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(54) **Titre : COMPOSITIONS ADHESIVES PRENANT A BASSE TEMPERATURE**
(54) **Title: LOW TEMPERATURE CURABLE ADHESIVE COMPOSITIONS**

(57) **Abrégé/Abstract:**

The present invention is concerned with curable adhesive compositions for anchoring elements in a structural body that exhibit low temperature versus standard temperature degree of cures that are at least 50% or higher. The compositions include, in a first component, a reactive resin, an acetoacetoxy functional monomer and a silane monomer. By using phthalate-free constituents in the formulation, a further 10% increase in strength and durability of the resins at standard temperatures may be realized after curing at low temperatures.



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(54) Title: LOW TEMPERATURE CURABLE ADHESIVE COMPOSITIONS

(57) Abstract: The present invention is concerned with curable adhesive compositions for anchoring elements in a structural body that exhibit low temperature versus standard temperature degree of cures that are at least 50% or higher. The compositions include, in a first component, a reactive resin, an acetoacetoxy functional monomer and a silane monomer. By using phthalate-free constituents in the formulation, a further 10% increase in strength and durability of the resins at standard temperatures may be realized after curing at low temperatures.

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UNITED STATES PATENT AND TRADEMARK OFFICE

Title: LOW TEMPERATURE CURABLE ADHESIVE COMPOSITIONS

BACKGROUND OF THE INVENTION

1. Field of the Invention

[0001] The present invention relates to adhesive compositions suitable for anchoring or fixing elements in a base or structural body, and to methods of anchoring. More specifically, the present invention is directed towards adhesive compositions and methods that are especially well suited for curing such compositions at lower temperatures, without compromising desirable characteristics such as strength and durability.

2. Discussion of the Related Art

[0002] It is well known that adhesive systems are useful for fixing or anchoring materials in or to rock, masonry, and concrete. Such systems typically involve the use of synthetic resins and monomers that are maintained separately from a hardening or curing agent until they are combined at or near the point of fastening. A variety of additional and often optional adjuvants may also be used with adhesive systems.

[0003] By way of example, U.S. Patent 5,157,072 to Hense, *et al.*, teaches ethylenically unsaturated, substituted cycloaliphatic compounds as monomers and resins for minimizing shrinkage of the adhesive when used for anchoring bolts in bore holes. However, Hense, *et al.*, is silent on low shrinkage stress. U.S. Pat. No. 5,288,767 to Cramer, *et al.*, teaches a methacrylate monomer in the first component together with diluent monomers. One of the stated goals of this patent is to eliminate styrene as a co-monomer, but Cramer, *et al.*, is silent on the subject of low-temperature curing. U.S. Pat. No. 6,037,408 to Weber, *et al.*, is similar to the Cramer '767 patent, but it requires the use

of very high levels of monomer and is silent on the affects of low temperature cure. Variously, U.S. Pat. No. 6,583,259, Weber, *et al.*, is concerned with adhesives to bond to wet bore holes; U.S. Pat. No. 7,544,739, to Liu, *et al.* teaches a composition for use under conditions of elevated temperatures; and U.S. Pat. No. 5,077,324 to Kistner, *et al.*, is concerned with extending the shelf life the formulation prior to use. Neither any of the foregoing, nor a great many other references are directed towards adhesive compositions that are suitable for curing at low temperatures.

[0004] It is often the case that adhesives must be applied to anchoring elements in concrete and masonry under adverse weather conditions involving low temperatures and/or excess moisture.

Unfortunately, it is not until the arrival of warmer weather at some later point in time that weakness or failure of the anchoring elements are observed. The effects of warming the substrate have been largely ignored in the past. Often, products that are developed for cold environments make the assumption that the substrate will not warm appreciably. Another tactic that has often been employed is to produce multiple variations of a product where several closely related compositions are developed, each associated with a specific temperature range. Under new protocols, however, the costs for testing can be prohibitive for a product line with multiple adhesives.

SUMMARY

[0005] In light of the foregoing, it is desirable to provide an adhesive composition that not only can be cured at low temperatures, but that also exhibits good strength and structural integrity over a wide range of temperature conditions. Moreover, another disadvantage of many adhesive compositions that are currently commercially available is that they contain or include phthalates. Phthalates, or phthalate esters, are often used in adhesive formulations as phlegmatizing agents to prevent the rapid and explosive reaction of certain curing agents when they are physically disturbed. Over concerns related to health reasons, however, phthalates are being phased out of many products in the United States, Canada, Europe and elsewhere in the world. Accordingly, it is desirable to provide an adhesive composition that does not include phthalates yet does not compromise safety.

[0006] The present disclosure provides an adhesive composition suitable for anchoring materials in or to concrete or masonry that comprises from about 20% to 80% by weight of the entire composition of a reactive resin monomer/acetoacetoxy monomer/silane monomer solution; and a curing agent. In one aspect, the present disclosure provides a composition suitable for anchoring materials in or to concrete or masonry that is made by mixing a first composition and a second composition. The first composition comprises from about 20% to 80% by weight of the entire composition of a reactive resin/acetoacetoxy monomer/silane monomer solution; in addition to an accelerant; inhibitor; and filler.

The second composition comprises a curing agent; diluents as required to provide a phlegmatizing agent or flow; and filler.

[0007] According to another aspect, the present disclosure provides a phthalate-free composition suitable for anchoring materials in or to concrete or masonry that is made by mixing a first composition and a second composition. The first composition comprises from about 20% to 80% by weight of the entire composition of a phthalate-free methacrylate monomer/acetoacetoxy monomer/silane monomer solution; in addition to an accelerant; an inhibitor; a filler and optional adjuncts. The second composition comprises a free radical initiator; phthalate-free diluents as required to provide a phlegmatizing agent or flow; and optional adjuncts.

[0007a] Various embodiments of the claimed invention relate to a curable adhesive composition for anchoring elements in a structural body, comprising: a. at least one reactive resin comprising a polymerizable monomer; b. at least one acetoacetoxy functional monomer; and c. at least one silane monomer. The structural body may be concrete, masonry or a combination thereof.

[0007b] Various embodiments of the claimed invention relate to a curable adhesive composition for anchoring structural materials in concrete or masonry comprising: a. from 10-25 wt % of at least one reactive resin comprising a polymerizable monomer; b. from 1-5 wt % of at least one acetoacetoxy functional monomer; and c. from 0.1-5 wt % of at least one silane monomer; wherein the strength of the composition at 23 °C after cure at -10 °C compared to the strength of the composition at 23 °C after cure at 23 °C is greater than 50%.

[0007c] Various embodiments of the claimed invention relate to a curable adhesive composition for anchoring structural materials in concrete or masonry comprising: a. from 10-25 wt % of at least one reactive resin comprising a polymerizable monomer; b. from 1-5 wt % of at least one acetoacetoxy functional monomer; and c. from 0.1-5 wt % of at least one silane monomer; wherein the strength of the composition at 23 °C after cure at -10 °C compared to the strength of the composition at 23 °C after cure at 23 °C is greater than 50%, and wherein the composition contains no phthalates.

[0007d] Various embodiments of the claimed invention relate to a curable adhesive composition, comprising: a. at least one reactive resin comprising a polymerizable monomer; b. at least one acetoacetoxy functional monomer; c. at least one silane monomer; d. a free radical initiator; and e. an accelerant; in which the free radical initiator is dibenzoyl peroxide, and the accelerant is selected from the group consisting: of N,N-diisopropanol-p-toluidine; N,N-dihydroxyethyl-p-toluidine; N,N-methylhydroxyethyl-p-toluidine; and mixtures thereof. The composition may be for anchoring structural materials in concrete, masonry or a combination thereof.

[0007e] Various embodiments of the claimed invention relate to a curable adhesive composition consisting essentially of: a. an ethoxylated bisphenol A dimethacrylate; b. acetoacetoxyethyl methacrylate; c. methacryloxypropyl trimethoxysilane; d. phthalate-free dibenzoyl peroxide; and e. an accelerant that is: N,N-diisopropanol-p-toluidine; N,N-dihydroxyethyl-p-toluidine; N,N-methylhydroxyethyl-p-toluidine; or a mixture thereof. The composition may be for anchoring structural materials in concrete, masonry or a combination thereof.

[0007f] Various embodiments of the claimed invention relate to a method for manufacturing an adhesive composition, comprising: a. presenting a first portion, the first portion comprising: 1) at least one reactive resin comprising a polymerizable monomer; 2) at least one acetoacetoxy functional monomer; 3) at least one silane monomer; and 4) at least one accelerant; b. presenting a separately arranged second portion, the second portion comprising: 5) a free radical initiator; and c. combining the first portion with the second portion; wherein the free radical initiator is dibenzoyl peroxide and the accelerant is selected from the group consisting of N,N-diisopropanol-p-toluidine, N,N-dihydroxyethyl-p-toluidine, N,N-methylhydroxyethyl-p-toluidine, and mixtures thereof. The composition may be for anchoring structural materials in concrete, masonry or a combination thereof.

[0007g] Various embodiments of the claimed invention relate to a method for anchoring an element in a structural body, comprising: a. providing a first portion, the first portion comprising: 1) an ethoxylated bisphenol A dimethacrylate; 2) acetoacetoxyethyl methacrylate; 3) methacryloxypropyl trimethoxysilane; and 4) an accelerant selected from the group consisting of N,N-diisopropanol-p-toluidine, N,N-dihydroxyethyl-p-toluidine, N,N-methylhydroxyethyl-p-toluidine, and combinations thereof; b. providing a separately arranged second portion, the second portion comprising: 5) phthalate-free dibenzoyl peroxide; c. combining the first portion with the second portion forming an adhesive composition; and d. anchoring the element in the structural body using the adhesive composition. The structural body may be concrete, masonry or a combination thereof.

[0007h] Various embodiments of the claimed invention relate to a method for anchoring an element in a structural body, comprising: a. providing a first portion, the first portion comprising: 1) an ethoxylated bisphenol A dimethacrylate; 2) acetoacetoxyethyl methacrylate; 3) methacryloxypropyl trimethoxysilane; and 4) N,N-diisopropanol-p-toluidine; and b. providing a separately arranged second portion, the second portion comprising: 5) phthalate-free dibenzoyl peroxide; c. combining the first portion with the second portion producing an adhesive composition; and d. anchoring the element in the structural body using the adhesive composition.

[0007i] Various embodiments of the claimed invention relate to a kit for an adhesive composition, comprising: a. a first portion having: 1) at least one reactive resin comprising a functional

monomer; 2) at least one acetoacetoxy functional monomer; 3) at least one silane monomer; and 4) at least one accelerant selected from the group consisting of N,N-diisopropanol-p-toluidine, N,N-dihydroxyethyl-p-toluidine, N,N-methylhydroxyethyl-p-toluidine, and combinations thereof; b. a separately-maintained second portion comprising: 5) dibenzoyl peroxide; and c. instructions for use.

- 5 The composition may be for anchoring structural materials in concrete, masonry or a combination thereof.

DETAILED DESCRIPTION OF THE INVENTION

[0008] The present disclosure provides an adhesive composition for anchoring materials in or
10 to concrete or masonry. The materials to be anchored in or to concrete or masonry include, but are not limited to: metallic objects such as steel rods and steel bolts; ceramics; other concrete or masonry members; plastics; glasses; and woods.

[0009] As indicated above, one of the motivating factors for the present disclosure was to develop an adhesive composition that cured at low temperatures without compromising strength of the
15 adhesive. In the course of developing such a composition, it was also recognized that it might also be possible to impart other desirable features to the adhesive composition. Thus, it was postulated that the inclusion of a silane group, for example, might help promote adhesion of the composition to a cementitious substrate in wet or humid conditions. In addition, it was felt that an acetoacetoxy functional group might help promote adhesion of the composition to the insert, the substrate, or both.
20 Under most conditions, these two monomers do not appear to significantly improve performance of an anchoring adhesive. Surprisingly, however, it was found that the

the first portion with the second portion forming an adhesive composition; and d. anchoring the element in the structural body using the adhesive composition.

[0007H] Various embodiments of this invention provide a method for anchoring an element in a structural body, comprising: a. providing a first portion, the first portion comprising: 1) an ethoxylated bisphenol A dimethacrylate; 2) acetoacetoxyethyl methacrylate; 3) methacryloxypropyl trimethoxysilane; and 4) phthalate-free dibenzoyl peroxide; and b. providing a separately arranged second portion, the second portion comprising: 5) N,N-diisopropanol-p-toluidine; c. combining the first portion with the second portion producing an adhesive composition; and d. anchoring the element in the structural body using the adhesive composition.

10 [0007I] Various embodiments of this invention provide a kit for an adhesive composition, comprising: a. a first portion having: 1) at least one reactive resin comprising a functional monomer; 2) at least one acetoacetoxy functional monomer; 3) at least one silane monomer; and 4) at least one accelerant selected from the group consisting of N,N-diisopropanol-p-toluidine, N,N-dihydroxyethyl-p-toluidine, N,N-methylhydroxyethyl-p-toluidine, and combinations thereof; b. a separately-maintained second portion comprising: 5) dibenzoyl peroxide; and c. instructions for use.

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presence of both an acetoacetoxy moiety and a silane moiety can provide a synergistic effect when curing takes place at low temperatures. Use of these monomers has unexpectedly resulted in demonstrably better curing at low temperatures. For instance, when acetoacetoxyethyl methacrylate and methacryloxypropyl trimethoxysilane (MPTMS) are used together in a first adhesive composition, a 20% improvement in mechanical strength has been observed when the adhesive was cured at low temperatures and then warmed to standard temperature.

[0010] Quite surprisingly, during the development of the inventive adhesive compositions described herein, it has also been discovered that the synergistic effect obtained upon the combination of silane and acetoacetoxy moieties is unexpectedly enhanced by the presence of a phthalate-free free radical initiator. Remarkably, the inventive adhesive compositions described herein have been shown to be curable at low temperatures, without any compromise as to strength, durability or structural integrity whether at low, moderate or elevated temperatures. In other words, the inventive silane-containing, and acetoacetoxy-containing compositions described herein, which can additionally be prepared phthalate-free, may be cured at low temperatures and yet retain the ability to perform at least as well as--if not better than--commercially available adhesive compositions, whether at low, moderate or elevated temperatures. The use of phthalate-free components in the inventive formulations can result in an approximately 10% increase in strength and durability characteristics following cure at low temperatures.

Reactive Resin

[0011] In discussing resins and monomers herein, it is to be understood that these terms may be used interchangeably. The molecules which are often referred to as resins are in reality high molecular weight monomers, from a chemistry standpoint. However, the terms resin and monomer are often used interchangeably in the adhesives trade and thus the terms are used without chemical distinction herein. No limitation(s) are intended or implied in the inventive adhesive compositions based on such terminology.

[0012] The inventive adhesive compositions comprise, in a first component or first composition, at least one synthetic resin or polymerizable monomer selected from among: acrylate monomers; allylic resins; bismaleimide resins; epoxy acrylate resins; epoxy methacrylate resins; methacrylate monomers; phenolic-based acrylates; phenolic-

based methacrylates; unsaturated polyester resins; urethane acrylate resins; urethane methacrylate resins; and vinyl ester resins. In one embodiment, one of the synthetic resins is preferably an alkoxyated bisphenol or a novolac compound having one or more functional acrylate or methacrylate groups. A novolac—also spelled novolak—is a phenol-aldehyde condensation prepolymer obtained by condensing phenolic monomers with a stoichiometric deficiency of aldehydes.

[0013] In one aspect, an adhesive composition of the present invention includes at least one polymerizable monomer that contains or includes at least one functional group selected from among: acrylates; methacrylates; as well as combinations thereof; in combination with a phenolic selected from among: bisphenol A; bisphenol F; bisphenol S; novolac monomers; and combinations thereof. In a preferred aspect of the invention, the reactive resin includes an alkoxy group. In a more preferred aspect of the invention, the alkoxy group(s) is positioned in the reactive resin between the phenolic and the acrylate or methacrylate group(s). Especially preferred for use with the present invention are alkoxyated methacrylates and alkoxyated dimethacrylates, with ethoxyated bisphenol A dimethacrylate being particularly preferred.

[0014] Ethoxyated bisphenol A dimethacrylate resins with no more than 4 mole ethoxylation are particularly suitable for use in the first composition of the inventive adhesive formulations of the present invention. Degrees of condensation of ethylene oxide groups from about 1.0 mole to about 4.0 mole are preferred, with an average degree of condensation of about 2.0 mole to above 4.0 mole being more preferred. This resin is difunctional and has relatively few ethoxylate groups, thus it has good crosslink density, which results in high mechanical strength. This monomer also has a high glass transition temperature, T_g , which allows for higher end use temperatures of the adhesive. It also has a very high molecular weight and subsequently exhibits very low shrinkage stress. Without being bound by theory, the ethoxylate groups are believed to help promote adhesion to cementitious substrates.

Diluent Monomer

[0015] Diluent monomers, also called reactive diluents, are often used in adhesive compositions to bring the viscosity of a reaction mixture into a desirable range. Such diluents are also used to incorporate functionality to improve the adhesion of these

compositions to the insert, the substrate, or both. Both multifunctional and monofunctional diluents may be used with the low temperature curable compositions of the present invention. Multifunctional diluents can be used to impart greater crosslink density which can improve chemical resistance, moisture tolerance and performance at higher use temperatures. Accordingly, either liquid or solid reactive organic diluents may be used with the reactive resins described herein to provide viscosity control, impart functionality, and/or increase the cross-linking density of the reaction mixture; as such, use of diluent monomers is only required for reaction mixtures in which the aforementioned properties must be altered. If a diluent monomer is used it is therefore desirable that the diluent monomer contain at least one functional group that is reactive with the polymerizable monomer described above. High molecular weight is also desirable in a diluent monomer; high molecular weight minimizes shrinkage stress and imparts low volatility. Reactive diluents are optional for the present invention; however, those reactive diluents suitable for use with the adhesive compositions of the present invention include ethylenically unsaturated monomers. Among ethylenically unsaturated monomer diluents that can be used with the present invention, it is preferred that the reactive organic diluent include at least one monofunctional monomer to lower viscosity and at least one multi-functional monomer to increase crosslink density. As with the reactive resin, polar groups such as alkoxylates; carbonyls; ether linkages; ester linkages; hydroxyls; amines; and amides are believed to improve adhesion to the substrate.

[0016] As indicated above, monofunctional monomers may also be used with the inventive adhesive formulations. Suitable monofunctional monomers for use with the present invention include, but are not limited to: methyl methacrylate, isopropyl methacrylate, isobutyl methacrylate, tert-butyl methacrylate, steryl methacrylate, 2-phenoxyethyl methacrylate, tetrahydrofurfuryl methacrylate, glycidyl methacrylate, isobornyl methacrylate, hydroxyethyl methacrylate, hydroxypropyl methacrylate, hydroxybutyl methacrylate, benzyl methacrylate, dicyclopentyl methacrylate, tert-butyl acrylate, steryl acrylate, 2-phenoxyethyl acrylate, tetrahydrofurfuryl acrylate, isobornyl acrylate, hydroxybutyl methacrylate, benzyl acrylate, dicyclopentyl acrylate, and the like, as well as combinations thereof.

[0017] Multifunctional monomers that are suitable for use with the present invention include, but are not limited to: ethylene glycol dimethacrylate, diethylene

glycol dimethacrylate, triethylene glycol dimethacrylate, dipropylene glycol dimethacrylate, 1,3-butylene glycol dimethacrylate, 1,4-butanediol dimethacrylate, 1,6-hexanediol dimethacrylate, neopentyl glycol dimethacrylate, cyclohexane dimethanol dimethacrylate, dicyclopentyl dimethacrylate, glyceryl trimethacrylate, trimethylolpropane trimethacrylate, pentaerythritol trimethacrylate, pentaerythritol tetramethacrylate, dipentaerythritol pentamethacrylate, ethylene glycol diacrylate, diethylene glycol diacrylate, triethylene glycol diacrylate, dipropylene glycol diacrylate, 1,3-butylene glycol diacrylate, 1,4-butanediol diacrylate, 1,6-hexanediol diacrylate, neopentyl glycol diacrylate, cyclohexane dimethanol diacrylate, dicyclopentyl diacrylate, glyceryl triacrylate, trimethylolpropane triacrylate, pentaerythritol triacrylate, pentaerythritol tetraacrylate, dipentaerythritol pentaacrylate, tris(2-hydroxy ethyl)isocyanurate triacrylate, alkoxylated variations of the foregoing monomers, and the like, as well as any combinations thereof. Additionally metallic acrylates and methacrylates can be used to increase crosslink density these include, but are not limited to acrylates and methacrylates of zinc, magnesium and calcium.

[0018] Other monomers, such as vinyl, allylic and acrylamide monomers may also be used. Examples of these monomers which can be used with the present invention include, but are not limited to: styrene; vinyl toluene; methyl styrene; divinyl benzene; allyl methacrylate; allyl cinnamate; allyl glycidyl ether; acrylamide; methacrylamide; N-methylol acrylamide; N-methylol methacrylamide; as well as combinations thereof. The use of vinyl, allylic, and acrylamide monomers with the inventive compositions described herein is not preferred, however, due to possible health concerns.

[0019] Preferred diluent monomers for the present invention include: hydroxypropyl methacrylate, isobornyl methacrylate, tert-butyl methacrylate, methyl methacrylate, tetrahydrofurfuryl methacrylate, benzyl methacrylate, ethylene glycol dimethacrylate, trimethylolpropane trimethacrylate, tris(2-hydroxyethyl) isocyanurate triacrylate, and trimethylolpropane triacrylate. Tetrahydrofurfuryl methacrylate and trimethylolpropane trimethacrylate are particularly preferred.

Acetoacetoxy Functional Monomer

[0020] As indicated above, the use of an acetoacetoxy functional monomer has surprisingly been found to provide an unexpected, beneficial synergistic effect with

respect to curing at low temperature when used in the presence of a monomer that contains a cross-linkable silane group. In addition to the main monomer described above, the adhesive compositions of the present invention therefore also comprise an ethylenically unsaturated monomer that contains at least one cross-linkable acetoacetoxy functional group. Acetoacetoxy functionality can be incorporated into the polymer matrix in the inventive adhesives using acetoacetoxy alkyl acrylates such as, but not limited to: acetoacetoxyethyl acrylate; acetoacetoxyethyl methacrylate; acetoacetoxy vinyl ether; as well as combinations of any of the foregoing. A preferred reactive monomer diluent is acetoacetoxyethyl methacrylate, often abbreviated AAEM.

Silane Monomer

[0021] As indicated above, the adhesive compositions of the present invention also comprise an ethylenically unsaturated monomer that contains at least one cross-linkable silane group. Cross-linkable silane groups that are preferred for use with the inventive compositions comprise hydrolyzable alkoxy groups. Examples of hydrolyzable alkoxy groups that are suitable for use with the present invention may be selected from among: hydroxy group; halogen atom; alkoxy group; and acyloxy group; as well as combinations of any of the foregoing. Silane monomers having alkoxy groups are preferred.

[0022] Examples of monomers having both a point of polymerizable unsaturation and a cross-linkable silicon group include: methacryloxypropyl polyalkoxy silanes such as methacryloxypropyl trimethoxysilane, methacryloxypropylmethyl dimethoxy silane and methacryloxypropyl triethoxy silane; acryloxypropyl polyalkoxy silanes such as acryloxypropyl trimethoxy silane, acryloxypropylmethyl dimethoxy silane, and acryloxypropyl triethoxy silane; vinylalkyl polyalkoxy silanes such as vinyl trimethoxysilane, vinylmethyl dimethoxy silane and vinyl triethoxy silane; as well as combinations of any of the foregoing.

Curing Agent

[0023] Curing agents in the present invention are free-radical initiators used with adhesive compositions in order to initiate polymerization and provide cross-linking of the adhesive. Free radical initiators that are suitable for use with the present invention may be selected from among: peroxides; peracids; peresters; and peroxy maleates; as well as

combinations of any of the foregoing. In addition, the adhesive compositions may also be cured by using physical curing techniques such as, but not limited to: radiant energy; thermal energy; as well as combinations thereof. Combinations of free radical initiators with physical techniques may also be appropriate for use with the low temperature adhesive compositions provided herein. Examples of peroxides that are suitable for use with the present invention include, but are not limited to: cumene hydroperoxide; cyclohexanone peroxide; diacyl peroxide; benzoyl peroxide; dibenzoyl peroxide; diisopropylbenzene dihydroperoxide; hydroperoxide; lauryl peroxide; methyl ethyl ketone peroxide; p-butyl hydroperoxide; and mixtures thereof. Dibenzoyl peroxides are preferred peroxides.

[0024] Non-reactive diluents are often used with dibenzoyl peroxide to add stability to the product. Examples of non-reactive diluents used to stabilize dibenzoyl peroxide include, but are not limited to: di-n-butyl phthalate; diisobutyl phthalate; dicyclohexyl phthalate; butylbenzylphthalate; trialkylphosphates; triarylphosphates; alkylarylphosphates; alkyl ethers of mono and diethylene glycols, alkyl ethers of mono and dipropylene glycols; benzoates of mono and diethylene glycols; benzoates of mono and dipropylene glycols; water; and the like. Additionally, non-reactive diluents such as ethylene glycol, propylene glycol, glycerol, urea and the like are often used to lower the freezing point of benzoyl peroxide mixtures. In one aspect of the present invention phthalate-free dibenzoyl peroxide mixtures are preferred.

Accelerants

[0025] Accelerants may be used with the adhesive compositions of the present invention. As will be understood by those skilled in the relevant art, the accelerant(s) that is appropriate for use with the low temperature adhesive compositions of the present invention will vary, depending upon selection of a free radical initiator. Accelerants that are suitable for curing via free radical mechanism include, but are not limited to organic compounds selected from among: thioamides such as thiourea, acyl thiourea, tetramethyl thiourea, diethylthiourea, dibutyl thiourea, ethylene thiourea, trimethyl thiourea, triphenyl thiourea and trioxy thiourea; mercaptobenzimidazol; tertiary amines such as N,N-dialkyl toluidines, where the alkyl group is selected from among methyl, ethyl, hydroxyethyl, hydroxyl propyl, isopropyl and mixtures thereof; trialkyl amines, where alkyl is selected from among ethyl, propyl, and ethyl diethanol; N,N-dialkylanilines such as N,N-

dimethylaniline and N,N-diethylaniline; 4,4-bis(dimethylamino) diphenylmethane; and mixtures thereof.

[0026] Inorganic materials as well as organic salts may also be used as accelerants with the present invention. Examples of inorganics and organic salts that are suitable for use with the inventive adhesives include, but are not limited to: magnesium; tin; and certain salts such as cobalt naphthenate. It is also possible to use more than one accelerant with the inventive adhesives. Accordingly, in one aspect, the inventive adhesive compositions may include an organic compound, an inorganic, an organic salt as well as combinations of any of the foregoing.

[0027] In the course of the inventive work described herein, it has also been found that formulations including dibenzoyl peroxide also preferably contain an accelerating agent in the first component with the resin and monomers. Accelerators suitable for use herein may be selected from among: N,N-diisopropanol-p-toluidine, N,N-dihydroxyethyl-p-toluidine; N,N-methylhydroxyethyl-p-toluidine; and mixtures of the foregoing.

Fillers

[0028] Adhesive compositions that are used for anchoring members often contain fillers to both impart strength and reduce cost. As will be appreciated by those knowledgeable in the relevant art, fillers can also be used to control viscosity. Fillers that are appropriate for use with the present invention include, but are not limited to: silica fume; quartz sand; finely ground quartz; a metal oxide such as magnesium oxide, iron oxide, aluminum oxide, and calcium oxide; clinker; calcium carbonate; metal shavings or particles; barium sulfate; aluminum trihydrate; wollastonite; kaolin clay; mica; feldspar; nepheline syenite; glass beads; corundum; talc; chalk; ceramic microspheres; and cement; in addition to combinations of any of the foregoing. In one aspect, either the first composition or the second composition comprising the inventive adhesives contains at least one filler, which may comprise the same or different fillers. In another aspect, both the first composition and the second composition contain fillers. In yet another aspect of the invention, the first component preferably contains at least one filler that is reactive with water, examples of which include cement and metal oxides. Cement is often a preferred filler, as it ties up water in the adhesive system and allows for better performance when an anchor is exposed to elevated temperatures after cure. As will be

understood by those skilled in the relevant art, fillers may be mixed into the first, monomer component and/or the second, curing agent component of the inventive adhesives.

Inhibitors

5 [0029] Inhibitors are required to prevent polymerization of the monomers and resins of the first component during storage. Inhibitors are present in reactive resins and monomers as they are received from manufacturers; however, additional inhibitor is often required to improve shelf life of the final product or to counteract the presence of the accelerator. Polymerization inhibitors appropriate for the present invention include, but
10 are not limited to: methyl hydroquinone, hydroquinone, catechol, hydroquinone monomethyl ether, mono-tert-butyl hydroquinone, di-tert-butyl hydroquinone, p-benzoquinone, 2,5-diphenyl-p-benzoquinone, p-benzoquinone, trimethyl hydroquinone, naphthaquinone, di-tert-butyl methylphenol, and combinations of any of the foregoing.

Thixotropic Agents

15 [0030] Thixotropic agents are often used in adhesive compositions to reduce the tendency of the liquid resin to flow or drain from vertical surfaces. Thixotropic agents that are suitable for use with adhesive compositions of the present invention include, but are not limited to: fumed silica, organosilicas, clays and silicic acid. Commercially available fumed silicas that are particularly suitable for use with the present invention are
20 sold under such trademarks as Aerosil® available from Evonik Industries, and Cab-o-Sil® available from Cabot Corp.

Adjuncts

[0031] It is recognized that other components or adjuvants known to those skilled in the art may also optionally be included in the inventive adhesive compositions. Such
25 components may include, but are not limited to: antifoaming agents; catalysts; coupling agents; non-reactive diluents; dyes; fillers; fungicides; impact modifiers; odor maskants; pigments; solvents; stabilizers; surfactants; wetting agents; as well as combinations of any of the foregoing.

Formulations

[0032] A number of different formulations that included varying amounts of the above active and optional ingredients were prepared and evaluated for curing at low and medium temperatures, and testing at low, medium and high temperatures. The term “low temperature” as used herein is understood to indicate temperatures on the order of approximately $-10^{\circ}\text{C} \pm 3^{\circ}\text{C}$ ($14^{\circ}\text{F} \pm 4^{\circ}\text{F}$). The term “medium temperature,” “ambient temperature,” “standard temperature” or “average temperature” as used herein is understood to refer to room temperature or temperatures of approximately $23^{\circ}\text{C} \pm 3^{\circ}\text{C}$ ($72^{\circ}\text{F} \pm 4^{\circ}\text{F}$). The term “high” or “elevated temperatures” as used herein is understood to indicate temperatures on the order of approximately $82^{\circ}\text{C} \pm 3^{\circ}\text{C}$ ($180^{\circ}\text{F} \pm 4^{\circ}\text{F}$). Thus, a variety of different reactive main monomers were used in combinations with acetoacetoxy-containing monomers, both with and without monomers that contained silane groups.

Phthalate-Free Compositions

[0033] As indicated above, formulations that comprised a reactive resin to which an acetoacetoxy-silane monomer combination was added were found to exhibit remarkably good strength and durability characteristics at room medium temperatures following curing at low temperatures. In many instances, the performance of these inventive adhesive compositions showed nearly a two-fold improvement over other formulations that did not include the acetoacetoxy-silane monomer combination. Even more unexpectedly, however, a further improvement in performance characteristics was observed when adhesive compositions were formulated without the presence of any phthalate moieties. Phthalate-free adhesive compositions of the present invention have surprisingly been found to be especially well-suited for curing at low temperatures. On average, the removal of phthalates from the inventive reactive resin/acetoacetoxy/silane monomer combination resulted in a 10% improvement in performance over adhesive compositions in which phthalates were included.

[0034] Phthalates are typically introduced into adhesive compositions with the free radical initiators that are used. According to one aspect of the present invention, therefore, noticeable improvements in adhesive performance can be observed in formulations at standard temperatures following cure at low temperatures when free

radical initiators are used in the inventive adhesives that are phthalate-free. Examples of phthalate-free free-radical initiators that are suitable for use with the present inventive include dibenzoyl peroxides. Phthalate-free dibenzoyl peroxides are commercially available under a variety of brand names such as, but not limited to, the Perkadox® series of free radical initiators available from Akzo Nobel and Luperox® series of free radical initiators from Elf Atochem.

EXAMPLES

[0035] A number of adhesive compositions were prepared in accordance with the teaching of the present invention for use in comparison to commercially available adhesive compositions. Performance characteristics were evaluated after cure at standard room temperature of 23 ± 4 °C (73 ± 8 °F) and at lower temperatures of -10 °C (14 °F) to mimic curing in cold conditions. Test members were prepared as follows. A channel or bore hole was created in a formed or smooth steel-troweled face of a Portland cement-based concrete test member of compressive strength in the range of 25.3 to 28.0 MPa (3,666 to 4,059 psi). The bore hole was made using a rotary-hammer drill with a 17.5 mm (11/16 inch) diameter carbide bit meeting the requirements of American National Standards Institute Bulletin 212.15 (ANSI B212.15, available in the United States from the Cemented Carbide Producers' Association). The bore hole was drilled to a depth of 79.4 mm (3.125 inch) embedment, perpendicular to the test surface. The channel chamber was then cleaned by blowing compressed air at 0.59 MPa (85 psi) into the hole for four seconds, followed by brushing the bore hole for four complete strokes using a nylon brush of greater diameter than the bore hole, followed by blowing compressed air at 0.59 MPa (85 psi) into the hole a second time, also for four seconds. The anchoring adhesive to be tested was then injected into the bore hole in such a manner as to ensure that the bore hole was evenly filled from the bottom of the chamber to a point approximately two-thirds full. A 15.9 mm (5/8 inch) diameter threaded metal rod was then inserted into the adhesive with a slight twisting motion and the adhesive and insert were allowed to cure undisturbed for one hour. After one hour, a load was placed on the metal rod anchors in tension until the point of failure in accordance with test methods in ASTM E488 as modified by ICC-ES Acceptance Criteria AC308. Tensile testing was performed using an in-house confined or restrained tension testing rig using a 13.6 kg (30 ton) hydraulic ram and a 22.7 kg (50 ton) load cell, in compliance with ASTM E488 as

modified by ICC-ES Acceptance Criteria AC308. The confined test setup was used to maximize strain on the adhesive while minimizing the risk of concrete failure.

[0036] For the evaluation of inventive formulations after cure at lower temperature, another series of smooth-faced, steel-troweled Portland cement-based concrete test members were prepared in a manner identical to the procedure outlined immediately above. The prepared test members were then placed into a controlled temperature chamber maintained at -10 °C (14 °F) and allowed to come to temperature equilibrium over the course of several days. The anchoring adhesive was then injected into the bore hole in the temperature controlled chamber, filling the drilled cavity from the bottom of the bore hole to a point approximately two-thirds full. A 15.9 mm (0.625 inch) diameter threaded metal rod was then inserted into the adhesive with a slight twisting motion and the adhesive and insert were left undisturbed and permitted to cure at - 10 °C (14°F) for twenty-four hours. At the end of that period, the test member was removed from the controlled temperature chamber and allowed to come to room temperature of approximately 23 ± 4 °C (73 ± 8 °F). The anchors were again loaded in tension until the point of failure in accordance with test methods in ASTM E488 as modified by ICC-ES Acceptance Criteria AC308, as indicated above. Tensile testing was performed using a confined or restrained tension test. The confined test setup was used to maximize strain on the adhesive while minimizing the risk of concrete failure.

[0037] Tables 1, 2 and 3 below contain the results of tensile tests performed on a variety of adhesive compositions that were cured at different temperatures in the manner described above. The compositions that were evaluated include commercially-available adhesive products as indicated in Table 1. Tables 2 and 3 contain a summary of a number of different formulations that were evaluated during the development of the inventive low-temperature cure compositions described herein.

[0038] Specifically and with reference to Table 1, the commercially available adhesives that were evaluated include: 1) HY 150 Max, manufactured by Hilti Aktiengesellschaft of Schaan, Liechtenstein, available in the United States online and through various distributors; 2) AC100+ Gold™, available from Powers Fasteners, Inc., of Brewster, NY; 3) FIS VW from Fischerwerke GmbH and Co. KG of Waldachtal, Deutschland, not available in the United States; and 4) Sikadur® AnchorFix-1, from Sika AG of Baar, Switzerland, and available through various distributors in the United States.

Both HY 150 Max and AC100+ Gold™ have approvals in the United States for installations under low temperature cure conditions. HY 150 Max, FIS VW and AnchorFix-1 have approvals in Europe for installations under low temperature cure conditions.

Table 1 Test Results for Competitive Products

Bond Strength After Cure (MPa)				
Company	Hilti	Powers	Fischer	Sika
Product	HY150 Max	AC100+ Gold	FIS VW	Anchorfix-1
Cure at 23°C, Test at 82°C	16.69	9.09	14.77	12.12
Cure at 23°C, Test at 23°C	21.95	16.32	18.62	15.44
Cure at -10°C, Test at 23°C	14.52	9.40	10.69	9.58
Cure at -10°C, Test at -10°C	19.71	NE ^a	NE ^a	12.17
Low Temperature vs. Standard Temperature Degree of Cure ^b				
	66.2%	57.6%	57.4%	60.3%
Phthalates present?	Yes	Yes	Yes	Yes

Notes to Table 1

^aNE – Not Evaluated

^bThis calculated value is the ratio of the strength at 23 °C after cure at -10 °C compared to the strength at 23 °C after cure at 23 °C, expressed in percent.

[0039] Table 2 contains a summary of representative formulations that were tested over a range of different concentrations combinations. The Examples in Table 2 are comparable in strength to the competitive products shown in Table 1.

Table 2 Formulations and Test Results of Example Compositions

Example	1	2	3	4	5	6
First Component						
Reactive Resin	22.4%	17.5%	22.3%	17.1%	17.1%	17.0%
Diluent monomer	15.2%	25.0%	15.1%	20.8%	20.8%	20.2%
Filler	60.2%	54.3%	59.8%	59.3%	59.2%	59.7%
Inhibitor	<0.1%	<0.1%	<0.1%	<0.1%	<0.1%	<0.1%
Accelerator	0.2%	0.3%	0.8%	0.3%	0.4%	0.6%
Miscellaneous ^a	2.0%	2.9%	2.0%	2.5%	2.5%	2.5%
Second Component						
Free radical initiator	11.9%	13.0%	14.8%	14.6%	21.3%	14.5%
Nonreactive diluent	36.9%	40.2%	33.0%	35.6%	35.7%	35.6%
Filler	48.0%	43.5%	48.9%	45.6%	45.9%	45.3%
Miscellaneous ^a	3.2%	3.3%	3.3%	4.2%	5.1%	4.6%
Bond Strength After Cure (MPa)						
Cure at 23°C, Test at 82°C	13.04	10.31	10.99	11.05	9.57	12.88
Cure at 23°C, Test at 23°C	15.78	10.46	16.31	15.03	15.32	21.83
Cure at -10°C, Test at 23°C	7.99	4.96	11.52	10.26	9.21	13.50
Low Temperature vs. Standard Temperature Degree of Cure ^b						
	50.6%	47.4%	70.7%	68.3%	60.1%	61.9%
Phthalates present?	Yes	Yes	Yes	Yes	Yes	Yes

Notes to Table 2

^aSelected from among: pigments; thixotropes; dyes and colorants; etc.

^bThis value, calculated for the entries in the table from their bond strengths, is the ratio of the strength at 23 °C after cure at -10 °C compared to the strength at 23 °C after cure at 23 °C, expressed in percent.

[0040] Following the initial discovery that acetoacetoxy-silane monomers imparted discernable low-temperature cure improvements to the main reactive resins, a series of experiments were conducted using phthalate-free initiators. As these latter adhesive formulations exhibited even more remarkable strength characteristics at medium temperatures following low temperature cure, a number of experiments were conducted in order to evaluate alternate adhesive compositions. The results of these studies are summarized in Table 3 below. Examples A through C of Table 3 represent a preferred aspect of the present invention, in that they provide phthalate-free compositions well-

suitied for low temperature cure. In examples A and B the phthalate-free radical initiator used was Perkadox® L-40 RPS; and in example C the free radical initiator used was Perkadox® BTW50. Examples D through G represent an alternate aspect of the present invention in which the adhesive composition is not phthalate-free. Perkadox® 40e was used as the free radical initiator in examples D through G.

Table 3 Formulations and Test Results for Sample Compositions

Example	A	B	C	D	E	F	G
First Component							
Reactive Resin	18.0%	18.0%	18.0%	18.0%	16.8%	16.8%	13.6%
Acetoacetoxy monomer	1.7%	1.7%	1.7%	1.7%	3.2%	0%	0%
Silane monomer	0.5%	0.5%	0.5%	0.5%	0.9%	0.9%	0.0%
Diluent monomer	19.4%	19.4%	19.4%	19.4%	16.8%	20.0%	23.3%
Filler	57.3%	57.3%	57.3%	57.3%	59.2%	59.2%	59.3%
Inhibitor	<0.1%	<0.1%	<0.1%	<0.1%	<0.1%	<0.1%	<0.1%
Accelerator	0.9%	0.9%	0.9%	0.9%	0.6%	0.6%	0.5%
Miscellaneous ^a	2.4%	2.4%	2.4%	2.4%	2.5%	2.5%	2.3%
Second Component							
Free radical initiator	14.5%	13.3%	14.6%	14.5%	14.5%	14.5%	14.6%
Nonreactive diluent	38.5%	39.0%	36.9%	35.6%	35.6%	35.6%	35.9%
Filler	41.9%	42.9%	43.7%	45.3%	45.3%	45.3%	45.5%
Miscellaneous ^a	5.1%	4.8%	4.8%	4.6%	4.6%	4.6%	4.0%
Bond Strength After Cure (MPa)							
Cure at 23°C, Test at 82°C	15.36	15.14	13.45	14.56	12.84	12.38	10.65
Cure at 23°C, Test at 23°C	22.28	20.77	18.98	21.49	21.55	21.07	20.35
Cure at -10°C, Test at 23°C	21.28	20.42	18.97	19.80	19.49	18.30	16.32
Cure at -10°C, Test at -10°C	22.10	21.73	NE ^b	21.65	NE ^b	NE ^b	NE ^b
Low Temperature vs. Standard Temperature Degree of Cure ^c							
	95.5%	98.3%	99.9%	92.1%	90.5%	86.9%	80.2%
Phthalates present?	No	No	No	Yes	Yes	Yes	Yes

Notes to Table 3

^aSelected from among: pigments; thixotropes; dyes and colorants; etc.

^bNE – Not Evaluated

^cThis value, calculated for the entries in the table from their bond strengths, is the ratio of the strength at 23 °C after cure at -10 °C compared to the strength at 23 °C after cure at 23 °C, expressed in percent.

[0041] A number of different formulations were tried and evaluated for strength and performance characteristics after curing at different temperatures. In one series of experiments, adhesive formulations with different ratios/levels of AAEM and silane were prepared and evaluated. The different combinations that were tested include (expressed in terms of weight % composition): a) 1.67% AAEM with 0.5% silane; b) 1.67% AAEM with 1.5% silane; c) 5% AAEM with 1.67% silane and d) 5 % AEM with 1.5% silane). All of the foregoing formulations gave equivalent bond strengths when cured at -10°C and tested at 23°C.

[0042] As a result of the foregoing work and in accordance with one aspect of the present invention, a first component of the low-temperature curable reaction mixtures comprises 30-70% of a mixture comprising at least one reactive resin, at least one acetoacetoxy monomer, and at least one silane monomer, with the balance selected from at least one of: accelerators, diluent monomers, inhibitors, dyes, fillers, pigments, and thixotropic agents; as well as combinations of the foregoing. A second component of the low-temperature curable reaction mixtures comprises 10-25% of a free radical initiator with the balance selected from at least one of: non-reactive diluents, dyes, fillers, pigments, and thixotropic agents, as well as combinations of the foregoing.

[0043] Additionally, according to another aspect of the present invention and as a result of the foregoing work, a first component of the low-temperature curable reaction mixtures comprises 30-70% of a phthalate-free mixture comprising at least one reactive resin, at least one acetoacetoxy monomer, and at least one silane monomer, with the balance selected from at least one of: accelerators, diluent monomers, inhibitors, dyes, fillers, pigments, and thixotropic agents; as well as combinations of the foregoing. A second component of the low-temperature curable reaction mixtures comprises 10-25% of a phthalate-free mixture comprising of at least one free radical initiator with the balance selected from at least one of: non-reactive diluents, dyes, fillers, pigments, and thixotropic agents, as well as combinations of the foregoing.

[0044] In a preferred aspect of the invention, the first component of the inventive adhesive composition comprises 4 mole ethoxylated bisphenol A dimethacrylate, 2-(acetoacetoxy)ethyl methacrylate, methacryloxypropyl trimethoxysilane; and at least one diluent monomer, and the second component comprises dibenzoyl peroxide. According

to another aspect, a first component of the inventive adhesive compositions additionally comprises the reactive diluent monomers tetrahydrofurfuryl methacrylate and trimethylolpropane trimethacrylate. According to yet another aspect of the invention, the second component comprises a phthalate-free dibenzoyl peroxide composition.

Delivery Method

[0045] Many methods of delivery for adhesive compositions may be contemplated. For instance, adhesive components may be stored in relatively small amounts in multi-chambered cartridges from which components are dispensed simultaneously. Mixing may take place manually or through a static mixing nozzle. Alternately, the components may be stored separately in large containers and mixed with mechanical dispensers just prior to use. Often, the selection of reactive resin and any diluent monomers may need to reflect the delivery method or tool that will be used to introduce the adhesive into a substrate. Dispensing with manual tools presents challenges, especially for low temperature cure adhesives. It is therefore desirable that the viscosities of such adhesive formulations can be adjusted in order to enable the end user to easily install the adhesive under low temperature conditions. In general, low viscosity reactive resins are preferred for such applications. However, low viscosity can also be achieved through a combination of choice of reactive resin, choice and amount of diluent monomer, and amount of filler. Accordingly, and as will be understood by those skilled in the relevant art, the ingredients of the present invention may be formulated over a wide range in order to meet a variety of viscosity criteria from water-thin to thick paste.

[0046] Without limiting the scope of the present invention, in one aspect a delivery method for the inventive adhesive compositions comprises using a dual chamber cartridge to dispense the composition through a static mixing nozzle using a dispensing tool. The dispensing tool can be of any power configuration including, but not limited to manual, electric, battery operated or pneumatic. In one aspect of the present invention, the first and second components are each prepared separately and then combined by mixing their ingredients in a large mechanical mixer. In one embodiment, the components are placed in separated multi-component, side-by-side or coaxial adhesive cartridges for use in the field where they are dispensed through a static mixing nozzle using a dispensing tool.

[0047] An alternate delivery method for an adhesive composition prepared according to the present invention may involve delivering the two separate components in the field using dual tank bulk dispensing equipment. Yet another delivery method for an adhesive composition according to the present invention would involve the use of frangible capsules. Thus a first, sealed capsule containing a first component of the inventive formulations may be situated inside a second, larger capsule. The second capsule also contains the second component of the formulation and is also sealed. In the field, such a dual capsule would be placed into a bore hole and broken by either driving an anchor element through the dual capsule or spinning the anchor element into the dual capsule. In such a frangible capsule delivery system, the dual capsules become part of the adhesive and serve as a filler. Regardless of the delivery technique employed, according to one aspect of the present invention, the first and second components are mixed in amounts such that the weight ratio of the first component to the second component is approximately ten to one. In another aspect of the present invention, the first component makes up approximately 91% of the total composition and the second component makes up approximately 9% of the total composition.

[0048] In one aspect, the formulations of the present invention improve upon adhesives of the prior art by providing an adhesive formulation that has high internal mechanical strength, high bond strength with the base and the anchor, absorbs little water, has low toxicity, a viscosity appropriate for filling bore holes, and at the same is suitable for curing at low temperatures. In another aspect, the formulations of the present invention, when applied and cured at low temperature, exhibit strength and durability characteristics at both room temperatures and elevated temperatures that are at least equivalent to adhesives that are currently commercially available. That is, equivalent strength and durability characteristics of the instant formulations can be realized both at room temperatures and elevated temperatures as compared to commercially available adhesives, without the need for formulating compositions differently for use at different temperatures. Moreover, the inventive adhesive compositions provide the added advantage that they are phthalate free.

[0049] The present invention has been described above in detail with reference to specific embodiments, Tables and Examples. These specific embodiments should not be construed as narrowing the scope of the invention, but rather as illustrative examples.

Although preferred embodiments of the invention are specifically disclosed and described above, it is to be understood that various modifications and substitutions are anticipated and may be made to the described compositions, as well as to materials, methods of manufacture and use, without departing from the scope of the invention contemplated herein.

WHAT IS CLAIMED:

1. A curable adhesive composition for anchoring elements in a structural body, comprising:
 - a. at least one reactive resin comprising a polymerizable monomer;
 - b. at least one acetoacetoxy functional monomer; and
 - c. at least one silane monomer.
2. The composition of claim 1, wherein the strength of the composition at 23 °C after cure at -10 °C compared to the strength of the composition at 23 °C after cure at 23 °C is greater than 50%.
3. A curable adhesive composition for anchoring structural materials in concrete or masonry comprising:
 - a. from 10-25 wt % of at least one reactive resin comprising a polymerizable monomer;
 - b. from 1-5 wt % of at least one acetoacetoxy functional monomer; and
 - c. from 0.1-5 wt % of at least one silane monomer;wherein the strength of the composition at 23 °C after cure at -10 °C compared to the strength of the composition at 23 °C after cure at 23 °C is greater than 50%.
4. A curable adhesive composition for anchoring structural materials in concrete or masonry comprising:
 - a. from 10-25 wt % of at least one reactive resin comprising a polymerizable monomer;
 - b. from 1-5 wt % of at least one acetoacetoxy functional monomer; and
 - c. from 0.1-5 wt % of at least one silane monomer;wherein the strength of the composition at 23 °C after cure at -10 °C compared to the strength of the composition at 23 °C after cure at 23 °C is greater than 50%, and wherein the composition contains no phthalates.

5. The composition of any one of claims 1 to 4, wherein the strength of the composition at 23 °C after cure at -10 °C compared to the strength of the composition at 23 °C after cure at 23 °C is greater than 60%.
6. The composition of any one of claims 1 to 4, wherein the strength of the composition at 23 °C after cure at -10 °C compared to the strength of the composition at 23 °C after cure at 23 °C is greater than 70%.
7. The composition of any one of claims 1 to 4, wherein the strength of the composition at 23 °C after cure at -10 °C compared to the strength of the composition at 23 °C after cure at 23 °C is greater than 80%.
8. The composition of any one of claims 1 to 7, wherein after curing at -10 °C, the composition exhibits a bond strength at 23 °C that is greater than 10 MPa.
9. The composition of any one of claims 1 to 7, wherein after curing at -10 °C, the composition exhibits a bond strength at 23 °C that is greater than 12 MPa.
10. The composition of any one of claims 1 to 7, wherein after curing at -10 °C, the composition exhibits a bond strength at 23 °C that is greater than 14 MPa.
11. The composition of any one of claims 1 to 7, wherein after curing at -10 °C, the composition exhibits a bond strength at 23 °C that is greater than 16 MPa.
12. The composition of any one of claims 1 to 11, wherein:
 - a. the reactive resin is selected from: acrylate monomers; allylic resins; bismaleimide resins; epoxy acrylate resins; epoxy methacrylate resins; methacrylate monomers; phenolic-based acrylates; phenolic-based methacrylates; unsaturated polyester resins; urethane acrylate resins; urethane methacrylate resins; vinyl ester resins; and any combination of the foregoing;

b. the acetoacetoxy functional monomer is selected from: acetoacetoxyethyl acrylate; acetoacetoxyethyl methacrylate; acetoacetoxy vinyl ether; and any combination of the foregoing; and

c. the silane monomer is selected from: methacryloxypropyl trimethoxysilane; methacryloxypropylmethyl dimethoxy silane; methacryloxypropyl triethoxy silane; acryloxypropyl trimethoxy silane; acryloxypropylmethyl dimethoxy silane; acryloxypropyl triethoxy silane; vinyl trimethoxysilane; vinylmethyl dimethoxy silane; vinyl triethoxy silane; and any combination of the foregoing.

13. The composition of any one of claims 1 to 12, further comprising:

d. at least one reactive diluent monomer, wherein the diluent monomer is selected from: monofunctional monomers, multifunctional monomers, and any combination of the foregoing;

wherein:

i. the monofunctional monomer is selected from: methyl methacrylate; isopropyl methacrylate; isobutyl methacrylate; tert-butyl methacrylate; steryl methacrylate; 2-phenoxyethyl methacrylate; tetrahydrofurfuryl methacrylate; glycidyl methacrylate; isobornyl methacrylate; hydroxyethyl methacrylate; hydroxypropyl methacrylate; hydroxybutyl methacrylate; benzyl methacrylate; dicyclopentyl methacrylate; tert-butyl acrylate; steryl acrylate; 2-phenoxyethyl acrylate; tetrahydrofurfuryl acrylate; isobornyl acrylate; hydroxybutyl methacrylate; benzyl acrylate; dicyclopentyl acrylate; styrene; vinyl toluene; methyl styrene; allyl glycidyl ether; acrylamide; methacrylamide; N-methylol acrylamide; N-methylol methacrylamide; and any combination of the foregoing; and

ii. the multifunctional monomer is selected from: divinyl benzene; allyl methacrylate; allyl cinnamate; ethylene glycol dimethacrylate; diethylene glycol dimethacrylate; triethylene glycol dimethacrylate; dipropylene glycol dimethacrylate; 1,3-butylene glycol dimethacrylate; 1,4-butanediol dimethacrylate; 1,6-hexanediol dimethacrylate; neopentyl glycol dimethacrylate; cyclohexane dimethanol dimethacrylate; dicyclopentyl dimethacrylate; glyceryl trimethacrylate; trimethylolpropane trimethacrylate; pentaerythritol trimethacrylate; pentaerythritol

tetramethacrylate; dipentaerythritol pentamethacrylate; ethylene glycol diacrylate; diethylene glycol diacrylate; triethylene glycol diacrylate; dipropylene glycol diacrylate; 1,3-butylene glycol diacrylate; 1,4-butanediol diacrylate; 1,6-hexanediol diacrylate; neopentyl glycol diacrylate; cyclohexane dimethanol diacrylate; dicyclopentyl diacrylate; glyceryl triacrylate; trimethylolpropane triacrylate; pentaerythritol triacrylate; pentaerythritol tetraacrylate; dipentaerythritol pentaacrylate; tris(2-hydroxyethyl)isocyanurate triacrylate; alkoxylated versions of any of the foregoing; metallic acrylates and methacrylates of zinc, magnesium or calcium; and any combination of the foregoing.

14. A curable adhesive composition, comprising:

- a. at least one reactive resin comprising a polymerizable monomer;
- b. at least one acetoacetoxy functional monomer;
- c. at least one silane monomer;
- d. a free radical initiator; and
- e. an accelerant;

in which the free radical initiator is dibenzoyl peroxide, and the accelerant is selected from the group consisting: of N,N-diisopropanol-p-toluidine; N,N-dihydroxyethyl-p-toluidine; N,N-methylhydroxyethyl-p-toluidine; and mixtures thereof.

15. The composition of claim 14, wherein the strength of the composition at 23 °C after cure at -10 °C compared to the strength of the composition at 23 °C after cure at 23 °C is greater than 50%.

16. The composition of claim 14, wherein the strength of the composition at 23 °C after cure at -10 °C compared to the strength of the composition at 23 °C after cure at 23 °C is greater than 60%.

17. The composition of claim 14, wherein the strength of the composition at 23 °C after cure at -10 °C compared to the strength of the composition at 23 °C after cure at 23 °C is greater than 70%.

18. The composition of claim 14, wherein the strength of the composition at 23 °C after cure at -10 °C compared to the strength of the composition at 23 °C after cure at 23 °C is greater than 80%.
19. The composition of any one of claims 14 to 18, wherein after curing at -10 °C, the composition exhibits a bond strength at 23 °C that is greater than 10 MPa.
20. The composition of any one of claims 14 to 18, wherein after curing at -10 °C, the composition exhibits a bond strength at 23 °C that is greater than 12 MPa.
21. The composition of any one of claims 14 to 18, wherein after curing at -10 °C, the composition exhibits a bond strength at 23 °C that is greater than 14 MPa.
22. The composition of any one of claims 14 to 18, wherein after curing at -10 °C, the composition exhibits a bond strength at 23 °C that is greater than 16 MPa.
23. The composition of any one of claims 14 to 22, wherein:
- a. the reactive resin is selected from: acrylate monomers; allylic resins; bismaleimide resins; epoxy acrylate resins; epoxy methacrylate resins; methacrylate monomers; phenolic-based acrylates; phenolic-based methacrylates; unsaturated polyester resins; urethane acrylate resins; urethane methacrylate resins; vinyl ester resins; and any combination of the foregoing;
 - b. the acetoacetoxy functional monomer is selected from: acetoacetoxyethyl acrylate; acetoacetoxyethyl methacrylate, acetoacetoxy vinyl ether; and any combination of the foregoing; and
 - c. the silane monomer is selected from: methacryloxypropyl trimethoxysilane; methacryloxypropylmethyl dimethoxy silane; methacryloxypropyl triethoxy silane; acryloxypropyl trimethoxy silane; acryloxypropylmethyl dimethoxy silane; acryloxypropyl triethoxy silane; vinyl trimethoxysilane; vinylmethyl dimethoxy silane; vinyl triethoxy silane; and any combination of any of the foregoing.

24. The composition of any one of claims 14 to 23, wherein the polymerizable monomer is an ethoxylated bisphenol A dimethacrylate.
25. The composition of any one of claims 14 to 24, wherein the acetoacetoxy functional monomer is acetoacetoxyethyl methacrylate.
26. The composition of any one of claims 14 to 25, wherein the silane monomer is methacryloxypropyl trimethoxysilane.
27. The composition of any one of claims 14 to 26, wherein the dibenzoyl peroxide is phthalate free.
28. The composition of any one of claims 14 to 22, wherein the polymerizable monomer is an ethoxylated bisphenol A dimethacrylate; the acetoacetoxy functional monomer is acetoacetoxyethyl methacrylate; the silane monomer is methacryloxypropyl trimethoxysilane; and, the dibenzoyl peroxide is phthalate free.
29. The composition of any one of claims 14 to 28, further comprising:
- f. at least one reactive diluent monomer, where the diluent monomer is selected from: monofunctional monomers, multifunctional monomers, and any combination of the foregoing; wherein:
 - 1) the monofunctional monomer is selected from: methyl methacrylate; isopropyl methacrylate; isobutyl methacrylate; tert-butyl methacrylate; steryl methacrylate; 2-phenoxyethyl methacrylate; tetrahydrofurfuryl methacrylate; glycidyl methacrylate; isobornyl methacrylate; hydroxyethyl methacrylate; hydroxypropyl methacrylate; hydroxybutyl methacrylate; benzyl methacrylate; dicyclopentyl methacrylate; tert-butyl acrylate; steryl acrylate; 2-phenoxyethyl acrylate; tetrahydrofurfuryl acrylate; isobornyl acrylate; hydroxybutyl methacrylate; benzyl acrylate; dicyclopentyl acrylate; styrene; vinyl toluene; methyl styrene; allyl glycidyl

ether; acrylamide; methacrylamide; N-methylol acrylamide; N-methylol methacrylamide; and any combination of the foregoing; and

2) the multifunctional monomer is selected from: divinyl benzene; allyl methacrylate; allyl cinnamate; ethylene glycol dimethacrylate; diethylene glycol dimethacrylate; triethylene glycol dimethacrylate; dipropylene glycol dimethacrylate; 1,3-butylene glycol dimethacrylate; 1,4-butanediol dimethacrylate; 1,6-hexanediol dimethacrylate; neopentyl glycol dimethacrylate; cyclohexane dimethanol dimethacrylate; dicyclopentyl dimethacrylate; glyceryl trimethacrylate; trimethylolpropane trimethacrylate; pentaerythritol trimethacrylate; pentaerythritol tetramethacrylate; dipentaerythritol pentamethacrylate; ethylene glycol diacrylate; diethylene glycol diacrylate; triethylene glycol diacrylate; dipropylene glycol diacrylate; 1,3-butylene glycol diacrylate; 1,4-butanediol diacrylate; 1,6-hexanediol diacrylate; neopentyl glycol diacrylate; cyclohexane dimethanol diacrylate; dicyclopentyl diacrylate; glyceryl triacrylate; trimethylolpropane triacrylate; pentaerythritol triacrylate; pentaerythritol tetraacrylate; dipentaerythritol pentaacrylate; tris(2-hydroxy ethyl)isocyanurate triacrylate; alkoxylated versions of any of the foregoing; and metallic acrylates and methacrylates of zinc, magnesium or calcium; and any combination of the foregoing.

30. A curable adhesive composition consisting essentially of:

- a. an ethoxylated bisphenol A dimethacrylate;
- b. acetoacetoxyethyl methacrylate;
- c. methacryloxypropyl trimethoxysilane;
- d. phthalate-free dibenzoyl peroxide; and
- e. an accelerant that is: N,N-diisopropanol-p-toluidine; N,N-dihydroxyethyl-p-toluidine; N,N-methylhydroxyethyl-p-toluidine; or, a mixture thereof.

31. The curable adhesive composition of any one of claims 14 to 30, wherein the accelerant is N,N-diisopropanol-p-toluidine.

32. A method for manufacturing an adhesive composition, comprising:
- a. presenting a first portion, the first portion comprising:
 - 1) at least one reactive resin comprising a polymerizable monomer;
 - 2) at least one acetoacetoxy functional monomer;
 - 3) at least one silane monomer; and
 - 4) at least one accelerant;
 - b. presenting a separately arranged second portion, the second portion comprising:
 - 5) a free radical initiator; and
 - c. combining the first portion with the second portion;
- wherein the free radical initiator is dibenzoyl peroxide and the accelerant is selected from the group consisting of N,N-diisopropanol-p-toluidine, N,N-dihydroxyethyl-p-toluidine, N,N-methylhydroxyethyl-p-toluidine, and mixtures thereof.
33. The method of claim 32, wherein the reactive resin is selected from the group consisting of: an acrylate monomer, an allylic resin, a bismaleimide resin, an epoxy acrylate resin, an epoxy methacrylate resin, a methacrylate monomer, a phenolic-based acrylate, a phenolic-based methacrylate, an unsaturated polyester resin, a urethane acrylate resin, a urethane methacrylate resin, a vinyl ester resin, and any combination of the foregoing.
34. The method of claim 32 or 33, wherein the acetoacetoxy functional monomer is selected from the group consisting: of an acetoacetoxyethyl acrylate, an acetoacetoxyethyl methacrylate, an acetoacetoxy vinyl ether, and any combination of the foregoing.
35. The method of claim 32, 33 or 34, wherein the silane monomer is selected from the group consisting of: a methacryloxypropyl trimethoxysilane, a methacryloxypropylmethyl dimethoxy silane, a methacryloxypropyl triethoxy silane, an acryloxypropyl trimethoxy silane, an acryloxypropylmethyl dimethoxy silane, an acryloxypropyl triethoxy silane, a vinyl trimethoxysilane, a vinylmethyl dimethoxy silane, a vinyl triethoxy silane, and any combination of the foregoing.

36. The method of any one of claims 32 to 35, wherein the polymerizable monomer is an ethoxylated bisphenol A dimethacrylate.

37. The method of any one of claims 32 to 36, wherein the acetoacetoxy functional monomer is acetoacetoxyethyl methacrylate.

38. The method of any one of claims 32 to 37, wherein the silane monomer is methacryloxypropyl trimethoxysilane.

39. The method of any one of claims 32 to 38, wherein the dibenzoyl peroxide is phthalate-free.

40. The method of claim 32, wherein the wherein the polymerizable monomer is an ethoxylated bisphenol A dimethacrylate, the acetoacetoxy functional monomer is acetoacetoxyethyl methacrylate, the silane monomer is methacryloxypropyl trimethoxysilane, and the dibenzoyl peroxide is phthalate-free.

41. The method of any one of claims 32 to 40, wherein the second portion further comprises:

6) at least one reactive diluent monomer selected from the group consisting of: a monofunctional monomer, a multifunctional monomer, and any combination of the foregoing, wherein

i) the monofunctional monomer is selected from the group consisting of: methyl methacrylate, isopropyl methacrylate, isobutyl methacrylate, tert-butyl methacrylate, steryl methacrylate, 2-phenoxyethyl methacrylate, tetrahydrofurfuryl methacrylate, glycidyl methacrylate, isobornyl methacrylate, hydroxyethyl methacrylate, hydroxypropyl methacrylate, hydroxybutyl methacrylate, benzyl methacrylate, dicyclopentyl methacrylate, tert-butyl acrylate, steryl acrylate, 2-phenoxyethyl acrylate, tetrahydrofurfuryl acrylate, isobornyl acrylate, hydroxybutyl methacrylate, benzyl acrylate, dicyclopentyl

acrylate, styrene, vinyl toluene, methyl styrene, allyl glycidyl ether, acrylamide, methacrylamide, N-methylol acrylamide, N-methylol methacrylamide, and any combination of the foregoing; and

ii) the multifunctional monomer is selected from the group consisting of: divinyl benzene, allyl methacrylate, allyl cinnamate, ethylene glycol dimethacrylate, diethylene glycol dimethacrylate, triethylene glycol dimethacrylate, dipropylene glycol dimethacrylate, 1,3-butylene glycol dimethacrylate, 1,4-butanediol dimethacrylate, 1,6-hexanediol dimethacrylate, neopentyl glycol dimethacrylate, cyclohexane dimethanol dimethacrylate, dicyclopentyl dimethacrylate, glyceryl trimethacrylate, trimethylolpropane trimethacrylate, pentaerythritol trimethacrylate, pentaerythritol tetramethacrylate, dipentaerythritol pentamethacrylate, ethylene glycol diacrylate, diethylene glycol diacrylate, triethylene glycol diacrylate, dipropylene glycol diacrylate, 1,3-butylene glycol diacrylate, 1,4-butanediol diacrylate, 1,6-hexanediol diacrylate, neopentyl glycol diacrylate, cyclohexane dimethanol diacrylate, dicyclopentyl diacrylate, glyceryl triacrylate, trimethylolpropane triacrylate, pentaerythritol triacrylate, pentaerythritol tetraacrylate, dipentaerythritol pentaacrylate, tris(2-hydroxy ethyl)isocyanurate triacrylate, alkoxylated versions of any of the foregoing, metallic acrylates and methacrylates of zinc, magnesium or calcium, and any combination of the foregoing.

42. A method for anchoring an element in a structural body, comprising:

a. providing a first portion, the first portion comprising:

- 1) an ethoxylated bisphenol A dimethacrylate;
- 2) acetoacetoxyethyl methacrylate;
- 3) methacryloxypropyl trimethoxysilane; and
- 4) an accelerant selected from the group consisting of N,N-diisopropanol-p-toluidine, N,N-dihydroxyethyl-p-toluidine, N,N-methylhydroxyethyl-p-toluidine, and combinations thereof;

- b. providing a separately arranged second portion, the second portion comprising:
 - 5) phthalate-free dibenzoyl peroxide;
 - c. combining the first portion with the second portion forming an adhesive composition; and
 - d. anchoring the element in the structural body using the adhesive composition.
43. A method for anchoring an element in a structural body, comprising:
- a. providing a first portion, the first portion comprising:
 - 1) an ethoxylated bisphenol A dimethacrylate;
 - 2) acetoacetoxyethyl methacrylate;
 - 3) methacryloxypropyl trimethoxysilane; and
 - 4) N,N-diisopropanol-p-toluidine; and
 - b. providing a separately arranged second portion, the second portion comprising:
 - 5) phthalate-free dibenzoyl peroxide;
 - c. combining the first portion with the second portion producing an adhesive composition; and
 - d. anchoring the element in the structural body using the adhesive composition.
44. The method of claim 42 or 43, wherein the element is selected from the group comprising a metallic object, a steel rod, a steel bolt, a ceramic member, a concrete member, a masonry member, a plastic member, a glass member, a wood member, and combinations thereof.
45. The method of claim 42, 43 or 44, wherein the structural body is selected from the group comprising concrete, masonry and combinations thereof.
46. The method of any one of claims 42 to 45, the first portion further comprising:
- 6) at least one reactive diluent monomer selected from the group consisting of: a monofunctional monomer, a multifunctional monomer, and combinations of the foregoing, wherein

i) the monofunctional monomer is selected from the group consisting of: methyl methacrylate, isopropyl methacrylate, isobutyl methacrylate, tert-butyl methacrylate, steryl methacrylate, 2-phenoxyethyl methacrylate, tetrahydrofurfuryl methacrylate, glycidyl methacrylate, isobornyl methacrylate, hydroxyethyl methacrylate, hydroxypropyl methacrylate, hydroxybutyl methacrylate, benzyl methacrylate, dicyclopentyl methacrylate, tert-butyl acrylate, steryl acrylate, 2-phenoxyethyl acrylate, tetrahydrofurfuryl acrylate, isobornyl acrylate, hydroxybutyl methacrylate, benzyl acrylate, dicyclopentyl acrylate, styrene, vinyl toluene, methyl styrene, allyl glycidyl ether, acrylamide, methacrylamide, N-methylol acrylamide, N-methylol methacrylamide, and any combination of the foregoing; and

ii) the multifunctional monomer is selected from the group consisting of: divinyl benzene, allyl methacrylate, allyl cinnamate, ethylene glycol dimethacrylate, diethylene glycol dimethacrylate, triethylene glycol dimethacrylate, dipropylene glycol dimethacrylate, 1,3-butylene glycol dimethacrylate, 1,4-butanediol dimethacrylate, 1,6-hexanediol dimethacrylate, neopentyl glycol dimethacrylate, cyclohexane dimethanol dimethacrylate, dicyclopentyl dimethacrylate, glyceryl trimethacrylate, trimethylolpropane trimethacrylate, pentaerythritol trimethacrylate, pentaerythritol tetramethacrylate, dipentaerythritol pentamethacrylate, ethylene glycol diacrylate, diethylene glycol diacrylate, triethylene glycol diacrylate, dipropylene glycol diacrylate, 1,3-butylene glycol diacrylate, 1,4-butanediol diacrylate, 1,6-hexanediol diacrylate, neopentyl glycol diacrylate, cyclohexane dimethanol diacrylate, dicyclopentyl diacrylate, glyceryl triacrylate, trimethylolpropane triacrylate, pentaerythritol triacrylate, pentaerythritol tetraacrylate, dipentaerythritol pentaacrylate, tris(2-hydroxy ethyl)isocyanurate triacrylate, alkoxylated versions of any of the foregoing, metallic acrylates and methacrylates of zinc, magnesium or calcium, and any combination of the foregoing.

47. The method of any one of claims 42 to 46, wherein the first portion and second portion are combined through a static mixing nozzle.
48. The method of any one of claims 42 to 47, wherein the amount of the first portion is in the range of about 30 wt% to about 70 wt%.
49. The method of any one of claims 42 to 48, wherein the amount of the second portion is in the range of about 10 wt% to 25 wt%.
50. The method of any one of claims 42 to 47, wherein the ratio of the first portion to the second portion is about 10:1 by weight.
51. A kit for an adhesive composition, comprising:
- a. a first portion having:
 - 1) at least one reactive resin comprising a functional monomer;
 - 2) at least one acetoacetoxy functional monomer;
 - 3) at least one silane monomer; and
 - 4) at least one accelerant selected from the group consisting of N,N-diisopropanol-p-toluidine, N,N-dihydroxyethyl-p-toluidine, N,N-methylhydroxyethyl-p-toluidine, and combinations thereof;
 - b. a separately-maintained second portion comprising:
 - 5) dibenzoyl peroxide; and
 - c. instructions for use.
52. The kit of claim 51, the first portion further comprising:
- 6) at least one reactive diluent monomer selected from the group consisting of: a monofunctional monomer, a multifunctional monomer, and combinations of the foregoing, wherein
 - i) the monofunctional monomer is selected from the group consisting of: methyl methacrylate, isopropyl methacrylate, isobutyl methacrylate, tert-butyl

methacrylate, steryl methacrylate, 2-phenoxyethyl methacrylate, tetrahydrofurfuryl methacrylate, glycidyl methacrylate, isobornyl methacrylate, hydroxyethyl methacrylate, hydroxypropyl methacrylate, hydroxybutyl methacrylate, benzyl methacrylate, dicyclopentyl methacrylate, tert-butyl acrylate, steryl acrylate, 2-phenoxyethyl acrylate, tetrahydrofurfuryl acrylate, isobornyl acrylate, hydroxybutyl methacrylate, benzyl acrylate, dicyclopentyl acrylate, styrene, vinyl toluene, methyl styrene, allyl glycidyl ether, acrylamide, methacrylamide, N-methylol acrylamide, N-methylol methacrylamide, and any combination of the foregoing; and

ii) the multifunctional monomer is selected from the group consisting of: divinyl benzene, allyl methacrylate, allyl cinnamate, ethylene glycol dimethacrylate, diethylene glycol dimethacrylate, triethylene glycol dimethacrylate, dipropylene glycol dimethacrylate, 1,3-butylene glycol dimethacrylate, 1,4-butanediol dimethacrylate, 1,6-hexanediol dimethacrylate, neopentyl glycol dimethacrylate, cyclohexane dimethanol dimethacrylate, dicyclopentyl dimethacrylate, glyceryl trimethacrylate, trimethylolpropane trimethacrylate, pentaerythritol trimethacrylate, pentaerythritol tetramethacrylate, dipentaerythritol pentamethacrylate, ethylene glycol diacrylate, diethylene glycol diacrylate, triethylene glycol diacrylate, dipropylene glycol diacrylate, 1,3-butylene glycol diacrylate, 1,4-butanediol diacrylate, 1,6-hexanediol diacrylate, neopentyl glycol diacrylate, cyclohexane dimethanol diacrylate, dicyclopentyl diacrylate, glyceryl triacrylate, trimethylolpropane triacrylate, pentaerythritol triacrylate, pentaerythritol tetraacrylate, dipentaerythritol pentaacrylate, tris(2-hydroxy ethyl)isocyanurate triacrylate, alkoxylated versions of any of the foregoing, metallic acrylates and methacrylates of zinc, magnesium or calcium, and any combination of the foregoing.

53. The kit of claim 51 or 52, wherein the first portion is contained in a first chamber and the second portion is contained in a second chamber.

54. The kit of claim 53, wherein the first chamber and the second chamber are in a co-axial or side-by-side arrangement.
55. The kit of claim 53 or 54, wherein at least one of the first chamber and the second chamber is a bulk tank.
56. The kit of claim 53, 54 or 55, wherein at least one of the first chamber and the second chamber is frangible.
57. The kit of claim 56, wherein the frangible chamber serves as a filler.
58. The kit of any one of claims 51 to 57, wherein the amount of the first portion is in the range of about 30 wt% to about 70 wt%.
59. The kit of any one of claims 51 to 58, wherein the amount of the second portion is in the range of about 10 wt% to 25 wt%.
60. The kit of any one of claims 51 to 57, wherein the ratio of the first portion to the second portion is about 10:1 by weight.