

## **LATENT ACRYLIC ADHESIVE**

### **CROSS-REFERENCE TO RELATED APPLICATION**

[0001] This application claims priority to US Pat. App. Ser. No. 63/528,491 filed July 24, 2023. The noted application is incorporated herein by reference.

### **FIELD**

[0002] The present disclosure is generally directed to a storage stable, reduced odor one-component acrylic-based adhesive composition which may be activated by a stimulus experienced during the manufacture of a structure of an article of manufacture (for e.g., a mechanical fastener of an automobile or airplane).

### **BACKGROUND**

[0003] Many different types of adhesives are known and currently used in a variety of industrial applications. For example, one-component adhesives may be formulated using epoxy resins and curing agents that are applied as liquids to substrate surfaces with elevated temperature, typically a minimum of 120°C for an hour or more, being required to effect curing of the epoxy resin and the formation of a strong adhesive bond between the substrates. In addition, polyurethane-based adhesive compositions suffer from being inherently hydrophilic and therefore exhibit poor corrosion resistance.

[0004] Acrylic adhesive compositions have been extensively used for bonding metal and plastic materials. The load-bearing and stress-relieving properties of acrylic adhesives, as well as their bond strength which can exceed the strength of the materials being bonded, make these adhesives attractive alternatives to or partial replacements for mechanical methods, such as riveting or spot welding, of joining materials. Their use can reduce or

eliminate costly finishing operations necessitated by mechanical joining methods, present a more pleasing exterior and at least reduce the possibility of corrosion of assemblies containing one or more metal components. Additionally, they can be used to bond a diversity of metals without extensive surface preparation. However, current state of the art acrylic adhesive compositions either lack sufficient storage stability, emit odor, are too viscous, or cure too slowly at room temperature making them unsuitable in current production cycles in highly industrialized processes (for e.g., bonding a fastener to an aerospace or automotive structure).

[0005] Accordingly, a need exists for the development of new acrylic adhesive compositions that are corrosion resistant, exhibit strong adhesion, have a fast reactivity at room temperature, a reduced odour or are odour-free and are storage stable until activated by an external stimulus.

#### SUMMARY

[0006] The present disclosure generally provides a one-component adhesive composition including: (a) a free radically polymerizable component comprising at least one free radically polymerizable compound; (b) an impact modifier; (c) an adhesion promoter; (d) a toughener; (e) a cure accelerant; (f) an encapsulated free radical forming compound; and optionally (g) a thixotropic modifier.

[0007] In another embodiment, there is provided a method of forming a structure of an article of manufacture including locating the one-component adhesive composition between a first substrate and a second substrate and activating the adhesive composition to cure between the first substrate and the second substrate by exposing the adhesive

composition to an external stimulus that causes the encapsulation of the free radical forming compound to fail.

[0008] The one-component adhesive composition may be applied to a variety of structures (e.g., one or more structural members) of a variety of articles of manufacture. Examples of such articles of manufacture include, but are not limited to, an automobile, a truck, a trailer, a train, a railroad car, an airplane, a body panel or part for any of the foregoing, a bridge, a pipeline, a pipe, a tubing, a boat, a ship, a storage container, a storage tank, an article of furniture, a window, a door, a railing, a functional or decorative architectural piece, a pipe railing, an electrical component, a conduit, a beverage container, a food container, or a foil. In other alternative embodiments, it is contemplated that the one-component adhesive composition may be employed in conjunction with one or more mechanical fasteners used in connection with such articles of manufacture.

#### .DETAILED DESCRIPTION

[0009] The present disclosure is generally directed to a one-component adhesive composition containing (a) a free radically polymerizable component comprising at least one free radically polymerizable compound, (b) an impact modifier, (c) an adhesion promoter, (d) a toughener, (e) a cure accelerant, (f) an encapsulated free radical forming compound, and optionally (g) a thixotropic modifier. The one-component adhesive composition of the present disclosure has been surprisingly found to exhibit excellent latency, corrosion resistance and strong adhesion (torque-out resistance) while also having reduced odor as compared to other state of the art (meth)acrylate adhesives. In addition, the one-component adhesive composition may be capable of maintaining high adhesive strength even when exposed to temperatures between -67°F and 350° F, or when exposed

to oils from human touch, aerospace greases, aerospace oils, jet fuel, silicone mold release agents and water.

[0010] The following terms shall have the following meanings:

[0011] The term "comprising" and derivatives thereof are not intended to exclude the presence of any additional component, step or procedure, whether or not the same is disclosed herein. In order to avoid any doubt, all compositions claimed herein through use of the term "comprising" may include any additional additive, adjuvant, or compound, unless stated to the contrary. In contrast, the term, "consisting essentially of" if appearing herein, excludes from the scope of any succeeding recitation any other component, step, or procedure, except those that are not essential to operability and the term "consisting of", if used, excludes any component, step or procedure not specifically delineated or listed. The term "or", unless stated otherwise, refers to the listed members individually as well as in any combination.

[0012] The articles "a" and "an" are used herein to refer to one or to more than one (i.e., to at least one) of the grammatical objects of the article. The phrases "in one embodiment", "according to one embodiment" and the like generally mean the particular feature, structure, or characteristic following the phrase is included in at least one embodiment of the present disclosure and may be included in more than one embodiment of the present disclosure. Importantly, such phrases do not necessarily refer to the same aspect. If the specification states a component or feature "may", "can", "could", or "might" be included or have a characteristic, that particular component or feature is not required to be included or have the characteristic.

[0013] The term “about” as used herein can allow for a degree of variability in a value or range, for example, it may be within 10%, within 5%, or within 1%, or within 0.5% of a stated value or of a stated limit of a range.

[0014] Values expressed in a range format should be interpreted in a flexible manner to include not only the numerical values explicitly recited as the limits of the range, but to also include all of the individual numerical values or sub-ranges encompassed within that range as if each numerical value and sub-range is explicitly recited. For example, a range such as from 1 to 6, should be considered to have specifically disclosed sub-ranges, such as, from 1 to 3, from 2 to 4, from 3 to 6, etc., as well as individual numbers within that range, for example, 1, 2, 3, 4, 5, and 6. This applies regardless of the breadth of the range.

[0015] The terms “preferred” and “preferably” refer to embodiments that may afford certain benefits, under certain circumstances. However, other embodiments may also be preferred, under the same or other circumstances. Furthermore, the recitation of one or more preferred embodiments does not imply that other embodiments are not useful and is not intended to exclude other embodiments from the scope of the present disclosure.

[0016] The term “one-component” composition refers to a composition which is contained in a single container, preferably a moisture-tight container, and which composition has certain storage stability. In comparison, a “two component” composition refers to a composition where two components (A and B) are physically separated from each other (for instance, in separate cartridges, compartments, totes, drums or other containers), where components A and B are physically combined (admixed) at the time the composition is to be used to form a cured resin.

[0017] The term "storage stabile" refers to the ability of a composition to be stored at ambient temperature in a suitable container under exclusion of moisture and external stimuli for a certain time interval, such as at least three months or at least four months or at least five months or at least six months, or at least 1 year without undergoing significant changes in application or end-use properties (for e.g. with minor (less than about 5% or less than about 4% or less than about 3%) or no crystallisation and/or with minor (less than about 5% or less than about 4% or less than about 3%) or no increase in viscosity).

[0018] The term "ambient temperature" refers to the temperature of the surrounding work environment (e.g., the temperature of the area, building or room where the composition is used), exclusive of any temperature changes that occur as a result of the direct application of heat to the composition to facilitate curing. The ambient temperature may be within a range from about 10°C to about 30°C, more specifically from about 15°C to about 25°C.

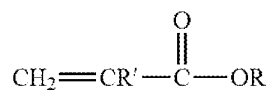
[0019] The term "optional" or "optionally" means that the subsequently described event or circumstance may or may not occur, and that the description includes instances where said event or circumstance occurs and instances where it does not.

[0020] The term "substantially free" refers to a composition in which a particular compound or moiety is present in an amount that has no material effect on the composition. In some embodiments, "substantially free" may refer to a composition in which the particular compound or moiety is present in the composition in an amount of less than 2% by weight, or less than 1% by weight, or less than 0.5% by weight, or less than 0.1% by weight, or less than 0.05% by weight, or even less than 0.01% by weight based on the total weight of the composition, or that no amount of that particular compound or moiety is present in the respective composition.

[0021] According to one embodiment, the present disclosure is directed to a one-component adhesive composition including: (a) a free radically polymerizable component comprising at least one free radically polymerizable compound; (b) an impact modifier; (c) an adhesion promoter; (d) a toughener; (e) a cure accelerant; and (f) a free radical forming compound.

[0022] The free radically polymerizable compound may be any monomer, oligomer or polymer which contains olefinic unsaturation and can polymerize by free-radical addition polymerization. Styrenic, vinyl, acrylic and methacrylic monomers and/or oligomers are suitable examples. These can include styrene, alpha-methyl styrene, vinyl esters such as vinyl neodecanoate and vinyl acetate, acrylic and methacrylic monomers or oligomers such as acrylic acid, acrylamide, acrylonitrile and acrylate. A variety of monomers can be used, and their choices will depend on the final adhesive properties desired and the substrates to be bonded.

[0023] Acrylic monomers include acrylamide and/or methylacrylamide monomers, acrylonitrile monomers, or acrylate monomers. In one non-limiting embodiment, the acrylic monomers can be acrylate monomers. The acrylate monomers can have the chemical structure



where R can be alkyl, cycloalkyl, or bicycloalkyl with or without other function groups such as hydroxyl, urethane, epoxy, or phenolic oligomers; and R' can be either hydrogen or a methyl group.

[0024] In one non-limiting embodiment, the acrylate monomers can include alkyl and cycloalkyl acrylates, alkyl methacrylates, and hydroxyl alkyl acrylates and methacrylates. Examples of the alkyl and cycloalkyl acrylates can include, but are not limited to, methyl acrylate, ethyl acrylate, n-propyl acrylate, n-butyl acrylate, t-butyl acrylate, isobutyl acrylate, isobornyl acrylate, n-octyl acrylate, 2-ethylhexyl acrylate, glycidyl acrylate, cyclohexyl acrylate, and tetrahydrofurfuryl acrylate.

[0025] The alkyl methacrylates can be selected from the group consisting of methyl methacrylate, ethyl methacrylate, n-butyl methacrylate, t-butyl methacrylate, isobutyl methacrylate, 2-ethylhexyl methacrylate, isobornyl methacrylate, decyl methacrylate, dodecyl methacrylate, glycidyl methacrylate, tetrahydrofurfuryl methacrylate, n-propyl methacrylate, and combinations thereof.

[0026] Examples of the hydroxyl alkyl acrylates and methacrylates can include, but are not limited to, hydroxy propyl acrylate, hydroxyl methyl methacrylate, hydroxyl ethyl methacrylate, hydroxy propyl methacrylate, and combinations thereof.

[0027] Acrylic and/or methacrylic oligomers can include acrylate terminated urethane, a methacrylate terminated urethane or mixtures thereof. Examples include an aliphatic polyether urethane acrylate or methacrylate, an aliphatic polyester urethane acrylate or methacrylate, an aromatic polyether urethane acrylate or methacrylate, an aromatic polyester urethane acrylate or methacrylate, an aliphatic polyether urethane diacrylate or dimethacrylate, an aliphatic polyester urethane diacrylate or dimethacrylate, an aromatic polyether urethane diacrylate or dimethacrylate, an aromatic polyester urethane diacrylate or dimethacrylate, an aliphatic polyether urethane polyacrylate or polymethacrylate, an aliphatic polyester urethane polyacrylate or polymethacrylate, an aromatic polyether

urethane polyacrylate or polymethacrylate, an aromatic polyester urethane polyacrylate or polymethacrylate (the term “polyacrylate” and “polymethacrylate” being used generally to include tri, tetra, penta, hexa, and higher functionality acrylates and methacrylates). Examples can include, but are not limited to, CN 1963 (an aliphatic polyester-based urethane dimethacrylate oligomer) and CN 1964 (a low molecular weight aliphatic urethane dimethacrylate) products.

[0028] Epoxy (meth)acrylates, including aromatic and aliphatic epoxy (meth)acrylates, are also suitable for use as the free radically polymerizable compound. Epoxy (meth)acrylates are the beta-hydroxy esters which are generated by the reaction of acrylic acid and/or methacrylic acid (or an equivalent thereof, such as an anhydride) with an epoxy compound, preferably an epoxy compound having an epoxy functionality of two or greater. Suitable epoxy (meth)acrylates include the relatively low viscosity epoxy (meth)acrylates derived from diglycidyl ethers obtained by reaction of epichlorohydrin with an aliphatic alcohol containing two or more hydroxyl groups per molecule. Suitable aliphatic alcohols include, for example, glycols such as ethylene glycol, 1,2-propanediol, 1,3-propanediol, 1,2-butanediol, 1,4-butanediol, 1,6-hexanediol, neopentylglycol and other linear and branched C<sub>2</sub>-C<sub>10</sub> aliphatic diols, triols such as glycerin, trimethylolpropane, trimethylolethane, butanetriols, and pentanetriols, tetrols such as pentaerythritol, as well as other polyfunctional alcohols such as dipentaerythritol, Sugar alcohols and the like and alkoxylated derivatives thereof (where the alcohol has been reacted with an alkylene oxide such as ethylene oxide or propylene oxide, including both oligomeric species such as diethylene glycol or tripropylene glycol as well as polymeric species such as polyethylene glycols or polypropylene glycols or block, capped or random copolymers of ethylene oxide

and propylene oxide). The alcohol may also be an aromatic alcohol such as bisphenol A, and bisphenol F. The epoxy compound reacted with the (meth)acrylic acid may also be an epoxidized unsaturated triglyceride such as epoxidized soybean oil or epoxidized linseed oil. In one embodiment, all or essentially all of the epoxy groups on the epoxy compound are ring-opened with the (meth)acrylic acid. Suitable epoxy (meth)acrylates thus may have two, three, or more (meth)acrylate groups and two, three, or more hydroxyl groups per molecule. Specific illustrative examples of epoxy compounds include bisphenol A diglycidyl ethers, bisphenol F diglycidyl ethers, hexanediol diglycidyl ethers, neopentylglycol diglycidyl ethers, and butanediol diglycidyl.

[0029] In another embodiment, the free radically polymerizable compound is a multifunctional acrylate or (meth)acrylate of low molecular weight which is understood to mean a compound having at least two acrylate or (meth)acrylate groups and a molecular weight below 2400 g/mol, such as below 800 g/mol. Such compounds which have two, three or more acrylate or (meth)acrylate groups per molecule have proven to be particularly advantageous.

[0030] Examples of multifunctional (meth)acrylates include difunctional compounds, such as ethylene glycol dimethacrylate, diethylene glycol dimethacrylate, triethylene glycol dimethacrylate, triethylene glycol diacrylate, tripropylene glycol dimethacrylate, 1,4-butanediol dimethacrylate, 1,3-butylene glycol dimethacrylate, 1,3-butanediol dimethacrylate, tricyclodecane dimethanol dimethacrylate, 1,10-dodecanediol dimethacrylate, 1,6-hexanediol dimethacrylate, 2-methyl-1,8-octanediol dimethacrylate, 1,9-nonanediol dimethacrylate, neopentyl glycol dimethacrylate and polybutylene glycol dimethacrylate.

[0031] Acrylates and (meth)acrylates of low molecular weight having three or more acrylate or (meth)acrylate groups are glycerol triacrylate, dipentaerythritol hexaacrylate, pentaerythritol triacrylate (TMM), tetramethylolmethane tetraacrylate (TMMT), trimethylolpropane triacrylate (TMPTA), pentaerythritol trimethacrylate, di(trimethylolpropane) tetraacrylate (TPMA), pentaerythritol tetraacrylate, trimethylolpropane trimethacrylate (TMPTMA), tri(2-acryloxyethyl) isocyanurate and tri(2-methacryloxyethyl) trimellitate as well as the ethoxylated and propoxylated derivatives thereof containing at most 35 EO units and/or at most 20 PO units.

[0032] According to one embodiment, the multifunctional acrylate or (meth)acrylate of low molecular weight is selected from triethylene glycol diacrylate, triethylene glycol dimethacrylate, trimethylolpropane triacrylate (TMPTA) and trimethylolpropane trimethacrylate (TMPTMA), pentaerythritol triacrylate (TMM), tetramethylolmethane tetraacrylate (TMMT), pentaerythritol trimethacrylate, di(trimethylolpropane) tetraacrylate (TPMA) and pentaerythritol tetraacrylate.

[0033] The free radically polymerizable compounds discussed above may be used in any combination. For example, in one embodiment the free radically polymerizable component may include (i) an acrylate terminated urethane, a methacrylate terminated urethane or mixture thereof, (ii) an epoxy (meth)acrylate and (iii) a multifunctional acrylate or (meth)acrylate. In some embodiments, the free radically polymerizable component may include at least about 70 wt.%, or at least about 80 wt.%, or at least about 85 wt.%, or at least 87.5 wt.%, based on the total weight of the free radically polymerizable component, of the acrylate terminated urethane, methacrylate terminated urethane or mixture thereof. In further embodiments, the free radically polymerizable component may include less than

about 20 wt.%, or less than about 15 wt.%, or less than about 12.5 wt.%, or less than about 10 wt.%, based on the total weight of the free radically polymerizable component, of the epoxy (meth)acrylate. In still a further embodiment, the free radically polymerizable component may include less than about 10 wt.%, or less than about 7.5 wt.%, or less than about 5 wt.%, or less than about 2.5 wt.%, based on the total weight of the free radically polymerizable component, of the multifunctional acrylate.

[0034] In one embodiment, the one-component adhesive composition contains at least about 30 wt.%, or at least about 40 wt.%, or at least about 50 wt.%, at least about 55 wt.%, based on the total weight of the one-component adhesive composition, of the free radically polymerizable component. In another embodiment, the one-component adhesive composition contains less than about 70 wt.%, or less than about 65 wt.%, or less than about 60 wt.%, based on the total weight of the one-component adhesive composition, of the free radically polymerizable component. In still another embodiment, the one-component adhesive composition contains the free radically polymerizable component in an amount of about 20 wt.% to about 80 wt.%, or about 30 wt.% to about 70 wt.%, or about 40 wt.% to about 60 wt.%, based on the total weight of the one component adhesive composition.

[0035] The one-component adhesive composition also includes an impact modifier. According to one embodiment, the impact modifier comprises a core-shell impact modifier which may be formed from graft copolymers. Such core-shell graft copolymers generally have a rubbery core, and an outer hard shell. The core or backbone polymer of the graft copolymers may have a glass transition temperature substantially below ambient

temperatures. The shell polymer which is grafted onto the backbone polymer may have a glass transition temperature substantially above ambient temperatures.

[0036] Examples of useful core-shell graft copolymers are those where hard monomers, such as styrene, acrylonitrile or methyl methacrylate, are grafted onto a rubbery core made from polymers of soft or elastomeric monomers, such as butadiene or ethyl acrylate. Examples of such core-shell copolymers may be found in U.S. Pat. Nos. 3,984,497, 3,985,703, 4,034,013, 4,096,202, 4,304,709, 4,942,201 and 5,112,691, which are incorporated herein by reference. In one embodiment, the core-shell impact modifiers are methacrylate-butadiene-styrene (MBS) graft copolymers, styrene-butadiene-styrene (SBS) graft copolymers, methyl methacrylate and ethyl acrylate, graft copolymers and acrylate-styrene-acrylic acid (ASA) graft copolymers. Examples of those commercially available impact modifiers include PARALOID® BTA-753 impact modifier (methyl methacrylate-butadiene-styrene), KANE ACE B-564 impact modifier (methyl methacrylate-butadiene-styrene) and FM-41 impact modifier (methyl methacrylate-ethyl acrylate) and Geloy 1020 impact modifier (acrylic-styrene-acrylonitrile).

[0037] The amount of core-shell impact modifier incorporated into the adhesive composition should be sufficient to provide toughness and is thus variable. In one embodiment, the one-component adhesive composition may include from about 5 wt.% to about 35 wt.%, or from about 10 wt.% to about 30 wt.% or from about 15 wt.% to about 20 wt.%, based on the total weight of the one-component adhesive composition, of the core-shell impact modifier.

[0038] The one-component adhesive composition also includes an adhesion promoter. Adhesion promoters useful herein include known phosphorus-containing compounds with

mono-esters of phosphinic, mono- and diesters of phosphonic and phosphoric acids having one unit of vinyl or allylic unsaturation present. Vinylic unsaturation is preferred. Representative of the phosphorus-containing adhesion promoters are, without limitation, phosphoric acid; 2-methacryloyloxyethyl phosphate; bis-(2-methacryloyloxyethyl)phosphate; 2-acryloyloxyethyl phosphate; bis-(2-acryloyloxyethyl)phosphate; methyl-(2-methacryloyloxyethyl)phosphate; ethyl methacryloyloxyethyl phosphate; methyl acryloyloxyethyl phosphate; ethyl acryloyloxyethyl phosphate; propyl acryloyloxyethyl phosphate, isobutyl acryloyloxyethyl phosphate, ethylhexyl acryloyloxyethyl phosphate, halopropyl acryloyloxyethyl phosphate, haloisobutyl acryloyloxyethyl phosphate or haloethylhexyl acryloyloxyethyl phosphate; vinyl phosphonic acid; cyclohexene-3-phosphonic acid; ( $\alpha$ -hydroxybutene-2 phosphonic acid; 1-hydroxy-1-phenylmethane-1,1-diphosphonic acid; 1-hydroxy-1-methyl-1-disphosphonic acid; 1-amino-1-phenyl-1,1-diphosphonic acid; 3-amino-3-hydroxypropane-1,1-disphosphonic acid; amino-tris(methylenephosphonic acid); gamma-amino-propylphosphonic acid; gamma-glycidoxypropylphosphonic acid; phosphoric acid-mono-2-aminoethyl ester; allyl phosphonic acid; allyl phosphinic acid;  $\beta$ -methacryloyloxyethyl phosphinic acid; diallylphosphinic acid; 3-methacryloyloxyethyl)phosphinic acid and allyl methacryloyloxyethyl phosphinic acid. A preferred adhesion promoter is 2-hydroxyethylmethacrylate phosphate (HEMA-phosphate).

[0039] Further adhesion promoters also include acids with acrylate functionality, including acrylic acid, methacrylic acid, crotonic acid, isocrotonic acid, fumaric acid, maleic acid, cinnamic acid, 2-methylmaleic acid, itaconic acid, 2-methylitaconic acid, sorbic acid, and

$\alpha$ - $\beta$ -methylene glutaric acid. Another class of adhesion promoters include metal dimethacrylates, such as zinc dimethacrylate.

[0040] In one embodiment, the one-component adhesive composition may include from about 1 wt.% to about 15 wt.%, or from about 2.5 wt.% to about 12.5 wt.% or from about 5 wt.% to about 10 wt.%, based on the total weight of the one-component adhesive composition, of the adhesion promoter.

[0041] The one-component adhesive composition also includes a toughener. In one embodiment, the toughener comprises an epoxy/carboxyl-terminated butadiene acrylonitrile (CTBN) adduct. In certain embodiments, CTBN liquid polymers undergo addition esterification reactions with epoxy resins, allowing them to serve as elastomeric modifiers to enhance impact strength, peel strength, and crack resistance.

[0042] Epoxy compounds that may be used to form the epoxy/CTBN adduct include epoxy-functional polymers that can be saturated or unsaturated, cyclic or acyclic, aliphatic, alicyclic, aromatic or heterocyclic. The epoxy-functional polymers can have pendant or terminal hydroxyl groups, if desired. They can contain substituents such as halogen, hydroxyl, and ether groups. A useful class of these materials includes polyepoxides comprising epoxy polyethers obtained by reacting an epihalohydrin (such as epichlorohydrin or epibromohydrin) with a di- or polyhydric alcohol in the presence of an alkali. Suitable polyhydric alcohols include polyphenols such as resorcinol, catechol, hydroquinone, bis(4-hydroxyphenyl)-2,2-propane, i.e., bisphenol A, bis(4-hydroxyphenyl)-1,1-isobutane, 4,4-dihydroxybenzophenone, bis(4-hydroxyphenol)-1,1-ethane, bis(2-hydroxyphenyl)-methane and 1,5-hydroxynaphthalene.

[0043] Frequently used polyepoxides include polyglycidyl ethers of Bisphenol A, such as Epon® 828 epoxy resin which has a number average molecular weight of about 400 and an epoxy equivalent weight of about 185-192. Other useful polyepoxides include polyglycidyl ethers of other polyhydric alcohols, polyglycidyl esters of polycarboxylic acids, polyepoxides that are derived from the epoxidation of an olefinically unsaturated alicyclic compound, polyepoxides containing oxyalkylene groups in the epoxy molecule, epoxy novolac resins, and polyepoxides that are partially defunctionalized by carboxylic acids, alcohol, water, phenols, mercaptans or other active hydrogen-containing compounds to give hydroxyl-containing polymers.

[0044] In certain embodiments, at least a portion, such as at least 5 percent by weight, of the polyepoxide has been reacted with a carboxy-terminated butadiene acrylonitrile polymer. In certain of these embodiments, the carboxy-terminated butadiene acrylonitrile polymers have an acrylonitrile content of about 10-26 percent by weight. Suitable CTBN compounds having an acrylonitrile content of about 10-26 percent by weight that may be used include Hypro 1300X8, Hypro 1300X9, Hypro 1300X13, Hypro 1300X18 and Hypro 1300X31 tougheners.

[0045] In certain other embodiments, the polyepoxide may be reacted with a mixture of different carboxy-terminated butadiene acrylonitrile polymers.

[0046] In certain embodiments, the functionality of the CTBN utilized is from 1.6 to 2.4, and the epoxy compound is reacted with the CTBN material in a stoichiometric amount to form the epoxy/CTBN adduct.

[0047] In one embodiment, the one-component adhesive composition may include from about 1 wt.% to about 30 wt.%, or from about 5 wt.% to about 25 wt.% or from about 10

wt.% to about 20 wt.%, based on the total weight of the one-component adhesive composition, of the toughener.

[0048] In still another embodiment, the one-component adhesive composition includes a cure accelerant. Examples of cure accelerants include, but are not limited to, N,N-dimethyl-para-toluidine (DMPT), N-(2-hydroxyethyl)-N-methyl-para-toluidine (MHPT), N-methyl-N-(2-hydroxypropyl)-p-toluidine (2HPMT), and N-ethyl-N-(2-hydroxyethyl)-p-toluidine (EHPT); more preferably N-methyl-para toluidine derivatives, N-(2-hydroxyethyl)-N-methyl-para-toluidine, N-ethyl-N-(2-hydroxyethyl)-p-toluidine, zinc di(meth)acrylate, aluminum di(meth)acrylate, magnesium di(meth)acrylate, organic transitional metal compounds, such as copper acetyl acetonate, vanadium acetyl acetonate, cobalt, nickel, manganese or iron naphthenate, copper octoate, copper acetylacetonate, iron hexoate and iron propionate. An example of other cure accelerants include metallocenes, such as ferrocenes (for e.g., alkyl ferrocene, ferrocene acetate, ferrocene carboxylate, alkyl ferrocene dimethylcarbox amide, acetyl ferrocene, propioly ferrocene, butyryl ferrocene, pentanoyl ferrocene, hexanoyl ferrocene, octanoyl ferrocene, benzoyl ferrocene, 1,1'-diacetyl ferrocene, 1,1'-dibutyryl ferrocene, 1,1'-dihexanoyl ferrocene, ethyl ferrocene, propyl ferrocene, n-butyl ferrocene, pentyl ferrocene, hexyl ferrocene, 1,1'-dimethyl ferrocene, 1,1'-diethyl ferrocene, 1,1'-dipropyl ferrocene, 1,1'-dibutyl ferrocene, 1,1'-dihexyl ferrocene, cyclopentenyl ferrocene, cyclohexenyl ferrocene, 3-ferrocenoyl propionic acid, 4-ferrocenoyl butyric acid, 4-ferrocenylbutyric acid, 5-ferrocenylvaleric acid, 3-ferrocenoyl propionic acid esters, 4-ferrocenoyl butyric acid esters, 4-ferrocenyl butyric acid esters, 5-ferrocenylvaleric acid esters and dimethylaminomethyl ferrocene).

[0049] In one embodiment, the one-component adhesive composition may include from about 0.01 wt.% to about 1 wt.%, or from about 0.1 wt.% to about 0.5 wt.%, based on the total weight of the one-component adhesive composition, of the cure accelerant.

[0050] The one-component adhesive composition further includes an encapsulated free radical forming compound. The encapsulated free radical forming compound is generally a peroxide although other free radical forming compounds, such as benzopinacol and azo compounds, may also be employed.

[0041] Any peroxide which is liquid or soluble in the one-component adhesive composition is suitable. Specific examples of such peroxides are methyl ethyl ketone peroxide, benzoyl peroxide, di-tert-butyl peroxide, tert-butyl hydroperoxide, isopropyl peroxydicarbonate, dichlorobenzoyl peroxide, lauroyl peroxide, acetyl peroxide, tert-butyl peracetate, tert-butyl perbenzoate, dicumyl peroxide, diethyl peroxide, di-tert-amyl peroxide, and cyclohexyl hydroperoxide. Specific examples of azo compounds include 2,2'-azobis[N-(2-propenyl)-2-methyl propionamide], 1-[(cyano-1-methyl ethyl)azo] formamide, 2,2'-azobis(N-butyl-2-methyl propionamide), 2,2'-azobis(N-cyclohexyl-2-methyl propionamide), 2,2'-azobis (2-methyl-N-[2-(1-hydroxybutyl)] propionamide), 2,2'-azobis(2-methyl-N-[2-(1-hydroxybutyl)]propionamide), and 2,2'-azobis(2-methyl-N-[1,1-bis(hydroxymethyl)-2-hydroxyethyl]propionamide).

[0042] Microencapsulation of the free radical forming compound may be attained through any of the known methods and using any of the known materials. While the following discussion is predominately directed towards the encapsulation of the free radical forming compound, the same is equally applicable to the encapsulation of other components of the adhesive compositions, where desired or applicable. Suitable techniques include

coacervation, interfacial polymerization, air suspension, centrifugal extrusion, spray drying, pan coating, in-situ polymerization, and by forming a dispersion of core material and shell material and applying a pressure shock wave to the dispersion as described in Redding Jr. (U.S. Pat. No. 5,271,881, incorporated herein by reference). The specific selection of the method and the materials depends upon the nature, including the physical state and/or chemistry, of the material to be encapsulated, e.g., whether the free radical forming compound is in a liquid form or a solid, semi-solid or gel-like particulate form. Exemplary methods and materials are set forth in the following paragraphs as well as in, for example, Schwantes (U.S. Pat. No. 6,592,990), Nagai et. al. (U.S. Pat. No. 4,708,924), Baker et. al. (U.S. Pat. No. 4,166,152), Wojciak (U.S. Pat. No. 4,093,556), Matsukawa et. al. (U.S. Pat. No. 3,965,033), Matsukawa (U.S. Pat. No. 3,660,304), Ozono (U.S. Pat. No. 4,588,639), Irgarashi et. al. (U.S. Pat. No. 4,610,927), Brown et. al. (U.S. Pat. No. 4,552,811), Scher (U.S. Pat. No. 4,285,720), Shioi et. al. (U.S. Pat. No. 4,601,863), Kiritani et. al. (U.S. Pat. No. 3,886,085), Jahns et. al. (U.S. Pat. Nos. 5,596,051 and 5,292,835), Matson (U.S. Pat. No. 3,516,941), Chao (U.S. Pat. No. 6,375,872), Foris et. al. (U.S. Pat. Nos. 4,001,140; 4,087,376; 4,089,802 and 4,100,103), Greene et. al. (U.S. Pat. Nos. 2,800,458 and 2,730,456), Clark (U.S. Pat. No. 6,531,156), Saeki et. al. (U.S. Pat. Nos. 4,251,386 and 4,356,109), Hoshi et. al. (U.S. Pat. No. 4,221,710), Hayford (U.S. Pat. No. 4,444,699), Hasler et. al. (U.S. Pat. No. 5,105,823), Stevens (U.S. Pat. No. 4,197,346), Riecke (U.S. Pat. No. 4,622,267), Greiner et al. (U.S. Pat. No. 4,547,429), and Tice et. al. (U.S. Pat. No. 5,407,609).

[0043] The first step in the encapsulation process is the preparation of the discrete particles, domains or beads of the free radical forming compound. Where such compounds are in

solution or liquid form and the encapsulation is to be by way of, e.g., coacervation, interfacial polymerization, etc., the solution or liquid containing the free radical forming compound is subjected to high shear mixing or agitation to create a suspension, emulsion or colloidal system of discrete domains of the free radical forming compound of the requisite size. Where the free radical forming compound is a heat sensitive material, e.g., a wax or wax-like material, the free radical forming compound is heated above its melt temperature and then subjected to a similar high shear mixing or agitation in a liquid medium, preferably water, to create discrete droplets of the free radical forming compound and then cooled to allow the solid particles to form, before encapsulating. Where the free radical forming compound is incorporated into a solid or substantially solid, the free radical forming compound may be ground and sorted to the desired particle size before encapsulation. Such methods, as well as additional alternative methods for preparation of the particles or discrete domains for encapsulation are widely used in industry and well known to those skilled in the art.

[0044] In one embodiment, the microencapsulation technique is coacervation where the free radical forming compound to be encapsulated is dispersed or emulsified in a liquid solution of a material to be used as the wall material. The solution is perturbed to cause a phase separation of the wall material, or at least a portion thereof, from the solvent with all or some of the wall material coating the dispersed free radical forming compound to be encapsulated. In this process, the wall forming material may directly separate out onto the emulsified or dispersed free radical forming compound or it may form its own emulsion with the droplets of the wall material subsequently depositing on the droplets of the free radical forming compound material. In either case, the liquid wall material deposits itself

as a continuous coating about the dispersed droplets of the internal phase or capsule free radical forming compound and the wall material is then solidified. Solution perturbation can be any that affects the solubility of the wall material including changes in temperature and addition of another solvent, including, for example, the addition of a non-solvent for the wall material. It should be readily understood by those skilled in the art that the foregoing may be accompanied by a pH shift with wall materials, such as gelatin, to promote the phase separation in the wall formation.

[0045] In coacervation encapsulation, the free radical forming compound to be coated is typically a liquid and is emulsified in the solvent to form droplets which are then coated with the wall material. Oftentimes it is advantageous to also employ an emulsification agent to assist with the emulsification of the free radical forming compound. Preferred emulsification agents that can be used are amphiphilic, that is, they contain both hydrophilic and hydrophobic groups in the same molecule. Exemplary emulsification agents include, but are not limited to, partially hydrolyzed polyvinyl alcohol, starch derivatives, cellulose derivatives, polyacrylamide, and the like. A preferred emulsification agent for use is partially hydrolyzed polyvinyl alcohol. In a preferred method, high shear agitation is provided to the aqueous mixture to achieve a droplet size of less than about 250 microns, preferably less than 100 microns.

[0046] The conditions for encapsulation will vary based upon the choice of the materials or compositions used for the capsule wall as well as the free radical forming compound to be encapsulated. Selection of the encapsulating materials or compositions depends upon a number of additional factors including the desired properties of the shell wall to be formed, the chemical composition and state of the free radical forming compound to

be encapsulated and the method employed for the encapsulation process. Desired properties of the shell wall include strength, breakability and impermeability. Suitable materials for the capsule walls include natural materials such as gelatin, gum arabic, starches, sugars, shellac, and rosin, cellulose derivatives, such as ethyl cellulose and carboxymethylcellulose, paraffin, tristearin, polymers such as polyvinyl alcohol, polyethylene, polypropylene, polystyrene, polyacrylamides, polyethers, polyesters, polyamides, polybutadiene, polyisoprene, silicones, epoxies, polyurethanes, formaldehyde resins such as reaction products of formaldehyde with phenols, urea, and melamine, and copolymers such as polyurethane copolyethers. Melamine-formaldehyde and polyvinyl alcohol are preferred wall materials.

[0047] Dyes, pigments, fillers, plasticizers, crosslinking agents, binding agents, and other additives can be incorporated in the capsule wall or applied to the capsule wall surface. One important parameter to keep in mind when formulating wall materials is permeability. Generally, the wall material should have low permeability, at least with respect to the free radical forming compound to be encapsulated. No or low permeability of the capsule wall is particularly important so as to prevent loss of the free radical forming compound and premature polymerization of the adhesive composition. Likewise, it may be important for the capsule wall to be impermeable or of low permeability to the free radical polymerizable component of the adhesive composition so as to prevent any ingress of the same into the encapsulated particles. It may also be desirable to formulate the wall material to have low permeability to certain gases, such as oxygen, or low permeability to liquids, such as water or solvents such as toluene or tetrahydrofuran. The requisite permeation rates will vary for each system, but can be met by judicious choice of the wall material and by degree of

crosslinking of the wall material. Generally, as crosslinking increases, the permeation rate decreases.

[0048] As noted above, any of a number of different processes may be used to encapsulate the free radical forming compound as well as other components of the adhesive compositions. One preferred technique is to polymerize the capsule wall material in-situ. In this technique, monomers or oligomers are dispersed on the free radical forming compound to be encapsulated and then polymerization is effected by addition of a reactive species, such as a co-monomer or radical initiator, a curing agent or by heat or ultraviolet radiation. Optionally, the capsule wall material may be crosslinked in-situ by addition of crosslinking agents or by treatment with heat or ultraviolet radiation or radical initiators. The method of polymerizing or crosslinking the capsule wall material will vary based upon the choice of wall materials and based upon the free radical forming compound being encapsulated.

[0049] When the walls of the microcapsules are comprised of polyamide or polyurea, a preferred encapsulation technique is interfacial polymerization. This can be effected by mixing the adhesive monomer or monomers to be microencapsulated together with either an acid chloride or an isocyanate. The resultant mixture is emulsified with an emulsification agent to obtain an on-in-water emulsion. A polyfunctional amino compound is then added into the emulsion, whereby microcapsule walls are formed around each microparticle of oil. When an acid chloride is mixed with the polyfunctional amino compound, a polyamide microcapsule is produced—when an isocyanate is used, polyurea capsules are formed. Though reference is made to microparticles of the oil phase, it is also

understood that the dispersed phase is also referred to herein as “domain”, “bead” or “droplet.”

[0050] Acid chlorides that can be used to produce polyamide microcapsules include, but are not limited to terephthaloyl chloride, isophthaloyl chloride, 1,3,5-benzenetricarboxylic acid chloride, sebacyl dichloride, 4,4-sulfonyldibenzoyl chloride, 1,3-benzenedisulfonyl chloride, 1,4-benzenedisulfonyl chloride, or mixtures thereof. A preferred acid chloride for use in the invention is a mixture of isophthaloyl chloride and terephthaloyl chloride.

[0051] Isocyanate compounds that can be used to produce polyurea microcapsules include, but are not limited to 2,4- and 2,6-diisocyanatotoluene, 4,4'-diisocyanatodiphenyl methane, 1,3,5-trimethylbenzene-2,4-diisocyanate, 1,6-diisocyanatohexane, polymethylene polyphenyl isocyanate, polyisocyanates which additionally contain biuret-, allophanate-, and carbodiimide groups.

[0052] Polymerization reactions in which the material to be encapsulated, or core material, is dissolved in an organic, hydrophobic oil phase which is dispersed in an aqueous phase may also be used. The aqueous phase has dissolved aminoplast resin forming materials which upon polymerization form the wall of the microcapsule. A dispersion of fine oil droplets is prepared using high shear agitation. Addition of an acid catalyst initiates the polycondensation forming the aminoplast resin within the aqueous phase, resulting in the formation of an aminoplast polymer which is insoluble in both phases. As the polymerization advances, the aminoplast polymer separates from the aqueous phase and deposits on the surface of the dispersed droplets of the oil phase to form a capsule wall at the interface of the two phases, thus encapsulating the free radical forming compound. Polymerizations that involve amines and aldehydes are known as aminoplast

encapsulations. Urea-formaldehyde, urea-resorcinol-formaldehyde, urea-melamine-formaldehyde, and melamine-formaldehyde, capsule formations proceed in a like manner. In interfacial polymerization, the materials to form the capsule wall are in separate phases, one in an aqueous phase and the other in an oil phase. Polymerization occurs at the phase boundary. Thus, a polymeric capsule shell wall forms at the interface of the two phases thereby encapsulating the free radical forming compound. Interfacial polymerization is particularly useful for wall materials such as polyesters, polyamides, and polyureas.

[0053] Gelatin and gelatin containing microcapsule wall materials are well known and may be used in coacervation and phase separation encapsulation processes. For example, one technique for gelatin/gum arabic encapsulation involves first emulsifying the free radical forming compound into a gelatin solution to obtain an oil-in-water emulsion. The emulsion is mixed with a gum arabic solution. The system is then pH adjusted or diluted to cause the gelatin/gum arabic to coacervate. Thereafter, the capsules are post-treated with a crosslinking agent, such as formaldehyde, glutaraldehyde, or other similar known compounds.

[0054] Wall materials made of melamine-formaldehyde can be made by first emulsifying the free radical forming compound into a carboxymethyl cellulose solution or a poly(styrene-maleic anhydride) solution to obtain an oil-in-water emulsion. The emulsion is then mixed with a melamine-formaldehyde precondensate solution. The system is then pH adjusted, followed by heating to initiate polymerization of the precondensate to a high molecular weight compound. The presence of the carboxyl methyl cellulose or poly(styrene-maleic anhydride) solution helps the polymerized melamine-formaldehyde to deposit onto the free radical forming compound surface, thereby encapsulating the free

radical forming compound. An alternative method polymerizes the melamine and formaldehyde in the presence of a styrene sulfonic acid. Yet, another alternative and a preferred embodiment of the melamine-formaldehyde resin wall forming process employs polyacrylic acid and/or polyacrylic acid derivatives as emulsifiers to assist in forming the oil in water emulsions. Such emulsifiers preferably have an HLB value of from about 8 to 18.

[0055] When the walls of the microcapsules are comprised of epoxies, suitable components include difunctional or polyfunctional epoxides such as vinylcyclohexene dioxide, 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexanecarboxylate and bis-phenol-A-diglycidyl ether. These can be used in combination with polyols such as glycerol. One convenient method of forming microcapsules involves forming an emulsion of the free radical forming compound to be encapsulated, adding a combination of the di- or polyfunctional epoxide with the polyol to coat the free radical forming compound to be encapsulated and then adding an acid to effect the polymerization and form the polyepoxide. Suitable acids include Bronsted acids such as hydrochloric acid or sulfuric acid and also Lewis acids such as boron trifluoride, antimony pentafluoride and the like.

[0056] Preferably the capsules employed are from about 0.1-100 microns, preferably about 1-50 microns, more preferably less than 40 microns, and most preferably less than 30 microns. Other sizes are possible for specific applications.

[0057] In one embodiment, the one-component adhesive composition includes less than about 5 wt.%, or less than about 4 wt.%, or less than about 3 wt.%, or less than about 2 wt.% or less than about 1 wt.%, based on the total weight of the one-component adhesive composition, of the encapsulated free radical forming compound. In another embodiment,

the one-component adhesive composition from about 0.01 wt.% to about 5 wt.%, or from about 0.1 wt.% to about 3 wt.%, based on the total weight of the one-component adhesive composition, of the encapsulated free radical forming compound.

[0058] According to another embodiment, the one-component acrylic adhesive composition may include a thixotropic modifier. Examples thixotropic modifiers include, but are not limited to, finely divided, high surface-area silica, fumed silica, sodium silicate, silicic acid, and combinations thereof. In one embodiment, the one-component adhesive composition includes less than about 5 wt.%, or less than about 4 wt.%, or less than about 3 wt.%, or less than about 2 wt.% or less than about 1.5 wt.%, based on the total weight of the one-component adhesive composition, of the thixotropic modifier. In another embodiment, the one-component adhesive composition from about 0.01 wt.% to about 5 wt.%, or from about 0.1 wt.% to about 3 wt.%, or from about 0.5% by weight to about 1.5% by weight, based on the total weight of the one-component adhesive composition, of the thixotropic modifier.

[0059] In further embodiments, the one-component adhesive composition may include one or more additives including, but not limited to, fillers, plasticizers, reactive and/or non-reactive diluents, flow auxiliaries, coupling agents, processing aids, wetting agents, tackifiers, flame retardants, thickeners, ageing and/or corrosion inhibitors, anti-oxidants, stabilizers and pigments.

[0060] In one embodiment, the one-component adhesive composition is formed as a material of substantially homogeneous composition. However, it is contemplated that various combining techniques may be used to increase or decrease the concentration of certain components in certain locations of the adhesive composition.

[0061] According to one embodiment, the one-component adhesive composition is formed by supplying the components of the adhesive composition in solid form, such as pellets, chunks, in liquid form or a combination thereof. The components are typically combined in one or more containers, such as large bins or other containers. Preferably, the containers can be used to intermix the components by rotating or otherwise moving the container or the material therein. Thereafter, heat, pressure or a combination thereof may be applied to soften or liquidize the components such that the components can be intermixed by stirring (or otherwise) into a single homogenous composition. When used, such heat and/or pressure are typically relatively low so as not to damage or rupture any encapsulations. Thus, it may be desirable for the free radically polymerizable compounds and/or other components of the adhesive composition to have relatively low viscosities for allowing mixing under lower pressure and lower heat conditions.

[0062] According to another embodiment, the adhesive composition may be formed by heating one or more of the components that is generally easier to soften or liquidize, such as the free radically polymerizable compounds to induce those components into a mixable state. Thereafter, the remaining components may then be intermixed with the softened components.

[0063] The one-component adhesive composition is typically activated to cure upon the exposure to an external stimulus. Although it is contemplated that various additional or alternative stimuli such as heat, moisture or the like may be employed, the adhesive material is activated to at least partially cure upon exposure to elevated pressure. Thus, the free radical forming compound is maintained separate from the free radically polymerizable compound in the one-component adhesive composition by encapsulation.

Upon application of sufficient pressure, the encapsulation will typically fail (e.g., rupture, melt, flow or the like) thereby exposing the free radically polymerizable compound(s) to the free radical forming compound to effectuate curing of the adhesive composition. As discussed above, various sizes, shapes and thickness, various different materials and combinations thereof for the encapsulation can provide or allow for rupture of the encapsulation at different pressure levels. Thus, rupture of the encapsulated free radical forming compound and, therefore, activation of the adhesive composition can occur at a variety of different pressures. Typically, the pressure of activation is at least greater than atmospheric pressure (e.g., at least about 20 psi, more typically at least about 30 psi and even more typically at least about 40 psi, such as between about 40 psi and about 80 psi). Typically, for the encapsulated free radical forming compound, it is preferable that the free radical forming compound can activate polymerization to effectuate curing at a temperature below about 100° C, more typically below about 70° C and even more typically below about 40° C. (for e.g., at about room temperature of around 22°-27°C).

[0064] In addition to polymerization, the adhesive composition may optionally also be activated to expand or foam and, therefore, may include a blowing agent (e.g., a physical or chemical blowing agent). Exemplary blowing agents can include one or more nitrogen containing groups such as amides or amines or can be thermoplastic encapsulated solvents or other chemicals. Typically, for a pressure activated system, it may be desirable for the blowing agent to create a blowing effect at a temperature below about 100°C, more typically below about 70°C and even more typically below about 40°C (e.g., about room temperature around 22°-27°C). Thus, when included, the blowing agent may be encapsulated in a manner as described for the free radical forming compound.

[0065] The one-component adhesive composition may be employed in connection with a variety of structural members of a variety of articles of manufacture. Generally, the one-component adhesive composition is located between at least one surface of a first substrate and at least one surface of a second substrate. Once between the substrates, and preferably contacting the surfaces of the substrates, the adhesive composition is typically exposed to an external stimulus, which is typically elevated pressure, that activates the adhesive composition to cure the adhesive composition. Such pressure may be applied by moving the surface of the first substrate toward the surface of the second substrate or vice versa or moving both surfaces toward each other.

[0066] Substrates used in the present disclosure may be made of the same material or dissimilar materials. The materials can include, but are not limited to, wood, metal (e.g., steel, aluminium, copper), coated or pretreated metal, plastic, filled plastic, thermoset materials, such as sheet molding compound, fiberglass and thermoplastics. The thermoplastics can include, but are not limited to, polypropylene, thermoplastic olefins, nylon, acrylonitrile-butadiene styrene or other thermoplastics known in the art. The one-component adhesive composition may be applied onto the surface of the substrate by any technique known in the art, for example, it can be pre-coated or applied before use by a robot, or by mechanical application methods or pressed into place by hand. The substrates may or may not be exposed to a surface treatment, such as a wipe on primer, plasma or corona surface treatment.

[0067] The one-component adhesive composition, in bonding the substrates together, can be used in the manufacture of various useful parts and/or articles of manufacture. It is generally contemplated that the one-component adhesive composition may be applied to a

variety of structural members of a variety of transportation vehicles (e.g., those described above) or other articles of manufacture, especially in situations where the adhesive composition is subject to elevated pressures caused by the assembly process thereof. For example, the one-component adhesive composition may be located between any two of the following: parts of a wing of an airplane, body panel of an automobile or airplane or other articles of manufacture, and a frame or structural members of an automobile, airplane or other articles of manufacture. In other alternative embodiments, it is contemplated that the one-component adhesive composition of the present disclosure may be employed in conjunction with one or more mechanical fasteners (e.g., threaded fasteners, such as nut and bolt assemblies, clamps or combinations thereof) used in connection with articles of manufacture. In such an embodiment, the adhesive composition is placed between two structures of an article of manufacture, or between two components (e.g., a nut and bolt) of the fastener, or between a component of the fastener and a structure of an article of manufacture or any combination thereof. Then, upon application of pressure applied to the fastener (e.g., upon tightening or clamping of the fastener), the adhesive composition is activated as described above to cure and adhere to the structure of the article of manufacture and/or the fastener.

[0068] Thus, the present disclosure further encompasses parts comprising two or more pieces that are adhered together, such as parts for vehicles (e.g., automobiles and other transportation vehicles like a motorcycle, bicycle, train, boat, airplane or other aerospace vehicle). The parts can comprise at least two substrates and one or more layers of the one-component adhesive composition which adhere the substrates to each other. The present

disclosure is also directed to an article of manufacture containing the one-component adhesive composition.

[0069] According to still another embodiment, there is provided a storage stable packaged product comprising: a) a container having at least an outlet; and b) the one-component adhesive composition of the present disclosure.

[0070] According to one embodiment, the packaged product comprises a container having a closure means, such as a lid, cover, cap, or plug to seal the container. In another embodiment, the sealed container also has a nozzle or pour spout. The sealed container may have the shape of a cylinder, oval, round, rectangle, canister, tub, square or jug and contains the one-component cationic polymerizable composition of the present disclosure.

[0071] In yet another embodiment, the container may be made from any material, such as steel, glass, aluminum, cardboard, tin-plate, plastics including, but not limited to, high density polyethylene (HDPE), polypropylene (PP), polyvinyl chloride (PVC), polyethylene terephthalate (PET), oriented polypropylene (OPP), polyethylene (PE) or polyamide and including mixtures, laminates or other combinations of these.

[0072] The present disclosure will now be further described with reference to the following non-limiting examples.

#### Examples

[0073] Examples 1 and 2. One-component adhesive composition according to the present disclosure.

As shown below in Tables 1 and 2, various amounts of each component were added to a vessel and mixed to form a one-component adhesive composition according to the present disclosure and a comparative adhesive composition. The lap shear strength, torque-

out strength and ambient storage stability for each composition were then determined and the results are shown below.

Table 1

| Component                                 | Comparative Example | Example 1 |
|-------------------------------------------|---------------------|-----------|
| Methacrylate terminated urethane          | 51.2                | 51.2      |
| Multifunctional acrylate                  | 1                   | 1         |
| Epoxy (meth)acrylate                      | 5                   | 5         |
| Impact modifier                           | 20                  | 20        |
| Adhesion Promoter                         | 7.5                 | 7.5       |
| Toughener                                 | 15                  | 15        |
| Cure Accelerant                           | 0.3                 | 0.3       |
| Benzoyl peroxide                          | 2                   |           |
| Encapsulated benzoyl peroxide             |                     | 2         |
| Total:                                    | 102                 | 102       |
| Lap shear strength (psi)                  | 1922 ± 41           | 1219 ± 31 |
| Torque-out strength (calculated, in-lbs.) | 481                 | 305       |
| Stability (time to full cure @ 25° C)     | 0.1 days            | >150 days |

Table 2

| Component                                 | Comparative Example | Example 2 |
|-------------------------------------------|---------------------|-----------|
| Methacrylate terminated urethane          | 54.9                | 54.9      |
| Multifunctional acrylate                  | 1                   | 1         |
| Epoxy (meth)acrylate                      | 5                   | 5         |
| Impact modifier                           | 10                  | 10        |
| Thixotropic modifier                      | 1                   | 1         |
| Adhesion Promoter                         | 7.5                 | 7.5       |
| Toughener                                 | 20                  | 20        |
| Cure Accelerant                           | 0.6                 | 0.6       |
| Benzoyl peroxide                          | 2                   |           |
| Encapsulated benzoyl peroxide             |                     | 2         |
| Lap shear strength (psi)                  | 2129 ± 84           | 1053 ± 21 |
| Torque-out strength (calculated, in-lbs.) | 532                 | 263       |
| Stability (time to full cure @ 25° C)     | 0.1 days            | >150 days |

[0074] Although making and using various embodiments of the present invention have been described in detail above, it should be appreciated that the present invention provides

many applicable inventive concepts that can be embodied in a wide variety of specific contexts. The specific embodiments discussed herein are merely illustrative of specific ways to make and use the invention, and do not delimit the scope of the invention.

## CLAIMS

What is claimed is:

1. A one-component adhesive composition comprising: (a) a free radically polymerizable component comprising at least one free radically polymerizable compound; (b) an impact modifier; (c) an adhesion promoter; (d) a toughener; (e) a cure accelerant; (f) an encapsulated free radical forming compound; and optionally (g) a thixotropic modifier.
2. The one-component adhesive composition of claim 1, wherein the free radically polymerizable compound comprises a (meth)acrylate terminated urethane.
3. The one-component adhesive composition of claim 2, wherein the free radically polymerizable component further comprises an epoxy (meth)acrylate.
4. The one-component adhesive composition of claim 3, wherein the free radically polymerizable component further comprises a multifunctional acrylate.
5. The one-component adhesive composition of claim 1, wherein the impact modifier comprises a core-shell impact modifier.
6. The one-component adhesive composition of claim 1, wherein the toughener comprises an epoxy/carboxyl-terminated butadiene acrylonitrile adduct.
7. The one-component adhesive composition of claim 1, wherein the free radical forming compound comprises a peroxide.
8. The one-component adhesive composition of claim 1, wherein the cure accelerant comprises a metallocene.
9. The one-component adhesive composition of claim 1, wherein the thixotropic modifier is present in an amount of from about 0.01 wt.% to about 5 wt.%, based on the total weight of the one-component adhesive composition.

10. The one-component cationic polymerizable composition of claim 1, further comprising one or more additives.
11. A packaged product comprising a) a container having at least an outlet; and b) the one-component adhesive composition of claim 1.
12. The packaged product of claim 11, wherein the one-component adhesive composition of claim 1 has a storage stability of at least 6 months.
13. A method of forming a structure of an article of manufacture comprising locating the one-component adhesive composition of claim 1 between a first substrate and a second substrate and activating the one-component adhesive composition to cure between the first substrate and the second substrate by exposing the one-component adhesive composition to an external stimulus that causes the encapsulation of the free radical forming compound to fail.
14. The method of claim 13, wherein the external stimulus is pressure.
15. The method of claim 14, wherein the pressure ranges from about 40 psi to about 80 psi.
16. A structure of an article of manufacture produced according to the method of claim 13.
17. The structure of claim 16, wherein the structure comprises a mechanical fastener and the article of manufacture is an automobile or an airplane.