rubber by weight) in bisphenol A diglycidyl ether (commercially available as Kane Ace MX 125), a core-shell styrene-butadiene rubber dispersion (25% core-shell rubber by weight) in bisphenol F diglycidyl ether (commercially available as Kane Ace MX 135), a core-shell styrene-butadiene rubber dispersion (25% core-shell rubber by weight) in D.E.N.™-438 phenolic novolac epoxy (commercially available as Kane Ace MX 215), a core-shell styrene-butadiene rubber dispersion (25% core-shell rubber by weight) in Araldite® MY-721 multi-functional epoxy (commercially available as Kane Ace MX 416), a core-shell styrene-butadiene rubber dispersion (25% core-shell rubber by

weight) in MY-0510 multi-functional epoxy (commercially available as Kane Ace MX 451), a core-shell styrene-butadiene rubber dispersion (25% core-shell rubber by weight) in Syna Epoxy 21 Cyclo-aliphatic Epoxy from Synasia (commercially available as Kane Ace MX 551), and a core-shell styrene-butadiene rubber dispersion (25% core-shell rubber by weight) in polypropylene glycol (MW 400) (commercially available as Kane Ace MX 715), each available from Kaneka Texas Corporation.

[0056] Exemplary non-limiting commercial core-shell elastomeric particle products using polysiloxane rubber particles that may be utilized in the coating composition include a core-shell polysiloxane rubber powder (commercially available as GENIOPERL[®] P52 from Wacker), a core-shell polysiloxane rubber dispersion (40% core-shell rubber by weight) in bisphenol A diglycidyl ether (commercially available as ALBIDUR[®] EP2240A from Evonik), a core-shell polysiloxane rubber dispersion (25% core-shell rubber by weight) in jERT[™]828 (commercially available as Kane Ace MX 960), a core-shell polysiloxane rubber dispersion (25% core-shell rubber by weight) in Epon[®] 863 (commercially available as Kane Ace MX 965) each available from Kaneka Texas Corporation.

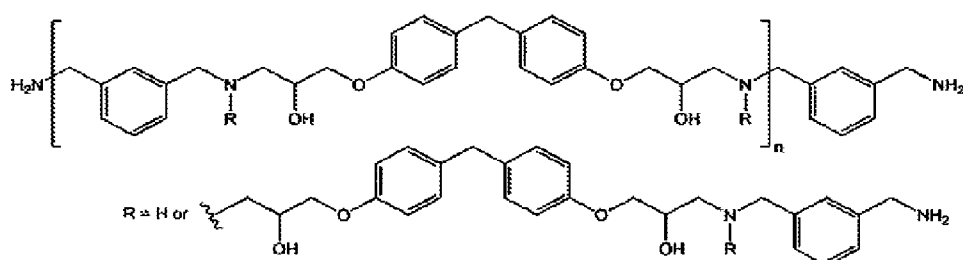
[0057] The average particle size of the elastomeric particles may be at least 20 nm, as measured by transmission electron microscopy (TEM), such as at least 30 nm, such as at least 40 nm, such as at least 50 nm, and may be no more than 400 nm, such as no more than 300 nm, such as no more than 200 nm, such as no more than 150 nm. The average particle size of the elastomeric particles may be 20 nm to 400 nm as measured by TEM, such as 30 nm to 300 nm, such as 40 nm to 200 nm, such as 50 nm to 150 nm. Suitable methods of measuring particle sizes by TEM include suspending elastomeric particles in a solvent selected such that the particles do not swell, and then drop casting the suspension onto a TEM grid which is allowed to dry under ambient conditions. For example, epoxy resin containing core-shell rubber elastomeric particles from Kaneka Texas Corporation can be diluted in butyl acetate for drop casting. Particle size measurements may be obtained from images acquired using a Tecnai T20 TEM operating at 200kV and analyzed using ImageJ software, or an equivalent instrument and software.

[0058] The composition also may further comprise a second component comprising a curing agent that chemically reacts with the epoxy-containing compound of the first component.

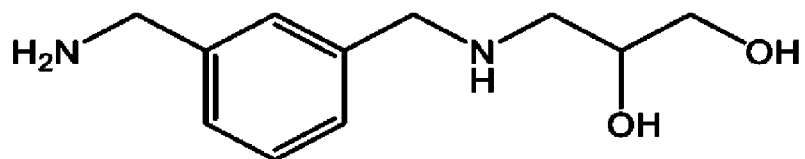
[0059] The curing agent of the second component comprises a diamine comprising a cyclic ring and/or a polyamine comprising a cyclic ring and includes ortho-, meta-, and para-isomers of aromatic diamines and polyamines or any mixtures of these isomers. The diamine and/or polyamine comprising a cyclic ring also includes amines containing non-aromatic ring structures such as aliphatic rings and/or heterocyclic rings. The diamine and/or the polyamine curing agent may be used to at least partially cure the composition by reacting with the epoxy-containing compound of the first component to form a polymeric matrix upon combining the first and second components of the composition.

[0060] In examples, the diamine and/or the polyamine may contain a cyclic ring. The cyclic ring may be intermolecular or may be pendant. For example, the diamine and/or the polyamine may comprise an aromatic ring such as xylylene diamine, phenylene diamine, methylenedianiline, diaminotoluene, diaminophenol, diamino diphenyl sulfone, 4,4'-oxydianiline, diethyl toluene diamine, methyl-bis(methylthio)benzenediamine (Ethacure 300, for example, available from Albemarle), aminobenzylamine, 5,5'-methylenedifurfurylamine, 5,5'-ethylenedifurfurylamine, or combinations thereof. The diamine and/or polyamine may also comprise a non-aromatic cyclic ring such as isophorone diamine, 4,4-diaminodicyclohexylmethane, diaminocyclohexane, bis(aminomethyl)norbornane, bis(aminomethyl)cyclohexane, piperazine, aminoethylpiperazine, bis(aminopropyl)piperazine, or combinations thereof.

[0061] In other examples, the curing agent of the second component may comprise an oligomeric cyclic ring-containing diamine or polyamine in addition to the diamine and/or the polyamine described above. As used herein, the term "oligomer" refers to a molecular complex of monomers having a finite number of repeating units. Optionally, the amino-functional oligomer may contain a cyclic ring. In an example, the amine-functional oligomer may comprise an oligomeric amine reaction product of xylylene diamine and epichlorohydrin, which is commercially available as Gaskamine 328 (Mitsubishi Gas). In an example, the amine-functional oligomer may have one of the following structures:



where n is at least 1 and the presence of R substituents on the amine demonstrate the possibility of branched structures (Structures I and II, respectively). In other examples, the curing agent of the second component may comprise a cyclic ring containing diamine partially reacted with a monofunctional epoxide. In an example, the curing agent of the second component may comprise the reaction product of excess xylylene diamine and glycidol, having the following structure:



(Structure III).

[0062] Optionally, in addition to the diamine or polyamine containing a cyclic ring, the second component may additionally comprise a monoamine, diamine, or polyamine. Useful monoamines include, but are not limited to, aniline, ethanolamine, N-methylethanolamine, butylamine, benzylamine, allylamine, ethylhexylamine, polypropylene glycol monoamines such as Jeffamine-M600 and Jeffamine M-2005 available from Huntsman, polyethylene glycol monoamines such as Jeffamine M-1000 and Jeffamine M-2070 available from Huntsman. Useful diamines include, but are not limited to, ethylenediamine, tetramethylenediamine, hexamethylenediamine, 2-methylpentamethylenediamine (available as Dytex A from Invista), polyether diamines such as those of the Jeffamine D, ED, or EDR series available from Huntsman. Useful polyamines include but are not limited to diethylenetriamine, triethylenetetramine, tetraethylenepentamine, tris(2-aminoethyl)amine, tris(3-aminopropyl)amine, and trifunctional polyether amines such as the Jeffamine T-403, Jeffamine T-3000, and Jeffamine T-5000 available from Huntsman.

[0063] Optionally, the curing agent of the second component may comprise a diamine comprising a cyclic ring and/or a polyamine comprising a cyclic ring in an amount of at least 20 percent by weight based on total weight of all monoamines, diamines and/or polyamines present

in the second component, such as at least 30 percent by weight, such as at least 40 percent by weight, such as at least 50 percent by weight, and may comprise a diamine comprising a cyclic ring and/or a polyamine comprising a cyclic ring in an amount of 100 percent by weight based on total weight of all monoamines, diamines and/or polyamines in the second component, such as no more than 90 percent by weight, such as no more than 80 percent by weight, such as no more than 70 percent by weight, such as no more than 60 percent by weight. The curing agent of the second component may comprise a diamine comprising a cyclic ring and/or a polyamine comprising a cyclic ring in an amount of 20 percent by weight to 100 percent by weight based on total weight of all monoamines, diamines, and/or polyamines in the second component, such as 30 percent by weight to 90 percent by weight, such as 40 percent by weight to 80 percent by weight, such as 50 percent by weight to 70 percent by weight. In an example, the cyclic ring may comprise a benzene. In an example, the diamine comprising a cyclic ring may comprise xylylene diamine.

[0064] The diamine and/or polyamine curing agent may be present in the composition in an amount sufficient to provide a molar ratio of epoxide functional groups from the epoxy-containing compound to amine-hydrogens from the diamine and/or polyamine curing agent of at least 0.5:1.0, such as at least 0.75:1.0, and may be present in the composition in amount to provide a molar ratio of epoxide functional groups from the epoxy-containing compound to amine-hydrogens from the diamine and/or polyamine curing agent of no more than 1.5:1.0, such as no more than 1.25 to 1.0. The diamine and/or polyamine curing agent may be present in the composition in an amount sufficient to provide a molar ratio of epoxide functional groups from the epoxy-containing compound to amine-hydrogens from the diamine and/or polyamine curing agent of 0.5:1.0 to 1.5:1.0, such as 0.75:1.0 to 1.25 to 1.0.

[0065] The second component of the composition may further comprise elastomeric particles. Useful elastomeric particles include those described above, including elastomeric particles having a core-shell structure. For example, the elastomeric particles may optionally be introduced into the second component of the coating composition as solid particles, such as core-shell elastomeric particles having an average particle size of 20 nm to 400 nm.

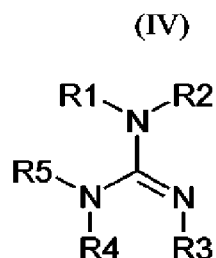
[0066] Elastomeric particles, if present at all, and whether present in the first component and/or the second component, may be present in the composition in a total amount of at least 1 percent by weight based on total weight of the composition, such as at least 3 percent

by weight, such as at least 5 percent by weight, and may be present in the composition in a total amount of no more than 50 percent by weight based on total weight of the composition, such as no more than 40 percent by weight, such as no more than 25 percent by weight. Elastomeric particles, if present at all, and whether present in the first component and/or the second component, may be present in the composition in a total amount of 1 percent by weight to 50 percent by weight based on total weight of the composition, such as 3 percent by weight to 40 percent by weight, such as 5 percent by weight to 25 percent by weight.

[0067] Optionally, the first component and/or the second component of the composition may further comprise an accelerator.

[0068] In examples, the accelerator may comprise, or consist essentially of, or consist of, a guanidine. It will be understood that “guanidine,” as used herein, refers to guanidine and derivatives thereof. For example, the curing agent that may be used includes guanidines, substituted guanidines, substituted ureas, melamine resins, guanamine derivatives, and/or mixtures thereof. Examples of substituted guanidines are methylguanidine, dimethylguanidine, trimethylguanidine, tetramethylguanidine, methylisobiguanidine, dimethylisobiguanidine, tetramethylisobiguanidine, hexamethylisobiguanidine, heptamethylisobiguanidine and, more especially, cyanoguanidine (dicyandiamide, e.g. Dyhard® available from AlzChem). Representatives of suitable guanamine derivatives which may be mentioned are alkylated benzoguanamine resins, benzoguanamine resins or methoxymethylethoxymethylbenzoguanamine.

[0069] For example, the guanidine may comprise a compound, moiety, and/or residue having the following general structure:

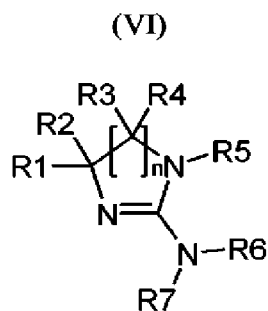
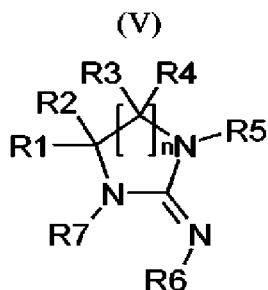


wherein each of R1, R2, R3, R4, and R5 (*i.e.*, substituents of structure (IV)) comprise hydrogen, (cyclo)alkyl, aryl, aromatic, organometallic, a polymeric structure, or together can form a cycloalkyl, aryl, or an aromatic structure, and wherein R1, R2, R3, R4, and R5 may be the same

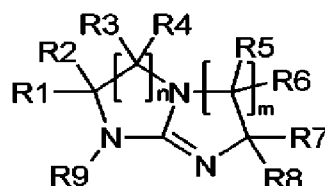
or different. As used herein, “(cyclo)alkyl” refers to both alkyl and cycloalkyl. When any of the R groups “together can form a (cyclo)alkyl, aryl, and/or aromatic group”, it is meant that any two adjacent R groups are connected to form a cyclic moiety, such as the rings in structures (V) – (VIII) below.

[0070] It will be appreciated that the double bond between the carbon atom and the nitrogen atom that is depicted in structure (IV) may be located between the carbon atom and another nitrogen atom of structure (IV). Accordingly, the various substituents of structure (IV) may be attached to different nitrogen atoms depending on where the double bond is located within the structure.

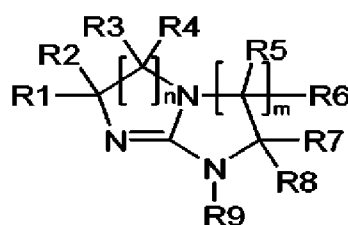
[0071] The guanidine may comprise a cyclic guanidine such as a guanidine of structure (IV) wherein two or more R groups of structure (IV) together form one or more rings. In other words, the cyclic guanidine may comprise ≥ 1 ring(s). For example, the cyclic guanidine may either be a monocyclic guanidine (1 ring) such as depicted in structures (V) and (VI) below, or the cyclic guanidine may be bicyclic or polycyclic guanidine (≥ 2 rings) such as depicted in structures (VII) and (VIII) below.



(VII)



(VIII)



[0072] Each substituent of structures (V) and/or (VI), R1-R7, may comprise hydrogen, (cyclo)alkyl, aryl, aromatic, organometallic, a polymeric structure, or together can form a cycloalkyl, aryl, or an aromatic structure, and wherein R1-R7 may be the same or different. Similarly, each substituent of structures (VII) and (VIII), R1-R9, may be hydrogen, alkyl, aryl, aromatic, organometallic, a polymeric structure, or together can form a cycloalkyl, aryl, or an aromatic structure, and wherein R1-R9 may be the same or different. Moreover, in some examples of structures (VI) and/or (VI), certain combinations of R1-R7 may be part of the same ring structure. For example, R1 and R7 of structure (V) may form part of a single ring structure. Moreover, it will be understood that any combination of substituents (R1-R7 of structures (V) and/or (VI) as well as R1-R9 of structures (VII) and/or (VIII)) may be chosen so long as the substituents do not substantially interfere with the catalytic activity of the cyclic guanidine.

[0073] Each ring in the cyclic guanidine may be comprised of ≥ 5 members. For example, the cyclic guanidine may comprise a 5-member ring, a 6-member ring, and/or a 7-member ring. As used herein, the term “member” refers to an atom located in a ring structure. Accordingly, a 5-member ring will have 5 atoms in the ring structure (“n” and/or “m”=1 in structures (V)-(VIII)), a 6-member ring will have 6 atoms in the ring structure (“n” and/or “m”=2

in structures (V)-(VIII)), and a 7-member ring will have 7 atoms in the ring structure ("n" and/or "m"=3 in structures (V)-(VIII)). It will be appreciated that if the cyclic guanidine is comprised of ≥ 2 rings (e.g., structures (VII) and (VIII)), the number of members in each ring of the cyclic guanidine can either be the same or different. For example, one ring may be a 5-member ring while the other ring may be a 6-member ring. If the cyclic guanidine is comprised of ≥ 3 rings, then in addition to the combinations cited in the preceding sentence, the number of members in a first ring of the cyclic guanidine may be different from the number of members in any other ring of the cyclic guanidine.

[0074] It will also be understood that the nitrogen atoms of structures (V)-(VIII) may further have additional atoms attached thereto. Moreover, the cyclic guanidine may either be substituted or unsubstituted. For example, as used herein in conjunction with the cyclic guanidine, the term "substituted" refers to a cyclic guanidine wherein R5, R6, and/or R7 of structures (V) and/or (VI) and/or R9 of structures (VII) and/or (VIII) is not hydrogen. As used herein in conjunction with the cyclic guanidine, the term "unsubstituted" refers to a cyclic guanidine wherein R1-R7 of structures (V) and/or (VI) and/or R1-R9 of structures (VII) and/or (VIII) are hydrogen.

[0075] The cyclic guanidine may comprise a bicyclic guanidine, and the bicyclic guanidine may comprise 1,5,7-triazabicyclo[4.4.0]dec-5-ene ("TBD" or "BCG") or 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (MTBD).

[0076] Other useful accelerators may comprise amidoamine or polyamide accelerators, such as, for example, one of the Ancamide® products available from Air Products, amine, amino-containing phenols, dihydrazide, imidazole, or dicyandiamide adducts and complexes, such as, for example, one of the Ajicure® products available from Ajinomoto Fine Techno Company, 3,4-dichlorophenyl-N,N-dimethylurea (A.K.A. Diuron) available from Alz Chem, or combinations thereof.

[0077] Useful accelerators that may be included in the second component of the composition may comprise secondary amines, tertiary amines, cyclic tertiary amines, amidines, or combinations thereof. The cyclic tertiary amine may comprise 1,4-diazabicyclo[2.2.2]octane ("DABCO"), 1,8-diazabicyclo[5.4.0]undec-7-ene ("DBU"), 1,5-diazabicyclo[4.3.0]non-5-ene ("DBN"), and combinations thereof. Additional examples of suitable accelerators include, pyridine, imidazole, dimethylaminopyridine, 1-methylimidazole, N,N'-carbonyldiimidazole,

[2,2]bipyridine, 2,4,6-tris(dimethylamino methyl)phenol, 3,5-dimethylpyrazole, and combinations thereof. Additional examples of useful accelerators include Mannich bases, tetraalkyl ammonium salts, metal salts, and strong bases.

[0078] The accelerator, if present at all, may be present in the second component of the composition in an amount of at least 0.5 percent by weight based on total weight of the composition, such as at least 1 percent by weight, and may be present in an amount of no more than 55 percent by weight based on total weight of the composition, such as no more than 20 percent by weight. The accelerator, if present at all, may be present in the second component of the composition in an amount of 0.5 percent by weight to 55 percent by weight based on total weight of the composition, such as 1 percent by weight to 20 percent by weight.

[0079] A filler material or more than one filler material may optionally be added to the first and/or second component of the composition. Useful fillers that may be introduced to provide improved mechanical 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. Additionally, filler material may optionally be graphene and graphenic carbon particles (for example, xGnP graphene nanoplatelets commercially available from XG Sciences, and/or for example, carbon particles having structures comprising one or more layers of one-atom-thick planar sheets of sp²-bonded carbon atoms that are densely packed in a honeycomb crystal lattice. The average number of stacked layers may be less than 100, for example, less than 50. The average number of stacked layers may be 30 or less, such as 20 or less, such as 10 or less, such as 5 or less. The graphenic carbon particles may be substantially flat; however, at least a portion of the planar sheets may be substantially curved, curled, creased, or buckled. The particles typically do not have a spheroidal or equiaxed morphology. Suitable graphenic carbon particles are described in U.S. Publication No. 2012/0129980, at paragraphs [0059]-[0065], the cited portion of which is incorporated herein by reference. Other suitable graphenic carbon particles are described in U.S. Pat. No. 9,562,175, at 6:6 to 9:52, the cited portion of which are incorporated herein by reference.

[0080] Organic and/or inorganic fillers, such as those that are substantially spherical, may optionally be added to the first and/or second component of the composition. Useful organic fillers that may be introduced include cellulose, starch, and acrylic. Useful inorganic

fillers that may be introduced include borosilicate, aluminosilicate, calcium inosilicate (Wollastonite), mica, silica and calcium carbonate. The organic and inorganic fillers may be solid, hollow, or layered in composition and may range in size from 10 nm to 1 mm in at least one dimension, measured, for example by TEM or SEM.

[0081] Optionally, additional fillers, thixotropes, colorants, tints and/or other materials also may be added to the first and/or second component of the composition.

[0082] Useful thixotropes that may be used include untreated fumed silica and treated fumed silica, castor wax, clay, organo clay and combinations thereof. In addition, fibers such as synthetic fibers like Aramid[®] fiber and Kevlar[®] fiber, acrylic fibers, and/or engineered cellulose fiber may also be utilized.

[0083] Useful colorants, dyes, or tints may include red iron pigment, titanium dioxide, calcium carbonate, and phthalocyanine blue and combinations thereof.

[0084] Useful fillers that may be used in conjunction with thixotropes may include inorganic fillers such as inorganic clay or silica and combinations thereof.

[0085] Exemplary other materials that may be utilized include, for example, calcium oxide and carbon black and combinations thereof.

[0086] Such fillers, if present at all, may be present in the first and/or second component of the composition in an amount of no more than 25 percent by weight based on total weight of the composition, such as no more than 15 percent by weight, such as no more than 10 percent by weight, such as no more than 5 percent by weight. Such fillers may be present in the first and/or second component of the composition an amount of 0 percent to 25 percent by weight based on total weight of the composition, such as 0.1 percent by weight to 15 percent by weight, such as 0.5 percent by weight to 10 percent by weight, such as 1 percent by weight to 5 percent by weight.

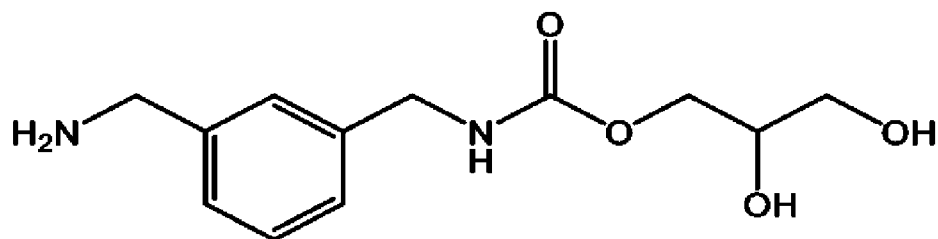
[0087] Optionally, the composition may be substantially free, or essentially free, or completely free, of platy fillers such as talc, pyrophyllite, chlorite, vermiculite, or combinations thereof. Optionally, the composition may be substantially free, or essentially free, or completely free, of alumina fillers, including plate-like alumina particles, spherical alumina particles, and/or amorphous alumina particles.

[0088] The composition may further comprise an additive or more than one additive. As used herein, the term “additives” refers to ingredients or components included in the first

and/or second component of the coating composition in addition to the epoxy-containing compound, the polyamine curing agent, the elastomeric particles, the accelerator (if any), and the fillers (if any) described herein. Exemplary non-limiting examples of such additives include flexibilizers such as Flexibilzer® DY 965 from Huntsman Corporation, reactive liquid rubber, non-reactive liquid rubber, epoxy-amine adducts (such as those described above but, when present, different from the epoxy-containing compound present in the coating composition), epoxy-thiol adducts, blocked isocyanates, capped isocyanates, epoxy-urethanes, epoxy-ureas, modified epoxies from Hexion, HELOXY™ modifiers from Hexion, adhesion promoters, silane coupling agents such as Silquest A-187 from Momentive, flame retardants, colloidal silica such as NANOPOX® dispersions from Evonik, thermoplastic resins, acrylic polymer beads such as ZEFIAC® beads from AICA Kogyo Co, or combinations thereof.

[0089] Such additives, if present at all, may be present in the first and/or second component of the composition in an amount of at least 1 percent by weight based on total weight of the composition, such as at least 2 percent by weight, and may be present in the composition in an amount of no more than 25 percent by weight based on total weight of the composition, such as no more than 10 percent by weight. Such additives, if present at all, may be present in the first and/or second component of the composition in an amount of 1 percent by weight to 25 percent by weight based on total weight of the composition, such as 2 percent by weight to 10 percent by weight.

[0090] The composition may further comprise a cyclic carbonate-functional molecule. The cyclic carbonate-functional molecule may be present in the first component and/or the second component. Useful examples of cyclic carbonate-functional molecules include glycerol carbonate, propylene carbonate, and combinations thereof. The cyclic carbonate-functional molecule may be present in the epoxy component or may be pre-reacted with the diamine or polyamine containing a cyclic ring. In an example, the curing agent may comprise the reaction product of excess xylylene diamine with glycerol carbonate having the following structure:



(Structure IX).

[0091] Such cyclic carbonate-functional molecule, if present at all, may be present in an amount of at least 0.1 percent by weight based on total weight of the composition, such as at least 1 percent by weight, such as at least 2 percent by weight, and may be present in an amount of no more than 10 percent by weight, such as no more than 8 percent by weight, such as no more than 6 percent by weight. Such cyclic carbonate-functional molecule, if present at all, may be present in an amount of 0.1 percent by weight to 10 percent by weight based on total weight of the composition, such as 1 percent by weight to 8 percent by weight, such as 2 percent by weight to 6 percent by weight.

[0092] The present invention also is directed to a method for treating a substrate comprising, or consisting essentially of, or consisting of, mixing one of the first components and one of the second components described above to form one of the compositions, and applying the composition to at least a portion of a substrate surface. The composition can be applied to the surface of the substrate in any number of different ways, non-limiting examples of which include brushes, rollers, films, pellets, spray guns, applicator guns, and injectors such that at least a portion of the surface is coated with the composition. Optionally, the composition may be contacted with a surface of a second substrate such that the composition is located between the first substrate and the second substrate and at least a portion of the surface of the first substrate and at least a portion of the second substrate is coated with the composition. Optionally, the composition may be injected into, on or around composite sheets, meshes, and the like.

[0093] Following application to a substrate surface, the composition may be at least partially cured at ambient or slightly thermal conditions. Optionally, the composition may be cured by a two-step curing process. As used herein, the term “two-step curing process” refers to a process comprising a first step during which the composition is allowed to cure at ambient or slightly thermal conditions followed by a second step during which the composition may be subjected to an external energy source to further react the components of the composition and effectuate additional cure of the composition. For example, the coating composition may be allowed to cure at room temperature or slightly thermal conditions during the first step. Next, the coating composition may be cured during the second step by baking and/or curing at elevated temperature, such as at a temperature of at least 50°C, such as at least 70°C, such as at least 80°C, such as at least 100°C, and in some cases at a temperature of no more than 250°C, such as no more than 200°C, such as no more than 180°C, such as no more than 170°C, such as no more

than 165°C, and in some cases at a temperature of from 50°C to 200°C, from 70°C to 180°C, from 80°C to 170°C, from 100°C to 165°C, and for any desired time period (e.g., from 5 minutes to 1 hour) sufficient to at least partially cure the coating composition on the substrate(s).

[0094] For example, the composition may be applied to a surface of either one or both of the substrate materials being bonded to form an adhesive bond therebetween and the substrates may be aligned and pressure and/or spacers may be added to control bond thickness.

[0095] The composition may be applied to cleaned or uncleaned (i.e., including oily or oiled) substrate surfaces. The composition may be cured to form a coating, layer or film on the substrate surface as described herein. The coating, layer or film, may be, for example, a sealant or an adhesive.

[0096] For example, the present invention may be a method for forming a bond between two substrates for a wide variety of potential applications in which the bond between the substrates provides particular mechanical properties related to both lap shear strength and displacement.

[0097] As stated above, the compositions of the present disclosure may form a coating, a seal, or an adhesive on a substrate or a substrate surface. The composition may be applied to substrate surfaces, including, by way of non-limiting example, a vehicle body, components of an automobile frame or an airplane, parts used in or on a vehicle, to armor assemblies such as those on a tank, or to protective clothing such as body armor, personal armor, suits of armor, and the like. The coating formed by the composition of the present invention provides sufficient lap shear strength and displacement. The composition may be applied alone or as part of a system. The composition may also be applied to a substrate that has been deoxidized, pretreated, coated with an electrodepositable coating, and/or coated with additional layers such as a primer, basecoat, or topcoat.

[0098] The present invention also is directed to a substrate having a surface, in which at least a portion of the surface is coated with one of the compositions of the present invention to form a coating thereon. The present invention also is directed to a part having a surface, in which at least a portion of the surface is coated with one of the compositions of the present invention to form a coating thereon. The present invention is also directed to an article comprising first and second substrates each having a surface, in which at least a portion of one of the surfaces is coated with one of the compositions of the present invention to form a coating

thereon between the first and second substrates. The present invention is also directed to a composition of the present invention injected into, on, and/or around a fibrous sheet or mesh. The fibrous sheet or mesh may be woven or non-woven.

[0099] As described above, substrates treated with the compositions of the present invention may have a film, coating, or the like formed by the coating composition, applied to at least a portion of the substrate surface. In examples, the coating composition may have a dry film thickness of at least 12.5 micrometers (0.5 mil), such as at least 25 micrometers (1 mil), such as at least 75 micrometers (3 mil), and in some instances may have a dry film thickness of no more than 1270 micrometers (50 mil), such as no more than 635 micrometers (25 mil), such as no more than 405 micrometers (16 mil). In examples, the coating composition may have a dry film thickness of 12.5 micrometers to 1270 micrometers, such as 25 micrometers to 635 micrometers, such as 75 micrometers to 405 micrometers.

[0100] The present invention is also directed to an adhesive having a lap shear displacement of at least 2.5 mm at failure, such as at least 3.0 mm, such as at least 3.1 mm and a lap shear strength of at least 30.0 MPa, such as at least 32 MPa, such as at least 35 MPa, wherein the lap shear displacement and the lap shear strength are measured according to ASTM D1002-10 using 2024-T3 aluminum substrate of 1.6 mm thickness, as measured by an INSTRON 5567 machine in tensile mode with a pull rate of 1.3 mm per minute.

[0101] It has been surprisingly discovered that the compositions of the present invention, in an at least partially cured state, may have a lap shear displacement at failure of at least 2.5 mm, such as at least 3.0 mm, such as at least 3.1 mm, and a lap shear strength of at least 30 MPa, such as at least 32 MPa, such as at least 35 MPa, wherein lap shear displacement and lap shear strength each are measured according to ASTM D1002-10 using 2024-T3 aluminum substrate of 1.6 mm thickness, as measured by an INSTRON 5567 machine in tensile mode with a pull rate of 1.3 mm per minute.

[0102] The substrates that may be coated by the compositions of the present invention are not limited. Suitable substrates useful in the present invention include, but are not limited to, materials such as metals or metal alloys, ceramic materials such as boron carbide or silicon carbide, polymeric materials such as hard plastics including filled and unfilled thermoplastic materials or thermoset materials, woven or non-woven fibrous sheets or meshes, or composite materials. Other suitable substrates useful in the present invention include, but are not limited to,

glass or natural materials such as wood. For example, suitable substrates include rigid metal substrates such as ferrous metals, aluminum, aluminum alloys, magnesium titanium, copper, and other metal and alloy substrates. The ferrous metal substrates used in the practice of the present invention may include iron, steel, and alloys thereof. Non-limiting examples of useful steel materials include cold rolled steel, galvanized (zinc coated) steel, electrogalvanized steel, stainless steel, pickled steel, zinc-iron alloy such as GALVANNEAL, and combinations thereof. Combinations or composites of ferrous and non-ferrous metals can also be used. Aluminum alloys of the 1XXX, 2XXX, 3XXX, 4XXX, 5XXX, 6XXX, 7XXX, or 8XXX series as well as clad aluminum alloys and cast aluminum alloys of the A356, 1XX.X, 2XX.X, 3XX.X, 4XX.X, 5XX.X, 6XX.X, 7XX.X, or 8XX.X series also may be used as the substrate. Magnesium alloys of the AZ31B, AZ91C, AM60B, or EV31A series also may be used as the substrate. The substrate used in the present invention may also comprise titanium and/or titanium alloys of grades 1-36 including H grade variants. Other suitable non-ferrous metals include copper and magnesium, as well as alloys of these materials. Suitable metal substrates for use in the present invention include those that are used in the assembly of vehicular bodies (e.g., without limitation, door, body panel, trunk deck lid, roof panel, hood, roof and/or stringers, rivets, landing gear components, and/or skins used on an aircraft), a vehicular frame, vehicular parts, motorcycles, wheels, and industrial structures and components. As used herein, “vehicle” or variations thereof includes, but is not limited to, civilian, commercial and military aircraft, and/or land vehicles such as cars, motorcycles, and/or trucks. The metal substrate also may be in the form of, for example, a sheet of metal or a fabricated part. It will also be understood that the substrate may be pretreated with a pretreatment solution including a zinc phosphate pretreatment solution such as, for example, those described in U.S. Patent Nos. 4,793,867 and 5,588,989, or a zirconium containing pretreatment solution such as, for example, those described in U.S. Patent Nos. 7,749,368 and 8,673,091. The substrate may comprise a composite material such as a plastic or a fiberglass composite. The substrate may be a fiberglass and/or carbon fiber composite. The compositions of the present invention are particularly suitable for use in various industrial or transportation applications including automotive, light and heavy commercial vehicles, marine, or aerospace.

[0103] The 2K compositions disclosed herein surprisingly may be used in any suitable additive manufacturing technology, such as extrusion, jetting, and binder jetting.

[0104] The present disclosure is directed to the production of structural articles, such as by way of non-limiting example, sound damping pads, using three-dimensional printing. A three-dimensional article may be produced by forming successive portions or layers of an article by depositing the composition of the present invention onto a substrate and thereafter depositing additional portions or layers of the composition over the underlying deposited portion or layer and/or adjacent the previously deposited portion or layer. Layers can be successively deposited adjacent to a previously deposited layer to build a printed article. First and second components of the composition can be mixed and then deposited or the first and second components of the composition can be deposited separately. When deposited separately, the first and second components can be deposited simultaneously, sequentially, or both simultaneously and sequentially.

[0105] By “portions of an article,” when used with respect to additive manufacturing, is meant subunits of an article, such as layers of an article. The layers may be on successive horizontal parallel planes. The portions may be parallel planes of the deposited material or beads of the deposited material produced as discreet droplets or as a continuous stream of material. The first and second components may each be provided neat or may also include a solvent (organic and/or water) and/or other additives as described below. First and second components provided by the present disclosure may be substantially free of solvent. By substantially free is meant that the first and second components comprise less than 5 wt%, less than 4 wt%, less than 2 wt%, or less than 1 wt% of solvent, where wt% is based on the total weight of the first component or the second component, as the case may be. Similarly, the composition provided by the present disclosure may be substantially free of solvent, such as having less than 5 wt%, less than 4 wt%, less than 2 wt%, or less than 1 wt% of solvent, where wt% is based on the total weight of the composition.

[0106] The first and second components may be mixed together and subsequently deposited as a mixture of components that react to form portions of an article. For example, two components may be mixed together and deposited as a mixture of components that react to form a thermoset by delivery of at least two separate streams of the components into a mixer such as a static mixer and/or a dynamic mixer to produce a single stream that is then deposited. The components may be at least partially reacted by the time a composition comprising the reaction mixture is deposited. The deposited reaction mixture may react at least in part after deposition

and may also react with previously deposited portions and/or subsequently deposited portions of the article such as underlying layers or overlying layers of the article.

[0107] Two or more components can be deposited using any suitable equipment. The selection of suitable deposition equipment depends on a number of factors including the deposition volume, the viscosity of the composition and the complexity of the part being fabricated. Each of the two or more components can be introduced into an independent pump and injected into a mixer to combine and mix the two components. A nozzle can be coupled to the mixer and the mixed composition can be pushed under pressure or extruded through the nozzle.

[0108] A pump can be, for example, a positive displacement pump, a syringe pump, a piston pump, or a progressive cavity pump. The two pumps delivering the two components can be placed in parallel or placed in series. A suitable pump can be capable of pushing a liquid or viscous liquid through a nozzle orifice. This process can also be referred to as extrusion. A component can be introduced into the mixer using two pumps in series.

[0109] For example, the first and second components can be deposited by dispensing materials through a disposable nozzle attached to a progressive cavity two-component dosing system such as a ViscoTec eco-DUO 450 precision dosing system, where the first and second components are mixed in-line. A two-component dosing system can comprise, for example, two progressive cavity pumps that separately dose reactants into a disposable static mixer dispenser or into a dynamic mixer. Other suitable pumps include positive displacement pumps, syringe pumps, piston pumps, and progressive cavity pumps. Upon dispensing, the materials of the first and second components form an extrudate which can be deposited onto a surface to provide an initial layer of material and successive layers on a base. The deposition system can be positioned orthogonal to the base, but also may be set at any suitable angle to form the extrudate such that the extrudate and deposition system form an obtuse angle with the extrudate being parallel to the base. The extrudate refers to the combined components, *i.e.*, a composition, that have been mixed, for example, in a static mixer or in a dynamic mixer. The extrudate can be shaped upon passing through a nozzle.

[0110] The base, the deposition system, or both the base and the deposition system may be moved to build up a three-dimensional article. The motion can be made in a predetermined

manner, which may be accomplished using any suitable CAD/CAM method and apparatus such as robotics and/or computerized machine tool interfaces.

[0111] An extrudate may be dispensed continuously or intermittently to form an initial layer and successive layers. For intermittent deposition, a dosing system may interface with a relay switch to shut off the pumps, such as the progressive cavity pumps and stop the flow of reactive materials. Any suitable switch such as an electromechanical switch that can be conveniently controlled by any suitable CAD/CAM methodology can be used.

[0112] A deposition system can include an in-line static and/or dynamic mixer as well as separate pressurized pumping compartments to hold the at least two components and feed the materials into the static and/or dynamic mixer. A mixer such as an active mixer can comprise a variable speed central impeller having high shear blades within a conical nozzle. A range of conical nozzles may be used which have an exit orifice dimension, for example, from 0.2 mm to 50 mm, from 0.5 mm to 40 mm, from 1 mm to 30 mm, or from 5 mm to 20 mm.

[0113] A range of static and/or dynamic mixing nozzles may be used which have, for example, an exit orifice dimension from 0.6 mm to 2.5 mm, and a length from 30 mm to 150 mm. For example, an exit orifice diameter can be from 0.2 mm to 4.0 mm, from 0.4 mm to 3.0 mm, from 0.6 mm to 2.5 mm, from 0.8 mm to 2 mm, or from 1.0 mm to 1.6 mm. A static mixer and/or dynamic can have a length, for example, from 10 mm to 200 mm, from 20 mm to 175 mm, from 30 mm to 150 mm, or from 50 mm to 100 mm. A mixing nozzle can include a static and/or dynamic mixing section and a dispensing section coupled to the static and/or dynamic mixing section. The static and/or dynamic mixing section can be configured to combine and mix the first and second components. The dispensing section can be, for example, a straight tube having any of the above orifice diameters. The length of the dispensing section can be configured to provide a region in which the components can begin to react and build viscosity before being deposited on the article. The length of the dispensing section can be selected, for example, based on the speed of deposition, the rate of reaction of the first and second components, and the desired viscosity.

[0114] First and second components can have a residence time in the static and/or dynamic mixing nozzle, for example, from 0.25 seconds to 5 seconds, from 0.3 seconds to 4 seconds, from 0.5 seconds to 3 seconds, or from 1 seconds to 3 seconds. Other residence times can be used as appropriate based on the curing chemistries and curing rates.

[0115] In general, a suitable residence time is less than the gel time of the composition. A suitable gel time can be less than 10 min, less than 8 min, less than 6 min, less than 5 min, less than 4 min, less than 3 min, less than 2 min, or less than 1 min. A gel time of the composition can be, for example, from 0.5 min to 10 min, from 1 min to 7 min, from 2 min to 6 min, or from 3 min to 5 min.

[0116] Compositions provided by the present disclosure can have a volume flow rate, for example, from 0.1 mL/min to 20,000 mL/min, such as from 1 mL/min to 12,000 mL/min, from 5 mL/min to 8,000 mL/min, or from 10 mL/min to 6,000 mL min. The volume flow rate can depend, for example, on the viscosity of the composition, the extrusion pressure, the nozzle diameter, and the reaction rate of the first and second components.

[0117] A composition can be used at a print speed, for example, from 1 mm/sec to 400 mm/sec, such as from 5 mm/sec to 300 mm/sec, from 10 mm/sec to 200 mm/sec, or from 15 mm/sec to 150 mm/sec. The printed speed can depend, for example, on the viscosity of the composition, the extrusion pressure, the nozzle diameter, and the reaction rate of the components. The print speed refers to the speed at which a nozzle used to extrude a composition move with respect to a surface onto which the composition is being deposited.

[0118] A composition can have a gel time, for example, less than 5 minutes, less than 4 minutes, less than 3 minutes, less than 2 minutes, less than 1 minute, less than 45 seconds, less than 30 seconds, less than 15 seconds, or less than 5 seconds. A composition can have a gel time, for example, from 0.1 seconds to 5 minutes, from 0.2 seconds to 3 minutes, from 0.5 seconds to 2 minutes, from 1 second to 1 minute, or from 2 seconds to 40 seconds. Gel time is considered as the time following mixing when the composition is no longer stirrable by hand.

[0119] A static and/or dynamic mixing nozzle can be heated or cooled to control, for example, the rate of reaction between the first and second components and/or the viscosity of the first and second components. An orifice of a deposition nozzle can have any suitable shape and dimensions. A system can comprise multiple deposition nozzles. The nozzles can have a fixed orifice dimension and shape, or the nozzle orifice can be controllably adjusted. The mixer and/or the nozzle may be cooled to control an exotherm generated by the reaction of the first and second components.

[0120] Methods provided by the present disclosure include printing the composition on a fabricated part. Methods provided by the present disclosure include directly printing parts.

[0121] Using the methods provided by the present disclosure parts can be fabricated. The entire part can be formed from one of the compositions disclosed herein, one or more portions of a part can be formed from one of the compositions disclosed herein, one or more different portions of a part can be formed using the compositions disclosed herein, and/or one or surfaces of a part can be formed from a composition provided by the present disclosure. In addition, internal regions of a part can be formed from a composition provided by the present disclosure.

[0122] Whereas specific aspects of the invention have been described in detail, it will be appreciated by those skilled in the art that various modifications and alternatives to those details could be developed in light of the overall teachings of the disclosure. Accordingly, the particular arrangements disclosed are meant to be illustrative only and not limiting as to the scope of the invention which is to be given the full breadth of the claims and aspects appended and any and all equivalents thereof.

ASPECTS

[0123] In the following, some non-limiting aspects of the present invention are summarized:

[0124] Aspect 1. A composition, comprising:
a first component comprising an epoxy-containing compound;
a second component that chemically reacts with the epoxy-containing compound, the second component comprising a diamine comprising a cyclic ring and/or a polyamine comprising a cyclic ring, wherein the cyclic ring of the diamine and/or the polyamine has at least one carbon positioned between the amino functional groups and the cyclic ring structure; and elastomeric particles.

[0125] Aspect 2. A composition comprising:
a first component comprising an epoxy-containing compound;
a second component that chemically reacts with the epoxy-containing compound, the second component comprising a diamine comprising a cyclic ring and/or a polyamine comprising a cyclic ring; and
elastomeric particles, wherein at least 50% by weight of the elastomeric particles comprise a styrene butadiene core based on total weight of the elastomeric particles.

[0126] Aspect 3. The composition of Aspect 1, wherein at least 50% by weight of the elastomeric particles comprise a styrene butadiene core based on total weight of the elastomeric particles.

[0127] Aspect 4. The composition of any of the preceding Aspects, wherein the epoxy-containing compound comprises bisphenol A, bisphenol F, a novolac resin, or combinations thereof.

[0128] Aspect 5. The composition of any of the preceding Aspects, wherein the diamine and/or the polyamine comprises xylylene diamine, bis(aminomethylcyclohexane), isophorone diamine, phenylene diamine, diaminotoluene, diaminophenol, diaminodiphenyl methane, or combinations thereof.

[0129] Aspect 6. The composition of any of the preceding Aspects, wherein the diamine comprising the cyclic ring and/or the polyamine comprising the cyclic ring is present in an amount sufficient to provide a molar ratio of epoxide functional groups from the epoxy-containing compound to amine-hydrogens from the diamine and/or polyamine of 0.5:1.0 to 1.5:1.0.

[0130] Aspect 7. The composition of any of the preceding Aspects, wherein at least 20 percent by weight of the second component, based on total weight of the all of the monoamines, diamines, and/or polyamines present in the second component, comprises the diamine and/or the polyamine comprising the cyclic ring.

[0131] Aspect 8. The composition of any of the preceding Aspects, wherein the diamine comprising the cyclic ring comprises xylylene diamine.

[0132] Aspect 9. The composition of any of the preceding Claims, wherein the second component further comprises an oligomeric cyclic ring-containing diamine or polyamine.

[0133] Aspect 10. The composition of any of the preceding Aspects, wherein the elastomeric particles comprise a core-shell structure.

[0134] Aspect 11. The composition of any of the preceding Aspects, wherein the elastomeric particles are present in the first component and are phase-separated from the epoxy-containing component.

[0135] Aspect 12. The composition of any of the preceding Aspects, wherein the elastomeric particles have a particle size of less than 300 nm as measured by TEM.

[0136] Aspect 13. The composition of any of the preceding Aspects, wherein at least 50% of the elastomeric particles have an average particle size of less than 150 nm as measured by transmission electron microscopy.

[0137] Aspect 14. The composition of any of the preceding Aspects, wherein no more than 50% by weight of the elastomeric particles comprise a polybutadiene core and/or a polysiloxane core based on total weight of the elastomeric particles.

[0138] Aspect 15. The composition of any of the preceding Aspects, wherein the elastomeric particles are present in the coating composition in an amount of 1 percent by weight to 50 percent by weight based on total weight of the coating composition.

[0139] Aspect 16. The composition of any of the preceding Aspects, wherein the second component further comprises an accelerator.

[0140] Aspect 17. The composition of Aspect 16, wherein the accelerator comprises a tris-(dimethylaminomethyl) phenol and/or a guanidine.

[0141] Aspect 18. The composition of Aspect 16 or Aspect 17, wherein the accelerator is present in the second component in an amount of no more than 10 percent by weight based on total weight of the coating composition.

[0142] Aspect 19. The composition of Aspect 16 or Aspect 17, wherein the accelerator is present in the second component in a total amount of 0.5 percent by weight to 55 percent by weight based on total weight of the coating composition.

[0143] Aspect 20. The composition of any of the preceding Aspects, further comprising a filler material in an amount of no more than 25 percent by weight based on total weight of the composition.

[0144] Aspect 21. The composition of any of the preceding Aspects, further comprising a filler material in an amount of no more than 10 percent by weight based on total weight of the composition.

[0145] Aspect 22. The composition of any of the preceding Aspects, further comprising additives in an amount of no more than 25 percent by weight based on total weight of the composition.

[0146] Aspect 23. The composition of any of the preceding Aspects, further comprising a cyclic carbonate-functional molecule.

[0147] Aspect 24. The composition of Aspect 23, wherein the cyclic carbonate-functional molecule comprises glycerol carbonate and/or propylene carbonate.

[0148] Aspect 25. The composition of Aspect 23 or Aspect 24, wherein the cyclic carbonate-functional molecule is present in an amount of 0.1 percent by weight to 10 percent by weight based on total weight of the composition.

[0149] Aspect 26. The composition of any of the preceding Aspects, wherein the composition is substantially free of platy fillers and/or alumina.

[0150] Aspect 27. The composition of any of the preceding Aspects, wherein the composition comprises a coating composition, an adhesive composition, or a sealant composition.

[0151] Aspect 28. A substrate comprising a surface, at least a portion of which is coated with or embedded in the composition of any of the preceding Aspects.

[0152] Aspect 29. The substrate of Aspect 28, wherein the substrate comprises a fibrous material, a sheet, or a mesh.

[0153] Aspect 30. The substrate of Aspect 29, wherein the fibrous material, the sheet, or the mesh comprises a woven material, sheet, or mesh.

[0154] Aspect 31. The substrate of Aspect 29, wherein the fibrous material, the sheet, or the mesh comprises a non-woven sheet or mesh.

[0155] Aspect 32. The substrate of any of Aspects 28 to 31, wherein the fibrous material, the sheet, or the mesh comprises carbon fibers, glass fibers, and/or nylon.

[0156] Aspect 33. The substrate of any of Aspects 28 to 32, positioned between a second substrate and a third substrate.

[0157] Aspect 34. Protective clothing comprising the substrate of any of Aspects 28 to 33.

[0158] Aspect 35. A part comprising a surface, at least a portion of which is coated with the composition of any of Aspects 1 to 27.

[0159] Aspect 36. An article, comprising:
the substrate of any of Claims 28 to 32; and
a second substrate;
wherein the composition is positioned between the substrate and the second substrate.

[0160] Aspect 37. The article of Aspect 36, wherein one of the substrates comprises a ceramic and the other of the substrates comprises aluminum or a composite.

[0161] Aspect 38. The substrate of any of Aspects 28 to 33, the protective clothing of Aspect 34, the part of Aspect 35, and/or the article of Aspect 36 or Aspect 37, wherein the composition, in an at least partially cured state, has a lap shear displacement of at least 2.5 mm at failure and a lap shear strength of at least 30.0 MPa, wherein the lap shear displacement and the lap shear strength are measured according to ASTM D1002-10 using 2024-T3 aluminum substrate of 1.6 mm thickness, as measured by an INSTRON 5567 machine in tensile mode with a pull rate of 1.3 mm per minute.

[0162] Aspect 41. An adhesive having a lap shear displacement of at least 2.5 mm at failure and a lap shear strength of at least 30.0 MPa, wherein the lap shear displacement and the lap shear strength are measured according to ASTM D1002-10 using 2024-T3 aluminum substrate of 1.6 mm thickness, as measured by an INSTRON 5567 machine in tensile mode with a pull rate of 1.3 mm per minute.

[0163] Aspect 42. A method for forming a coating on a surface of a substrate comprising:

mixing the first component and the second component of any of Aspects 1 to 27 to form the composition; and

applying the composition to the surface of the substrate, wherein at least a portion of the substrate is coated with the composition following the applying.

[0164] Aspect 43. The method of Aspect 42, further comprising contacting a surface of a second substrate to the composition such that the composition is located between the first substrate and the second substrate.

[0165] Aspect 44. The method of Aspect 42 or Aspect 43, further comprising at least partially curing the composition by exposing the composition to a temperature of at least 50°C.

[0166] Aspect 45. The method of Aspect 44, further comprising a second curing step comprising exposing the composition to a temperature of at least 120°C.

[0167] Aspect 46. A method of forming an article comprising extruding the composition of any of Aspects 1 to 27.

[0168] Aspect 47. The method of Aspect 46, wherein the extruding comprises three-dimensional printing.

[0169] Aspect 48. The method of Aspect 46 or Aspect 467, further comprising, before extruding, mixing the first component and the second component.

[0170] Aspect 49. The method of any of Aspects 46 to 48, wherein the extruding comprises applying successive layers to build the article.

[0171] Aspect 50. The article formed by the method of any of Aspects 46 to 49.

[0172] Aspect 51. Use of the composition according to any one of Aspects 1 to 27 for coating a surface of a substrate and/or the substrate is coated by a method for treating a substrate as described in any one of Aspects 42 to 45.

[0173] Aspect 52. Use of the composition according to any one of Aspects 1 to 27 for forming an article and/or the article is formed by a method as described in any one of Aspects 46 to 49.

[0174] Illustrating the invention are the following examples, which, however, are not to be considered as limiting the invention to their details. Unless otherwise indicated, all parts and percentages in the following examples, as well as throughout the specification, are by weight.

EXAMPLES

[0175] A deoxidizing composition (DEOX-1) was prepared in a clean 5-gallon plastic bucket to which 18.2 liters of deionized water, 180.5 g fluorosilicic acid (23% solution), 80 g fluorozirconic acid (45% solution), 11.61 g potassium bifluoride, and 31.6 g of Chemfil Buffer (commercially available from PPG Industries, Inc.) were added.

[0176] In each of the Examples below, 2024-T3 aluminum alloy panels measuring 25.4 mm×101.6 mm×1.6 mm (supplied by Online Metals) were used to prepare lap shear specimens according to ASTM D1002-10. Each panel was rinsed with acetone, then was immersed in deionized water for 1 minute, then was immersed in DEOX-1 (heated to 100°F) for 1 minute. Each panel was immersed in deionized water for 1 minute and then was dried at 70°C for at least 10 minutes.

[0177] Next, one of Compositions I through XXXVI below was prepared as described below. Glass beads averaging 4.1 mil in diameter were mixed into the composition in an amount of 2% by weight based on total weight of the composition. Composition was applied to one end of a panel covering the full 25.4 mm width and ≥ 12.7 mm from one end. A second pretreated aluminum panel was then placed over the composition layer in an end-to-end fashion, resulting

in a bond area of 25.4 mm×12.7 mm. Lap shear specimens were prepared at 50% relative humidity or lower. Lap joints were secured with metal clips and excess composition cleaned, leaving a 45° fillet. Lap joints were baked at 70°C for 60 minutes. The baked lap joint specimens were tested using an INSTRON model 5567 in tensile mode with 25.4 mm of aluminum substrate in each grip and at a pull rate of 1.3 mm per minute (in accordance with ASTM D1002-10).

Example 1

[0178] Compositions I-III were prepared from the mixtures of ingredients shown in Table 1. All compositions were prepared at a molar ratio of epoxide functional groups from the epoxy-containing compound to amine-hydrogens from the diamine or polyamine containing a cyclic ring of 1:1 (E:AH). Epoxy resins and fillers were premixed, then the curing agent, accelerators, and spacer beads were added, mixed for at least 1 minute at 2350 rpm using a DAC Speedmixer, and then lap shear specimens (described above) were immediately prepared.

Table 1. Compositions I-III			
Components	I (comparative)	II	III (comparative)
Kane Ace MX-135 ¹	15.25	15.25	15.25
Epon 863 ²	3.18	3.18	3.18
Acrosil R202 ³	0.57	0.57	0.57
Ancamine 1922A ⁴	4.85		
m-xylylenediamine ⁵		3.00	
Diethylenetriamine ⁶			1.82
Ancamine K54 ⁷	0.48	0.46	0.43
Total	24.33	22.46	21.25
Lap Joint Performance			
Lap Shear Strength [MPa]	35.3 ± 1.6	43.3 ± 0.9	31.9 ± 4.6
Displacement at Failure [mm]	2.60 ± 0.19	4.32 ± 0.25	2.20 ± 0.32
¹ Blend of bisphenol F epoxy resin and ~100 nm diameter core-shell styrene-butadiene rubber available from Kaneka Corporation (epoxy-containing compound with elastomeric particles) ² Liquid bisphenol F epoxy resin available from Hexion (epoxy-containing compound) ³ Hydrophobic fumed silica available from Evonik (filler) ⁴ Bis(3-aminopropyl)diethylene glycol ether available from Evonik (curing agent) ⁵ Available from Sigma-Aldrich (curing agent; diamine containing a cyclic ring) ⁶ Available from Acros Organics (curing agent) ⁷ 2,4,6-tris(N,N-dimethylaminomethyl)phenol available from Evonik (accelerator)			

[0179] The data from Example 1 demonstrate that curing of an epoxy resin containing elastomeric particles with m-xylylenediamine (a diamine containing a cyclic ring) (Composition II) forms an adhesive with improved lap shear strength and displacement compared to other amine-containing curing agents (Compositions I and III).

Example 2

[0180] Example 2 illustrates the effects of epoxy resin composition and core-shell elastomeric particle size and composition on lap joint performance.

[0181] Compositions IV-VIII were prepared from the mixtures of ingredients shown in Table 2. All compositions were prepared at an E:AH molar ratio of 1:1. Epoxy resins and fillers were premixed, then accelerators, curing agents, and spacer beads were added, mixed for at least 1 minute at 2350 rpm using a DAC Speedmixer, and then lap shear specimens were immediately prepared and tested in accordance with ASTM D1002-10 as described above.

Table 2. Compositions IV-VIII					
Components	IV	V	VI	VII	VIII
Epon 863	19.84	4.49	4.46	9.71	4.48
Kane Ace MX-135		16.00			
Kane Ace MX-136 ¹			16.00		
Kane Ace MX-267 ²				10.81	
Kane Ace MX-965 ³					16.00
Aerosil R 202	0.63	0.63	0.63	0.63	0.63
m-Xylylenediamine	4.03	3.38	3.41	3.35	3.39
Ancamine K-54	0.50	0.50	0.50	0.50	0.50
Total	25.00	25.00	25.00	25.00	25.00
Lap Joint Performance					
Lap Shear Strength [MPa]	22.4 ± 2.4	43.1 ± 1.8	44.8 ± 1.8	41.5 ± 1.1	30.5 ± 3.3
Displacement at Failure [mm]	1.38 ± 0.14	3.34 ± 0.57	2.89 ± 0.19	3.00 ± 0.32	1.92 ± 0.22
¹ Blend of bisphenol F epoxy resin and ~100 nm diameter core-shell polybutadiene rubber available from Kaneka Corporation					
² Blend of bisphenol F epoxy resin and ~200 nm diameter core-shell polybutadiene rubber available from Kaneka Corporation					
³ Blend of bisphenol F epoxy resin and ~300 nm diameter core-shell polysiloxane rubber available from Kaneka Corporation					

[0182] The data from Example 2 indicate that inclusion of elastomeric particles having an average particle diameter of less than 300 nm resulted in an adhesive having improved lap shear strength and displacement.

Example 3

[0183] Example 3 illustrates the effect that including an accelerator in the coating composition has on lap shear properties.

[0184] Compositions IX-XV were prepared from the mixtures of ingredients shown in Table 3. All compositions were prepared at an E:AH molar ratio of 1:1. Epoxy resins and fillers were premixed, then accelerators, curing agents, and spacer beads were added, mixed for at least 1 minute at 2350 rpm using a DAC Speedmixer, and then lap shear specimens were immediately prepared and tested in accordance with ASTM D1002-10, as described above.

Table 3. Compositions IX-XV							
Components	IX	X	XI	XII	XIII	XIV	XV
Kane Ace MX-135	15.25	15.25	15.25	15.25	15.25	15.25	15.25
Epon 863	3.18	3.18	3.18	3.18	3.18	3.18	3.18
Aerosil R202	0.57	0.57	0.57	0.57	0.57	0.57	0.57
m-xylylenediamine	3.00	3.00	3.00	3.00	3.00	3.00	3.00
Ancamine K-54	0.46						
Diazabicycloundecene ¹		0.46					
1-methylimidazole ²			0.46				
Triethanolamine ³				0.46			
Tetrabutylammonium Bromide ⁴					0.46		
Aminosaliclic Acid ⁵						0.46	
DABCO ⁶							0.46
Total	22.46	22.46	22.46	22.46	22.46	22.46	22.46
Lap Joint Performance							
Lap Shear Strength [MPa]	45.2 ± 0.8	44.0 ± 1.1	45.1 ± 0.8	21.1 ± 2.7	42.3 ± 1.3	29.5 ± 1.8	42.3 ± 0.1
Displacement at Failure [mm]	3.95 ± 0.47	3.14 ± 0.25	3.50 ± 0.28	1.17 ± 0.20	2.92 ± 0.21	1.66 ± 0.19	3.26 ± 0.42
¹ Amidine base available from Sigma-Aldrich (accelerator) ² Imidazole base available from Oakwood Products (accelerator) ³ Tertiary amine base available from Sigma-Aldrich (accelerator) ⁴ Ammonium salt available from Sigma-Aldrich (accelerator) ⁵ Multifunctional amine available from Sigma-Aldrich (accelerator); amine hydrogens omitted in calculated E:AH molar ratio ⁶ Tertiary amine base available from Sigma-Aldrich (accelerator)							

[0185] The data from Example 3 indicate that accelerators may further improve lap joint strength and displacement.

Example 4

[0186] Example 4 illustrates the effects of E:AH molar ratio and accelerator loading on lap joint performance.

[0187] Compositions XVI-XXIV were prepared from the mixtures of ingredients shown in Table 4. Each composition was prepared at the E:AH molar ratio shown in Table 4. Epoxy resins and fillers were premixed, then accelerators, curing agents, and spacer beads were added, mixed for at least 1 minute at 2350 rpm using a DAC Speedmixer, and then lap shear specimens were immediately prepared and tested in accordance with ASTM D1002-10, as described above.

Table 4. Compositions XVI-XXIV									
Components	XVI	XVII	XVIII	XIX	XX	XXI	XXII	XXIII	XXIV
Kane Ace MX-135	15.25	15.25	15.25	15.25	15.25	15.25	15.25	15.25	15.25
Epon 863	3.18	3.18	3.18	3.18	3.18	3.18	3.18	3.18	3.18
Aerosil R202	0.57	0.57	0.57	0.57	0.57	0.57	0.57	0.57	0.57
MXDA	3.00	2.40	4.00	3.00	2.40	4.00	3.00	2.40	4.00
Ancamine K54	0.23	0.22	0.24	0.46	0.44	0.46	0.92	0.89	0.95
Total	22.23	21.62	23.24	22.46	21.84	23.46	22.92	22.29	23.95
E:AH molar Ratio	1.0:1.0	1.25:1.0	0.75:1.0	1.0:1.0	1.25:1.0	0.75:1.0	1.0:1.0	1.25:1.0	0.75:1.0
Wt% Ancamine K54	1.0%	1.0%	1.0%	2.0%	2.0%	2.0%	4.0%	4.0%	4.0%
Lap Joint Performance									
Lap Shear Strength [MPa]	44.5 ± 0.7	43.1 ± 0.6	43.8 ± 2.0	45.3 ± 0.5	44.3 ± 1.7	46.8 ± 0.9	42.9 ± 1.3	40.4 ± 3.0	45.1 ± 2.0
Displacement at Failure [mm]	3.84 ± 0.32	3.33 ± 0.16	4.23 ± 0.46	4.19 ± 0.26	4.11 ± 0.53	4.88 ± 0.56	3.07 ± 0.22	2.74 ± 0.31	4.32 ± 0.84

[0188] The data from Example 4 demonstrate that E:AH molar ratios of 0.75:1.0 to 1.25:1.0 and accelerator loadings of 4 wt% or less give improved lap joint strength and displacement.

Example 5

[0189] Lap joint specimens (prepared according to ASTM D1002-10 as described above) were prepared using Loctite EA 9309, Loctite EA 9320, or Loctite EA 9395 (each commercially available from Henkel), DP460NS (commercially available from 3M), and with Composition II (prepared as described above) under identical conditions. In order to maintain a bondline thickness, 4.1 mil glass beads were added to each composition at 2% by weight based on total weight of the composition. Lap joint specimens were baked at 70°C for 60 minutes. Testing was conducted according to ASTM D1002-10.

Table 5. Lap Joint Performance					
Composition	Loctite EA9309 (comparative)	Loctite EA9320 (comparative)	Loctite EA9395 (comparative)	DP460NS (comparative)	II
Lap Shear Strength [MPa]	33.0 ± 0.8	36.1 ± 3.2	27.4 ± 2.2	36.4 ± 0.7	44.4 ± 2.3
Displacement at Failure [mm]	2.10 ± 0.05	2.31 ± 0.19	1.73 ± 0.13	1.80 ± 0.05	4.12 ± 0.60

[0190] The data from Example 5 demonstrate that Composition II, which is an epoxide-functional composition containing elastomeric particles cured with m-xylylenediamine and accelerator, had improved lap joint strength and displacement compared to commercially available adhesive compositions that do not contain a combination of core-shell rubber particles and diamine containing a cyclic ring or a polyamine containing a cyclic ring.

Example 6

[0191] Example 6 illustrates the effects of using an oligomer of m-xylylenediamine and epichlorohydrin to cure the adhesive composition.

[0192] Compositions XXV-XXVI were prepared from the mixtures of ingredients shown in Table 6. Each composition was prepared at an E:AH molar ratio of 1:1. Epoxy resins and fillers were premixed, then accelerators, curing agents, and spacer beads were added, mixed for at least 1 minute at 2350 rpm using a DAC Speedmixer, and then lap shear specimens were immediately prepared on ChemKleen 490MX or DEOX-1 treated aluminum in accordance with ASTM D1002-10 and tested in accordance with ASTM D1002-10, as described above. Aluminum panels were treated with ChemKleen 490MX (commercially available from PPG) as follows: rinsed panels with acetone, immersed in deionized water for 2 minutes, immersed in the ChemKleen 490MX (heated to 120°F) for 2 minutes, immersed in deionized water for 2 minutes, and dried at 70°C for 10 minutes.

Table 6. Compositions XXV-XXVI		
Components	XXV	XXVI
Kane Ace MX-135	9.16	9.16
Epon 863	9.16	9.16
Aerosil R202	0.65	0.65
m-xylylenediamine	3.26	
Gaskamine 328 ¹		5.27
Ancamine K54	0.46	0.50
Total	22.72	24.77
Lap Joint Performance		
Lap Shear Strength [MPa], ChemKleen	39.0 ± 3.2	37.5 ± 0.8
Displacement at Failure [mm], ChemKleen	2.66 ± 0.33	2.35 ± 0.11
Lap Shear Strength [MPa], DEOX-1	45.3 ± 0.7	43.1 ± 2.6
Displacement at Failure [mm], DEOX-1	4.02 ± 0.40	3.43 ± 0.64
¹ Oligomer of m-xylylenediamine and epichlorohydrin available from Mitsubishi Gas Chemical (oligomeric polyamine amine containing a cyclic ring)		

[0193] The data from Example 6 show that an oligomeric polyamine containing a cyclic ring performs substantially the same as a diamine containing a cyclic ring.

Example 7

[0194] Compositions XXVII-XXXIV were prepared from the mixtures of ingredients shown in Table 7. All compositions were prepared at an E:AH molar ratio of 1:1. Epoxy resins and fillers were premixed, then curing agents, accelerator, and spacer beads were added, mixed for at least 1 minute at 2350 rpm using a DAC Speedmixer, and then lap shear specimens (described above) were immediately prepared. Samples were baked at 70 °C for 60 minutes, and some samples were additionally baked at 150 °C for 180 minutes.

Table 7. Compositions XXVII-XXXIV								
Components	XXVII	XXVIII	XXIX	XXX (Comp)	XXXI	XXXII (Comp)	XXXIII	XXXIV
Kane Ace MX-135	13.50	8.10	13.50	13.50	13.50	13.50	13.50	13.50
Epon 863	4.50	2.70	4.39	4.88	3.90	4.28	3.94	3.76
Aerosil R202	0.44	0.26	0.44	0.44	0.44	0.44	0.44	0.44
m-xylylenediamine	3.00							
o-xylylenediamine ¹		1.80						
1,3-bis(aminomethyl)cyclohexane ²			3.11					

1,5-diamino-2-methylpentane ³				2.62				
Isophorone diamine ⁴					3.60			
Jeffamine EDR-148 ⁵						3.22		
Ancamine 1482 ⁶							3.56	
Ethacure 100-LC ⁷								3.74
Ancamine K-54	0.44	0.26	0.44	0.44	0.44	0.44	0.44	0.44
Lap Joint Performance								
Lap Shear Strength [MPa], 70 °C cure	48.6 ±1.5	46.5 ±1.5	46.3 ±1.2	44.3 ±1.3	33.2 ±2.3	42.7 ±0.7	35.9 ±5.4	16.4 ±5.5
Displacement at Failure [mm], 70 °C cure	4.04 ±0.67	3.30 ±0.68	3.11 ±0.44	2.58 ±0.32	1.39 ±0.11	2.27 ±0.14	1.60 ±0.30	0.72 ±0.32
Lap Shear Strength [MPa], 150 °C cure	46.5 ±1.0	46.4 ±0.6	44.8 ±0.9	42.7 ±1.5	45.2 ±0.7	40.8 ±0.7	45.5 ±1.5	44.5 ±1.5
Displacement at Failure [mm], 150 °C cure	4.43 ±0.53	4.51 ±0.23	3.68 ±0.60	2.79 ±0.46	3.61 ±0.31	2.32 ±0.10	3.96 ±0.78	3.51 ±0.52
¹⁻⁴ Available from Sigma-Aldrich ⁵ Bis(3-aminopropyl)diethylene glycol ether available from Evonik ⁶ Liquid eutectic mixture of cyclic polyamines available from Evonik ⁷ Mixture of isomers of diethyltoluenediamine available from Albemarle								

[0195] The data from Example 7 demonstrate that curing of an epoxy resin containing elastomeric particles with a diamine containing a cyclic structure forms an adhesive with improved lap shear strength and displacement compared to other amine-containing curing agents (Compositions XXX and XXXII).

Example 8

[0196] An amine functional adduct containing a cyclic ring was prepared using the components in Table 8 below in the amounts indicated. An appropriately sized round bottom flask was first equipped with an addition funnel and a stirrer. The flask was charged with m-xylylenediamine and blanketed with a nitrogen atmosphere. Epon 863 was charged into the addition funnel and added dropwise into the flask over a period of 30 minutes while stirring, resulting the heating of the reaction mixture to 100 °C. The resulting mixture was subsequently heated to 70 °C for 5 hours, then allowed to stand at room temperature overnight. Thin layer chromatography analysis indicated complete conversion of the epoxy. The reaction mixture was heated to 70 °C and poured into a suitable container. The resulting amine functional adduct was

Table 8. Composition XXXV	
Component	XXXV
m-xylylenediamine	167.1
Epon 863	83.0

Example 9

[0197] Compositions XXXVI and XXXVII were prepared from the mixtures of ingredients shown in Table 9. All compositions were prepared at an E:AH molar ratio of 1:1, after assuming each primary amine will react once with each cyclic carbonate functional group. Epoxy resins, cyclic carbonate monomer, and fillers were premixed, then curing agents, accelerators and spacer beads were added, mixed for at least 1 minute at 2350 rpm using a DAC Speedmixer, and then lap shear specimens (described above) were immediately prepared, except that panels were either immersed in DEOX-1 or were immersed in CHEMDEOX 395 (commercially available from PPG Industries, Inc. and prepared according to manufacturer's instructions).

Table 9. Compositions XXXVI-XXXVII		
Components	XXXVI	XXXVII
Kane Ace MX-135	12.08	15.25
Epon 863	2.52	3.18
Jeffsol GC ¹	1.04	
Aerosil R202	0.45	0.57
m-xylylenediamine	3.00	
Composition XXXV		5.02
Ancamine K-54	0.39	0.48
Lap Joint Performance		
Lap Shear Strength [MPa], treated with ChemDeox 395	45.3 ± 2.6	44.7 ± 1.8
Displacement at Failure [mm], treated with ChemDeox 395	3.77 ± 0.99	3.44 ± 0.49
Lap Shear Strength [MPa], treated with DEOX-1	47.8 ± 0.8	45.3 ± 1.0
Displacement at Failure [mm], treated with DEOX-1	4.96 ± 0.59	3.61 ± 0.31
¹ Glycerine carbonate available from Huntsman Corporation		

[0198] The data from Example 9 demonstrate the improved lap shear strength and displacement obtainable in a composition modified with a cyclic carbonate-functional molecule or in a composition cured with an oligomeric amine reaction product.

[0199] It will be appreciated by skilled artisans that numerous modifications and variations are possible in light of the above disclosure without departing from the broad inventive concepts described and exemplified herein. Accordingly, it is therefore to be

understood that the foregoing disclosure is merely illustrative of various exemplary aspects of this application and that numerous modifications and variations can be readily made by skilled artisans which are within the spirit and scope of this application and the accompanying claims.

We claim:

1. A composition, comprising:
a first component comprising an epoxy-containing compound;
a second component that chemically reacts with the epoxy-containing compound, the second component comprising a diamine comprising a cyclic ring and/or a polyamine comprising a cyclic ring, wherein the cyclic ring of the diamine and/or the polyamine has at least one carbon positioned between the amino functional groups and the cyclic ring structure; and
elastomeric particles.
2. A composition comprising:
a first component comprising an epoxy-containing compound;
a second component that chemically reacts with the epoxy-containing compound, the second component comprising a diamine comprising a cyclic ring and/or a polyamine comprising a cyclic ring; and
elastomeric particles, wherein at least 50% by weight of the elastomeric particles comprise a styrene butadiene core based on total weight of the elastomeric particles.
3. The composition of Claim 1, wherein at least 50% by weight of the elastomeric particles comprise a styrene butadiene core based on total weight of the elastomeric particles.
4. The composition of any of the preceding Claims, wherein the diamine and/or the polyamine comprises xylylene diamine, bis(aminomethylcyclohexane), isophorone diamine, phenylene diamine, diaminotoluene, diaminophenol, diaminodiphenyl methane, or combinations thereof.
5. The composition of any of the preceding Claims, wherein the diamine comprising the cyclic ring and/or the polyamine comprising the cyclic ring is present in an amount sufficient to provide a molar ratio of epoxide functional groups from the epoxy-containing compound to amine-hydrogens from the diamine and/or polyamine of 0.5:1.0 to 1.5:1.0.

6. The composition of any of the preceding Claims, wherein the second component further comprises an oligomeric cyclic ring-containing diamine or polyamine.
7. The composition of any of the preceding Claims, wherein the elastomeric particles comprise a core-shell structure.
8. The composition of any of the preceding Claims, wherein the elastomeric particles have a particle size of less than 300 nm as measured by TEM.
9. The composition of any of the preceding Claims, wherein at least 50% of the elastomeric particles have an average particle size of less than 150 nm as measured by transmission electron microscopy.
10. The composition of any of the preceding Claims, wherein no more than 50% by weight of the elastomeric particles comprise a polybutadiene core and/or a polysiloxane core based on total weight of the elastomeric particles.
11. The composition of any of the preceding Claims, wherein the second component further comprises an accelerator and/or an additive.
12. The composition of Claim 11, wherein the accelerator comprises a tris-(dimethylaminomethyl) phenol and/or a guanidine.
13. The composition of any of the preceding Claims, further comprising a filler material in an amount of no more than 25 percent by weight based on total weight of the composition.
14. The composition of any of the preceding Claims, further comprising a filler material in an amount of no more than 10 percent by weight based on total weight of the composition.
15. The composition of any of the preceding Claims, further comprising a cyclic carbonate-functional molecule.

16. The composition of Claim 15, wherein the cyclic carbonate-functional molecule is present in an amount of 0.1 percent by weight to 10 percent by weight based on total weight of the composition.
17. The composition of any of the preceding Claims, wherein the composition comprises a coating composition, an adhesive composition, or a sealant composition.
18. A substrate comprising a surface, at least a portion of which is coated with or embedded in the composition of any of the preceding Claims.
19. The substrate of Claim 18, wherein the substrate comprises a fibrous material, a sheet, or a mesh.
20. The substrate of Claim 18 or Claim 19, positioned between a second substrate and a third substrate.
21. Protective clothing comprising the substrate of any of Claims 18 to 20.
22. A part comprising a surface, at least a portion of which is coated with the composition of any of Claims 1 to 17.
23. An article, comprising:
 - the substrate of any of Claims 18 to 20; and
 - a second substrate;
 - wherein the composition is positioned between the substrate and the second substrate.
24. The substrate of any of Claims 18 to 20, the protective clothing of Claim 21, the part of Claim 22, and/or the article of Claim 23, wherein the composition, in an at least partially cured state, has a lap shear displacement of at least 2.5 mm at failure and a lap shear strength of at least 30.0 MPa, wherein the lap shear displacement and the lap shear strength are measured according

to ASTM D1002-10 using 2024-T3 aluminum substrate of 1.6 mm thickness, as measured by an INSTRON 5567 machine in tensile mode with a pull rate of 1.3 mm per minute.

25. An adhesive having a lap shear displacement of at least 2.5 mm at failure and a lap shear strength of at least 30.0 MPa, wherein the lap shear displacement and the lap shear strength are measured according to ASTM D1002-10 using 2024-T3 aluminum substrate of 1.6 mm thickness, as measured by an INSTRON 5567 machine in tensile mode with a pull rate of 1.3 mm per minute.

26. A method for forming a coating on a surface of a substrate comprising:
mixing the first component and the second component of any of Claims 1 to 17 to form the composition; and
applying the composition to the surface of the first substrate, wherein at least a portion of the substrate is coated with the composition following the applying.

27. The method of Claim 26, further comprising at least partially curing the composition by exposing the composition to a temperature of at least 50°C.

28. The method of Claim 27, further comprising a second curing step comprising exposing the composition to a temperature of at least 120°C

29. A method of forming an article comprising extruding the composition of any of Claims 1 to 17.

30. The method of Claim 29, wherein the extruding comprises three-dimensional printing.

31. The article formed by the method of Claim 29 or Claim 30.