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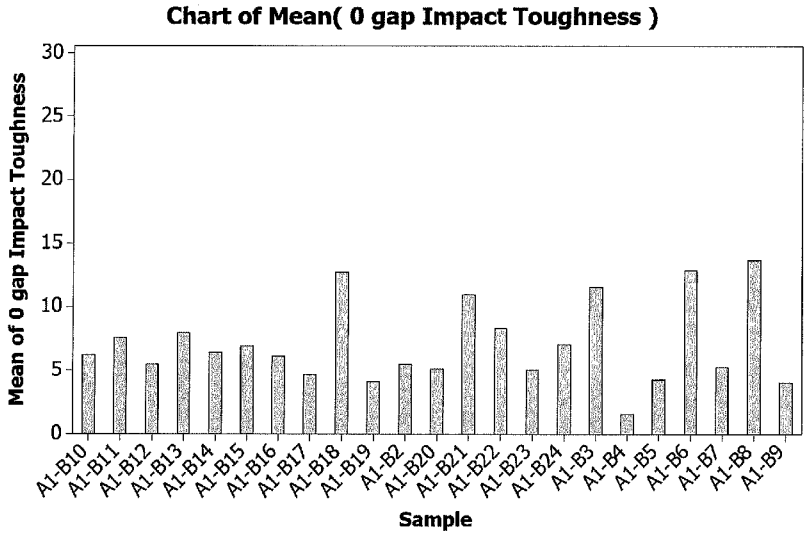


FIG. 1

(57) Abstract: Two-part cyanoacrylate/free radically curable adhesive systems demonstrating improved toughness are provided.

[Continued on next page]

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TWO-PART, CYANOACRYLATE/FREE RADICALLY CURABLE ADHESIVE SYSTEMS

BACKGROUND

Field

[0001] Two-part cyanoacrylate/free radically curable adhesive systems demonstrating improved toughness are provided.

Brief Discussion of Related Technology

[0002] Curable compositions such as cyanoacrylate adhesives are well recognized for their excellent ability to rapidly bond a wide range of substrates, generally in a number of minutes and depending on the particular substrate, often in a number of seconds.

[0003] Polymerization of cyanoacrylates is initiated by nucleophiles found under normal atmospheric conditions on most surfaces. The initiation by surface chemistry means that sufficient initiating species are available when two surfaces are in close contact with a small layer of cyanoacrylate between the two surfaces. Under these conditions a strong bond is obtained in a short period of time. Thus, in essence the cyanoacrylate often functions as an instant adhesive.

[0004] Cyanoacrylate adhesive performance, particularly durability, oftentimes becomes suspect when exposed to elevated temperature conditions and/or high relative humidity conditions. To combat these application-dependent shortcomings, a host of additives have been identified for inclusion in cyanoacrylate adhesive formulations. Improvements would still be seen as beneficial.

[0005] A variety of additives and fillers have been added to cyanoacrylate compositions to modify physical properties.

[0006] For instance, U.S. Patent No. 3,183,217 to Serniuk et al. discloses free radical polymerization of a methacrylic acid or methyl methacrylate monomer with a non-polar or mildly polar olefin where the monomer is complexed with a Friedel-Crafts halide.

[0007] U.S. Patent No. 3,963,772 to Takeshita discloses liquid telomers of alkylene and acrylic monomers which result in short chain alternating copolymers substantially terminated at one end of the polymer chains with the more reactive alkylene units. The liquid telomers are useful in making elastomeric polymers for high molecular weight rubbers which permit the ready incorporation of fillers, additives, and the like, due to its liquid phase.

[0008] U.S. Patent No. 4,440,910 to O'Connor is directed to cyanoacrylate compositions having improved toughness, achieved through the addition of elastomers, i.e., acrylic rubbers. These rubbers are either (i) homopolymers of alkyl esters of acrylic acid; (ii) copolymers of another polymerizable monomer, such as lower alkenes, with an alkyl ester of acrylic acid or with an alkoxy ester of acrylic acid; (iii) copolymers of alkyl esters of acrylic acid; (iv) copolymers of alkoxy esters of acrylic acid; and (v) mixtures thereof.

[0009] U.S. Patent No. 4,560,723 to Millet et al. discloses a cyanoacrylate adhesive composition containing a toughening agent comprising a core-shell polymer and a sustainer comprising an organic compound containing one or more unsubstituted or substituted aryl groups. The sustainer is reported to improve retention of toughness after heat aging of cured bonds of the adhesive. The core-shell polymer is treated with an acid wash to remove any polymerization-causing impurities such as salts, soaps or other nucleophilic species left over from the core-shell polymer manufacturing process.

[0010] U.S. Patent No. 5,340,873 to Mitry discloses a cyanoacrylate adhesive composition having improved toughness by including an effective toughening amount of a polyester polymer derived from a dibasic aliphatic or aromatic carboxylic acid and a glycol.

[0011] U.S. Patent No. 5,994,464 to Ohsawa et al. discloses a cyanoacrylate adhesive composition containing a cyanoacrylate monomer, an elastomer miscible or compatible with the cyanoacrylate monomer, and a core-shell polymer being compatible, but not miscible, with the cyanoacrylate monomer.

[0012] U.S. Patent No. 6,833,196 to Wojciak discloses a method of enhancing the toughness of a cyanoacrylate composition between steel and EPDM rubber substrates. The disclosed method is defined by the steps of: providing a cyanoacrylate component; and providing a toughening agent comprising methyl methacrylic monomer and at least one of butyl acrylic monomer and isobornyl acrylic monomer, whereby the acrylic monomer toughening agent enhances the toughness of the cyanoacrylate composition such that whereupon cure, the cyanoacrylate composition has an average tensile shear strength of over about 4400 psi after 72 hours at room temperature cure and 2 hours post cure at 121°C.

[0013] Reactive acrylic adhesives that cure by free radical polymerization of (meth)acrylic esters (i.e., acrylates) are known, but suffer from certain drawbacks. Commercially important acrylic adhesives tend to have an offensive odor, particularly those that are made from methyl methacrylate. Methyl methacrylate-based acrylic adhesives also have low flash points (approximately 59°F). Low flash points are particularly an issue during storage and transportation of the adhesives. If the flash point is 141°F or lower, the U.S. Department of Transportation classifies the product as "Flammable" and

requires marking and special storage and transportation conditions.

[0014] U.S. Patent No. 6,562,181 to Righettini intends to provide a solution to the problem addressed in the preceding paragraph by describing an adhesive composition comprising: (a) a trifunctional olefinic first monomer comprising an olefinic group that has at least three functional groups each bonded directly to the unsaturated carbon atoms of said olefinic group; (b) an olefinic second monomer that is copolymerizable with the first monomer; (c) a redox initiator system, and (d) a reactive diluent, where the composition is a liquid at room temperature is 100% reactive and substantially free of volatile organic solvent, and is curable at room temperature.

[0015] And more recently, U.S. Patent No. 9,371,470 to Burns describes and claims a two-part curable composition comprising: (a) a first part comprising a cyanoacrylate component and a peroxide catalyst; and (b) a second part comprising a free radical curable component and a transition metal. When mixed together the peroxide catalyst initiates cure of the free radical curable component and the transition metal initiates cure of the cyanoacrylate component. In a particular embodiment, the peroxide catalyst is t-butyl perbenzoate.

[0016] Notwithstanding the state of the art, it would be desirable to provide an adhesive system having both the features of an instant adhesive, such as in terms of the fast fixture times and ability to bond a wide range of substrates such as metals and plastics observed with cyanoacrylates, together with the improved bond strength over a greater variety and/or selection of substrates seen with (meth)acrylate compositions. And it would be desirable to provide a two-part reactive adhesive with reduced odor and flammability that could be mixed at a 1:1 volume ratio without comprising shelf life stability or

adhesive performance. In addition, it would be desirable for the two-part reactive adhesive to be toughened so that reaction products thereof can withstand exposure to a variety of extreme conditions without sacrificing useful bond strength.

SUMMARY

[0017] There is provided in one aspect a two-part cyanoacrylate/free radically curable composition comprising:

(a) a first part comprising a cyanoacrylate component and a peroxide catalyst; and

(b) a second part comprising a free radical curable component and a transition metal.

When mixed together, the peroxide catalyst of the first part initiates cure of the free radically curable component of the second part and the transition metal of the second part initiates cure of the cyanoacrylate of the first part.

[0018] Significantly, in at least one of the first part or the second part is further provided a (meth)acrylate-functionalized urethane resin having a polyurethane backbone, at least a portion of which includes a urethane linkage formed from isophorane diisocyanate.

[0019] The compositions, which are room temperature curable as the first part and the second part do not interact prior to use on mixing, provide good performance across substrates constructed from a wide variety of materials and provide improved durability performance over conventional cyanoacrylate compositions and improved fixture time and improved bond strength over conventional free radical curable compositions.

BRIEF DESCRIPTION OF THE FIGURES

[0020] FIGs. 1-2 depict bar charts of various adhesive systems used to bond metal (i.e., grit blasted mild steel and

aluminum) substrates shown on the X axis and impact toughness performance measured at 0 gap and 1 mm gap in Joules shown on the Y axis.

DETAILED DESCRIPTION

Part A

[0021] The cyanoacrylate component includes cyanoacrylate monomers, such as those represented by $H_2C=C(CN)-COOR$, where R is selected from C_{1-15} alkyl, C_{2-15} alkoxyalkyl, C_{3-15} cycloalkyl, C_{2-15} alkenyl, C_{7-15} aralkyl, C_{6-15} aryl, C_{3-15} allyl and C_{1-15} haloalkyl groups. Desirably, the cyanoacrylate monomer is selected from methyl cyanoacrylate, ethyl-2-cyanoacrylate ("ECA"), propyl cyanoacrylates, butyl cyanoacrylates (such as n-butyl-2-cyanoacrylate), octyl cyanoacrylates, allyl cyanoacrylate, ß-methoxyethyl cyanoacrylate and combinations thereof. A particularly desirable one is ethyl-2-cyanoacrylate.

[0022] The cyanoacrylate component should be included in the Part A composition in an amount within the range of from about 50 weight percent to about 99.98 weight percent, such as about 90 weight percent to about 99 weight percent being desirable, and about 92 weight percent to about 97 weight percent of the Part A composition being particularly desirable.

[0023] As the peroxide catalyst to be included in the Part A composition of the two-part adhesive system, perbenzoates should be used, such as t-butylperbenzoate.

[0024] Typically, the amount of peroxide catalyst should fall in the range of about 0.001 weight percent up to about 10.00 weight percent of the composition, desirably about 0.01 weight percent up to about 5.00 weight percent of the composition, such as about 0.50 to 2.50 weight percent of the composition.

[0025] Additives may be included in the Part A composition of the adhesive system to modify physical properties, such as

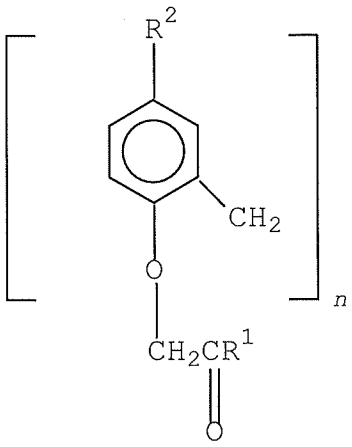
improved fixture speed, improved shelf-life stability, flexibility, thixotropy, increased viscosity, color, and improved toughness. Such additives therefore may be selected from accelerators, free radical stabilizers, anionic stabilizers, gelling agents, thickeners [such as PMMAs], thixotropy conferring agents (such as fumed silica), dyes, toughening agents, plasticizers and combinations thereof.

[0026] The toughening agent used in the Part A composition are those that have been found to be compatible with cyanoacrylate.

[0027] One or more accelerators may also be used in the adhesive system, particularly, in the Part A composition, to accelerate cure of the cyanoacrylate component. Such accelerators may be selected from calixarenes and oxacalixarenes, silacrowns, crown ethers, cyclodextrins, poly(ethyleneglycol) di(meth)acrylates, ethoxylated hydric compounds and combinations thereof.

[0028] Of the calixarenes and oxacalixarenes, many are known, and are reported in the patent literature. See e.g. U.S. Patent Nos. 4,556,700, 4,622,414, 4,636,539, 4,695,615, 4,718,966, and 4,855,461, the disclosures of each of which are hereby expressly incorporated herein by reference.

[0029] For instance, as regards calixarenes, those within the structure below are useful herein:

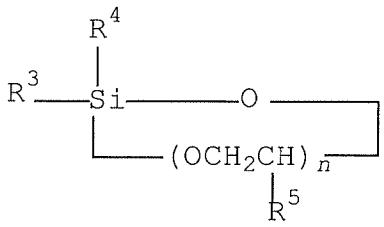


where R^1 is alkyl, alkoxy, substituted alkyl or substituted alkoxy; R^2 is H or alkyl; and n is 4, 6 or 8.

[0030] One particularly desirable calixarene is tetrabutyl tetra[2-ethoxy-2-oxoethoxy]calix-4-arene.

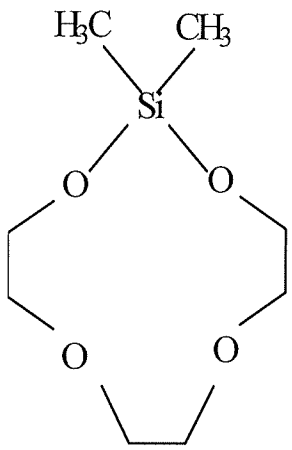
[0031] A host of crown ethers are known. For instance, examples which may be used herein either individually or in combination include 15-crown-5, 18-crown-6, dibenzo-18-crown-6, benzo-15-crown-5-dibenzo-24-crown-8, dibenzo-30-crown-10, tribenzo-18-crown-6, asym-dibenzo-22-crown-6, dibenzo-14-crown-4, dicyclohexyl-18-crown-6, dicyclohexyl-24-crown-8, cyclohexyl-12-crown-4, 1,2-decalyl-15-crown-5, 1,2-naphtho-15-crown-5, 3,4,5-naphtyl-16-crown-5, 1,2-methyl-benzo-18-crown-6, 1,2-methylbenzo-5, 6-methylbenzo-18-crown-6, 1,2-t-butyl-18-crown-6, 1,2-vinylbenzo-15-crown-5, 1,2-vinylbenzo-18-crown-6, 1,2-t-butyl-cyclohexyl-18-crown-6, asym-dibenzo-22-crown-6 and 1,2-benzo-1,4-benzo-5-oxygen-20-crown-7. See U.S. Patent No. 4,837,260 (Sato), the disclosure of which is hereby expressly incorporated here by reference.

[0032] Of the silacrowns, again many are known, and are reported in the literature. For instance, a typical silacrown may be represented within the structure below:

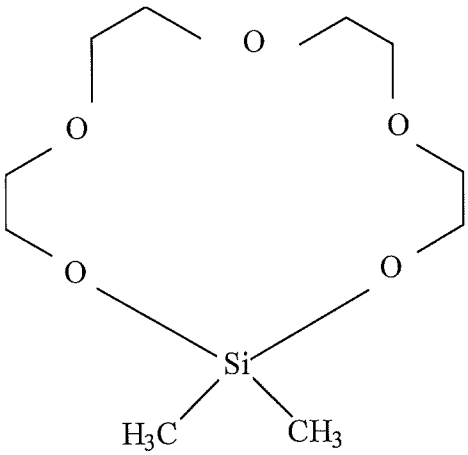


where R^3 and R^4 are organo groups which do not themselves cause polymerization of the cyanoacrylate monomer, R^5 is H or CH_3 and n is an integer of between 1 and 4. Examples of suitable R^3 and R^4 groups are R groups, alkoxy groups, such as methoxy, and aryloxy groups, such as phenoxy. The R^3 and R^4 groups may contain halogen or other substituents, an example being trifluoropropyl. However, groups not suitable as R^4 and R^5 groups are basic groups, such as amino, substituted amino and alkylamino.

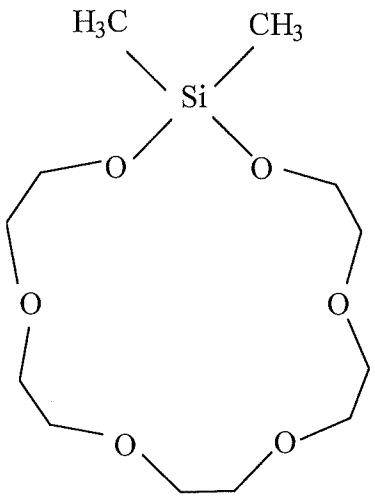
[0033] Specific examples of silacrown compounds useful in the inventive compositions include:



dimethylsila-11-crown-4;



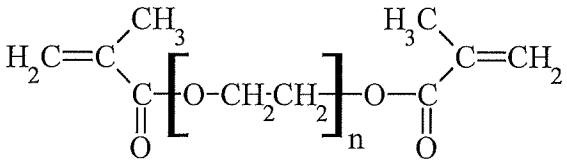
dimethylsila-14-crown-5;



and dimethylsila-17-crown-6. See e.g. U.S. Patent No. 4,906,317 (Liu), the disclosure of which is hereby expressly incorporated herein by reference.

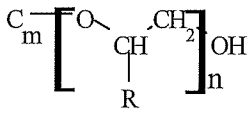
[0034] Many cyclodextrins may be used in connection with the present invention. For instance, those described and claimed in U.S. Patent No. 5,312,864 (Wenz), the disclosure of which is hereby expressly incorporated herein by reference, as hydroxyl group derivatives of an α, β or γ-cyclodextrin which is at least partly soluble in the cyanoacrylate would be appropriate choices for use herein as an accelerator component.

[0035] In addition, poly(ethylene glycol) di(meth)acrylates suitable for use herein include those within the structure below:



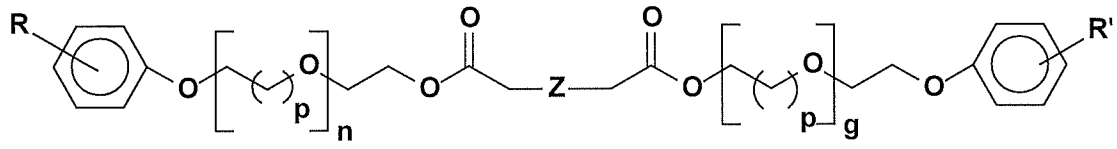
where n is greater than 3, such as within the range of 3 to 12, with n being 9 as particularly desirable. More specific examples include PEG 200 DMA (where n is about 4), PEG 400 DMA (where n is about 9), PEG 600 DMA (where n is about 14), and PEG 800 DMA (where n is about 19), where the number (e.g., 400) represents the average molecular weight of the glycol portion of the molecule, excluding the two methacrylate groups, expressed as grams/mole (i.e., 400 g/mol). A particularly desirable PEG DMA is PEG 400 DMA.

[0036] And of the ethoxylated hydric compounds (or ethoxylated fatty alcohols that may be employed), appropriate ones may be chosen from those within the structure below:



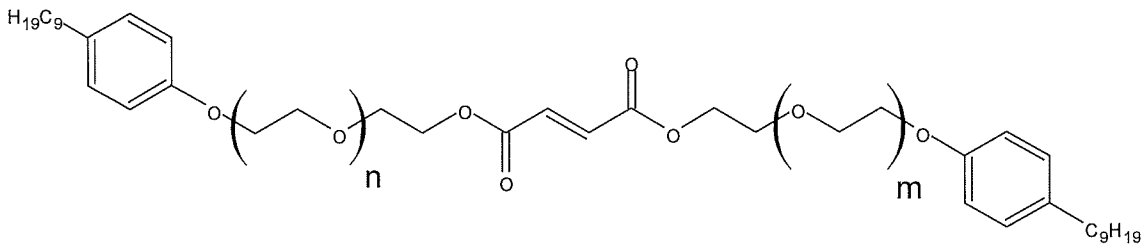
where C_m can be a linear or branched alkyl or alkenyl chain, m is an integer between 1 to 30, such as from 5 to 20, n is an integer between 2 to 30, such as from 5 to 15, and R may be H or alkyl, such as C_{1-6} alkyl.

[0037] In addition, accelerators embraced within the structure below:



where R is hydrogen, C_{1-6} alkyl, C_{1-6} alkyloxy, alkyl thioethers, haloalkyl, carboxylic acid and esters thereof, sulfinic, sulfonic and sulfurous acids and esters, phosphinic, phosphonic and phosphorous acids and esters thereof, Z is a polyether linkage, n is 1-12 and p is 1-3 are as defined above, and R' is the same as R, and g is the same as n.

[0038] A particularly desirable chemical within this class as an accelerator component is



where n and m combined are greater than or equal to 12.

[0039] The accelerator should be included in the composition in an amount within the range of from about 0.01 weight percent to about 10 weight percent, with the range of about 0.1 to about 0.5 weight percent being desirable, and about 0.4 weight percent of the total composition being particularly desirable.

[0040] Stabilizers useful in the Part A composition of the adhesive system include free-radical stabilizers, anionic stabilizers and stabilizer packages that include combinations thereof. The identity and amount of such stabilizers are well known to those of ordinary skill in the art. See e.g. U.S. Patent Nos. 5,530,037 and 6,607,632, the disclosures of each of which are hereby incorporated herein by reference. Commonly

used free-radical stabilizers include hydroquinone, while commonly used anionic stabilizers include boron triflouride, boron trifluoride-etherate, sulphur trioxide (and hydrolyis products thereof) and methane sulfonic acid.

Part B

[0041] Free radical curable monomers for use in the Part B composition of the adhesive system include (meth)acrylate monomers, maleimide-, itaconamide- or nadimide-containing compounds and combinations thereof.

[0042] (Meth)acrylate monomers for use in Part B of the composition of the adhesive system include a host of (meth)acrylate monomers, with some of the (meth)acrylate monomers being aromatic, while others are aliphatic and still others are cycloaliphatic. Examples of such (meth)acrylate monomers include di-or tri-functional (meth)acrylates like polyethylene glycol di(meth)acrylates, tetrahydrofuran (meth)acrylates and di(meth)acrylates, hydroxypropyl (meth)acrylate ("HPMA"), hexanediol di(meth)acrylate, trimethylol propane tri(meth)acrylate ("TMPTMA"), diethylene glycol dimethacrylate, triethylene glycol dimethacrylate ("TRIEGMA"), benzylmethacrylate, tetraethylene glycol dimethacrylate, dipropylene glycol dimethacrylate, di-(pentamethylene glycol) dimethacrylate, tetraethylene diglycol diacrylate, diglycerol tetramethacrylate, tetramethylene dimethacrylate, ethylene dimethacrylate, neopentyl glycol diacrylate, trimethylol propane triacrylate and bisphenol-A mono and di(meth)acrylates, such as ethoxylated bisphenol-A (meth)acrylate ("EBIPMA"), bisphenol-F mono and di(meth)acrylates, such as ethoxylated bisphenol-F (meth)acrylate, and (meth)acrylate-functionalized urethanes.

[0043] For instance, examples of such (meth)acrylate-functionalized urethanes include a tetramethylene glycol urethane acrylate oligomer and a propylene glycol urethane acrylate oligomer.

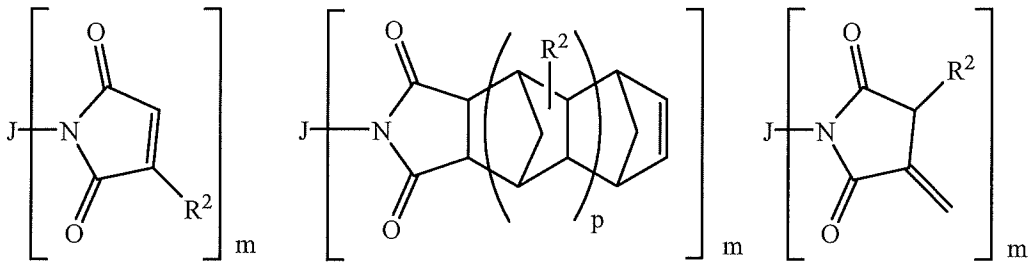
[0044] Other (meth)acrylate-functionalized urethanes are urethane (meth)acrylate oligomers based on polyethers or polyesters, which are reacted with aromatic, aliphatic, or cycloaliphatic diisocyanates and capped with hydroxy acrylates. For instance, difunctional urethane acrylate oligomers, such as a polyester of hexanedioic acid and diethylene glycol, terminated with isophorone diisocyanate, capped with 2-hydroxyethyl acrylate (CAS 72121-94-9); a polypropylene glycol terminated with tolyene-2,6-diisocyanate, capped with 2-hydroxyethylacrylate (CAS 37302-70-8); a polyester of hexanedioic acid and diethylene glycol, terminated with 4,4'-methylenebis(cyclohexyl isocyanate), capped with 2-hydroxyethyl acrylate (CAS 69011-33-2); a polyester of hexanedioic acid, 1,2-ethanediol, and 1,2 propanediol, terminated with tolylene-2,4-diisocyanate, capped with 2-hydroxyethyl acrylate (CAS 69011-31-0); a polyester of hexanedioic acid, 1,2-ethanediol, and 1,2 propanediol, terminated with 4,4'-methylenebis(cyclohexyl isocyanate, capped with 2-hydroxyethyl acrylate (CAS 69011-32-1); and a polytetramethylene glycol ether terminated with 4,4'-methylenebis(cyclohexylisocyanate), capped with 2-hydroxyethyl acrylate.

[0045] Still other (meth)acrylate-functionalized urethanes are monofunctional urethane acrylate oligomers, such as a polypropylene terminated with 4,4'-methylenebis(cyclohexylisocyanate), capped with 2-hydroxyethyl acrylate and 1-dodosanol.

[0046] They also include difunctional urethane methacrylate oligomers such as a polytetramethylene glycol ether terminated

with tolulene-2,4-diisocyanate, capped with 2-hydroxyethyl methacrylate; a polytetramethylene glycol ether terminated with isophorone diisocyanate, capped with 2-hydroxyethyl methacrylate; a polytetramethylene glycol ether terminated with 4,4'-methylenebis(cyclohexylisocyanate), capped with 2-hydroxyethyl methacrylate; and a polypropylene glycol terminated with tolylene-2,4-diisocyanate, capped with 2-hydroxyethyl methacrylate.

[0047] The maleimides, nadimides, and itaconimides include those compounds having the following structures **I**, **II** and **III**, respectively



I II III

where:

m = 1-15,

p = 0-15,

each R^2 is independently selected from hydrogen or lower alkyl, and

J is a monovalent or a polyvalent moiety comprising organic or organosiloxane radicals, and combinations of two or more thereof.

[0048] More specific representations of the maleimides, itaconimides and nadimides include those corresponding to structures **I**, **II**, or **III**, where m = 1-6, p = 0, R^2 is independently selected from hydrogen or lower alkyl, and J is a

monovalent or polyvalent radical selected from hydrocarbyl, substituted hydrocarbyl, heteroatom-containing hydrocarbyl, substituted heteroatom-containing hydrocarbyl, hydrocarbylene, substituted hydrocarbylene, heteroatom-containing hydrocarbylene, substituted heteroatom-containing hydrocarbylene, polysiloxane, polysiloxane-polyurethane block copolymer, and combinations of two or more thereof, optionally containing one or more linkers selected from a covalent bond, -O-, -S-, -NR-, -O-C(O)-, -O-C(O)-O-, -O-C(O)-NR-, -NR-C(O)-, -NR-C(O)-O-, -NR-C(O)-NR-, -S-C(O)-, -S-C(O)-O-, -S-C(O)-NR-, -S(O)-, -S(O)$_2$-, -O-S(O)$_2$-, -O-S(O)$_2$-O-, -O-S(O)$_2$-NR-, -O-S(O)-, -O-S(O)-O-, -O-S(O)-NR-, -O-NR-C(O)-, -O-NR-C(O)-O-, -O-NR-C(O)-NR-, -NR-O-C(O)-, -NR-O-C(O)-O-, -NR-O-C(O)-NR-, -O-NR-C(S)-, -O-NR-C(S)-O-, -O-NR-C(S)-NR-, -NR-O-C(S)-, -NR-O-C(S)-O-, -NR-O-C(S)-NR-, -O-C(S)-, -O-C(S)-O-, -O-C(S)-NR-, -NR-C(S)-, -NR-C(S)-O-, -NR-C(S)-NR-, -S-S(O)$_2$-, -S-S(O)$_2$-O-, -S-S(O)$_2$-NR-, -NR-O-S(O)-, -NR-O-S(O)-O-, -NR-O-S(O)-NR-, -NR-O-S(O)$_2$-, -NR-O-S(O)$_2$-O-, -NR-O-S(O)$_2$-NR-, -O-NR-S(O)-, -O-NR-S(O)-O-, -O-NR-S(O)-NR-, -O-NR-S(O)$_2$-O-, -O-NR-S(O)$_2$-NR-, -O-NR-S(O)$_2$-, -O-P(O)R$_2$-, -S-P(O)R$_2$-, -NR-P(O)R$_2$-, where each R is independently hydrogen, alkyl or substituted alkyl, and combinations of any two or more thereof.

[0049] When one or more of the above described monovalent or polyvalent groups contain one or more of the above described linkers to form the "J" appendage of a maleimide, nadimide or itaconimide group, as readily recognized by those of skill in the art, a wide variety of linkers can be produced, such as, for example, oxyalkyl, thioalkyl, aminoalkyl, carboxylalkyl, oxyalkenyl, thioalkenyl, aminoalkenyl, carboxyalkenyl, oxyalkynyl, thioalkynyl, aminoalkynyl, carboxyalkynyl, oxycycloalkyl, thiocycloalkyl, aminocycloalkyl,

carboxycycloalkyl, oxycloalkenyl, thiocycloalkenyl, aminocycloalkenyl, carboxycycloalkenyl, heterocyclic, oxyheterocyclic, thioheterocyclic, aminoheterocyclic, carboxyheterocyclic, oxyaryl, thioaryl, aminoaryl, carboxyaryl, heteroaryl, oxyheteroaryl, thioheteroaryl, aminoheteroaryl, carboxyheteroaryl, oxyalkylaryl, thioalkylaryl, aminoalkylaryl, carboxyalkylaryl, oxyarylalkyl, thioarylalkyl, aminoarylalkyl, carboxyarylalkyl, oxyarylalkenyl, thioarylalkenyl, aminoarylalkenyl, carboxyarylalkenyl, oxyalkenylaryl, thioalkenylaryl, aminoalkenylaryl, carboxyalkenylaryl, oxyarylalkynyl, thioarylalkynyl, aminoarylalkynyl, carboxyarylalkynyl, oxyalkynylaryl, thioalkynylaryl, aminoalkynylaryl or carboxyalkynylaryl, oxyalkylene, thioalkylene, aminoalkylene, carboxyalkylene, oxyalkenylene, thioalkenylene, aminoalkenylene, carboxyalkenylene, oxyalkynylene, thioalkynylene, aminoalkynylene, carboxyalkynylene, oxycycloalkylene, thiocycloalkylene, aminocycloalkylene, carboxycycloalkylene, oxycycloalkenylene, thiocycloalkenyle aminoalkylarylene, carboxyalkylarylene, oxyarylalkylene, thioarylalkylene, aminoarylalkylene, carboxyarylalkylene, oxyarylalkenylene, thioarylalkenylene, aminoarylalkenylene, carboxyarylalkenylene, oxyalkenylarylene, thioalkenylarylene, aminoalkenylarylene, carboxyalkenylarylene, oxyarylalkynylene, thioarylalkynylene, aminoarylalkynylene, carboxy arylalkynylene, oxyalkynylarylene, thioalkynylarylene, aminoalkynylarylene, carboxyalkynylarylene, heteroarylene, oxyheteroarylene, thioheteroarylene, aminoheteroarylene, carboxyheteroarylene, heteroatom-containing di- or polyvalent cyclic moiety, oxyheteroatom-containing di- or polyvalent cyclic moiety, thioheteroatom-containing di- or polyvalent cyclic moiety, aminoheteroatom-containing di- or polyvalent cyclic moiety, carboxyheteroatom-containing di- or polyvalent cyclic

moiety, disulfide, sulfonamide, and the like. ne, aminocycloalkenylene, carboxycycloalkenylene, oxyarylene, thioarylene, aminoarylene, carboxyarylene, oxyalkylarylene, thioalkylarylene,

[0050] In another embodiment, maleimides, nadimides, and itaconimides contemplated for use in the practice of the present invention have the structures **I**, **II**, and **III**, where m = 1-6, p = 0-6, and J is selected from saturated straight chain alkyl or branched chain alkyl, optionally containing optionally substituted aryl moieties as substituents on the alkyl chain or as part of the backbone of the alkyl chain, and where the alkyl chains have up to about 20 carbon atoms;

a siloxane having the structure: $-(C(R^3)_2)_d-[Si(R^4)_2-O]_f-Si(R^4)_2-(C(R^3)_2)_e-$, $-(C(R^3)_2)_d-C(R^3)-C(O)O-(C(R^3)_2)_d-[Si(R^4)_2-O]_f-Si(R^4)_2-(C(R^3)_2)_e-O(O)C-(C(R^3)_2)_e-$, or $-(C(R^3)_2)_d-C(R^3)-O(O)C-(C(R^3)_2)_d-[Si(R^4)_2-O]_f-Si(R^4)_2-(C(R^3)_2)_e-C(O)O-(C(R^3)_2)_e-$, where:

each R^3 is independently hydrogen, alkyl or substituted alkyl,

each R^4 is independently hydrogen, lower alkyl or aryl,

d = 1-10,

e = 1-10, and

f = 1-50;

a polyalkylene oxide having the structure:

$$[(CR_2)_r-O-]_f-(CR_2)_s-$$

where:

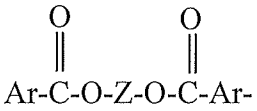
each R is independently hydrogen, alkyl or substituted alkyl,

r = 1-10,

s = 1-10, and

f is as defined above;

aromatic groups having the structure:



where:

each Ar is a monosubstituted, disubstituted or trisubstituted aromatic or heteroaromatic ring having in the range of 3 up to 10 carbon atoms, and

Z is:

saturated straight chain alkylene or branched chain alkylene, optionally containing saturated cyclic moieties as substituents on the alkylene chain or as part of the backbone of the alkylene chain, or

polyalkylene oxides having the structure:

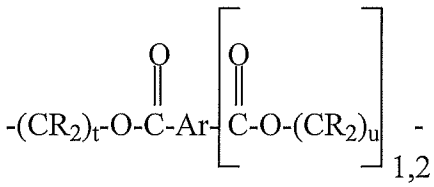
$$-[(CR_2)_r-O-]_q-(CR_2)_s-$$

where:

each R is independently hydrogen, alkyl or substituted alkyl, r and s are each defined as above, and

q falls in the range of 1 up to 50;

di- or tri-substituted aromatic moieties having the structure:



where:

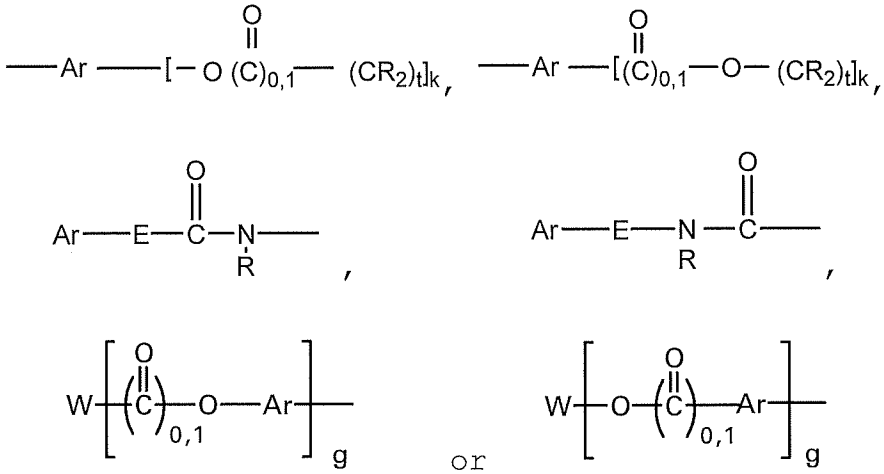
each R is independently hydrogen, alkyl or substituted alkyl,

t falls in the range of 2 up to 10,

u falls in the range of 2 up to 10, and

Ar is as defined above;

aromatic groups having the structure:



where:

each R is independently hydrogen, alkyl or substituted alkyl,

t = 2-10,

k = 1, 2 or 3,

g = 1 up to about 50,

each Ar is as defined above,

E is -O- or $-NR^5-$, where R^5 is hydrogen or lower alkyl; and

W is straight or branched chain alkyl, alkylene, oxyalkylene, alkenyl, alkenylene, oxyalkenylene, ester, or polyester, a siloxane having the structure $-(C(R^3)_2)_d-[Si(R^4)_2-O]_f-Si(R^4)_2-(C(R^3)_2)_e-$, $-(C(R^3)_2)_d-C(R^3)-C(O)O-(C(R^3)_2)_d-[Si(R^4)_2-O]_f-Si(R^4)_2-(C(R^3)_2)_e-O(O)C-(C(R^3)_2)_e-$, or $-(C(R^3)_2)_d-C(R^3)-O(O)C-(C(R^3)_2)_d-[Si(R^4)_2-O]_f-Si(R^4)_2-(C(R^3)_2)_e-C(O)O-(C(R^3)_2)_e-$, where:

each R^3 is independently hydrogen, alkyl or substituted alkyl,

each R^4 is independently hydrogen, lower alkyl or aryl,

d = 1-10,

e = 1-10, and

f = 1-50;

a polyalkylene oxide having the structure:

$$-[(CR_2)_r-O-]_f-(CR_2)_s-$$

where:

each R is independently hydrogen, alkyl or substituted alkyl,

r = 1-10,

s = 1-10, and

f is as defined above;

optionally containing substituents selected from hydroxy, alkoxy, carboxy, nitrile, cycloalkyl or cycloalkenyl;

a urethane group having the structure:

$R^7-U-C(O)-NR^6-R^8-NR^6-C(O)-(O-R^8-O-C(O)-NR^6-R^8-NR^6-C(O))_v-U-R^8-$

where:

each R^6 is independently hydrogen or lower alkyl,

each R^7 is independently an alkyl, aryl, or arylalkyl group having 1 to 18 carbon atoms,

each R^8 is an alkyl or alkyloxy chain having up to about 100 atoms in the chain, optionally substituted with Ar,

U is -O-, -S-, -N(R)-, or $-P(L)_{1,2}-$,

where R as defined above, and where each L is independently =O, =S, -OR -R; and

v = 0-50;

polycyclic alkenyl; or mixtures of any two or more thereof.

[0051] In a more specific recitation of such maleimide-, nadimide-, and itaconimide-containing compounds of structures **I**, **II** and **III**, respectively, each R is independently hydrogen or lower alkyl (such as C_{1-4}), -J- comprises a branched chain alkyl, alkylene, alkylene oxide, alkylene carboxyl or alkylene amido species having sufficient length and branching to render the maleimide, nadimide and/or itaconimide compound a liquid, and m is 1, 2 or 3.

[0052] Particularly desirable maleimide-containing compounds include those have two maleimide groups with an aromatic group therebetween, such as a phenyl, biphenyl, bisphenyl or napthyl linkage.

[0053] In addition to the free radical curable component, Part B also includes a transition metal compound. A non-exhaustive list of representative examples of the transition metal compounds are copper, vanadium, cobalt and iron compounds. For instance, as regards copper compounds, copper compounds where copper enjoys a 1+ or 2+ valence state are desirable. A non-exhaustive list of examples of such copper (I) and (II) compounds include copper (II) 3,5-diisopropylsalicylate hydrate, copper bis(2,2,6,6-tetramethyl-3,5-heptanedionate), copper (II) hydroxide phosphate, copper (II) chloride, copper (II) acetate monohydrate, tetrakis(acetonitrile)copper (I) hexafluorophosphate, copper (II) formate hydrate, tetrakisacetonitrile copper (I) triflate, copper(II)tetrafluoroborate, copper (II) perchlorate, tetrakis(acetonitrile)copper (I) tetrafluoroborate, copper (II) hydroxide, copper (II) hexafluoroacetylacetonate hydrate and copper (II) carbonate. These copper (I) and (II) compounds should be used in an amount such that when dissolved or suspended in a carrier vehicle, such as a (meth)acrylate, a concentration of about 100 ppm to about 5,000 ppm, such as about 500 ppm to about 2,500 ppm, for instance about 1,000 ppm is present in the solution or suspension.

[0054] As regards vanadium compounds, vanadium compounds where vanadium enjoys a 2+ and 3+ valence state are desirable. Examples of such vanadium (III) compounds include vanadyl naphthanate and vanadyl acetylacetonate. These vanadium (III) compounds should be used in an amount of 50 ppm to about 5,000 ppm, such as about 500 ppm to about 2,500 ppm, for instance about 1,000 ppm.

[0055] As regards cobalt compounds, cobalt compounds where cobalt enjoys a 2+ valence state are desirable. Examples of such cobalt (II) compounds include cobalt naphthenate, cobalt

tetrafluoroborate and cobalt acetylacetonate. These cobalt (II) compounds should be used in an amount of about 100 ppm to about 1000 ppm.

[0056] As regards iron compounds, iron compounds where iron enjoys a 3+ valence state are desirable. Examples of such iron (III) compounds include iron acetate, iron acetylacetonate, iron tetrafluoroborate, iron perchlorate, and iron chloride. These iron compounds should be used in an amount of about 100 ppm to about 1000 ppm.

[0057] As discussed above, additives may be included in either or both of the Part A or the Part B compositions to influence a variety of performance properties.

[0058] Fillers contemplated for use include, for example, aluminum nitride, boron nitride, silicon carbide, diamond, graphite, beryllium oxide, magnesia, silicas, such as fumed silica or fused silica, alumina, perfluorinated hydrocarbon polymers (i.e., TEFLON), thermoplastic polymers, thermoplastic elastomers, mica, glass powder and the like. Preferably, the particle size of these fillers will be about 20 microns or less.

[0059] As regards silicas, the silica may have a mean particle diameter on the nanoparticle size; that is, having a mean particle diameter on the order of 10^{-9} meters. The silica nanoparticles can be pre-dispersed in epoxy resins, and may be selected from those available under the tradename NANOPOCRYL, from Nanoresins, Germany. NANOCRYL is a tradename for a product family of silica nanoparticle reinforced (meth)acrylates. The silica phase consists of surface-modified, synthetic SiO_2 nanospheres with less than 50 nm diameter and an extremely narrow particle size distribution. The SiO_2 nanospheres are agglomerate-free dispersions in the (meth)acrylate matrix resulting in a low viscosity for resins containing up to 50 weight percent silica.

[0060] The silica component should be present in an amount in the range of about 1 to about 60 weight percent, such as about 3 to about 30 weight percent, desirably about 5 to about 20 weight percent, based on the total weight of the composition.

[0061] Toughеners contemplated for use particularly in the Part A composition include elastomeric polymers selected from elastomeric copolymers of a lower alkene monomer and (i) acrylic acid esters, (ii) methacrylic acid esters or (iii) vinyl acetate, such as acrylic rubbers; polyester urethanes; ethylene-vinyl acetates; fluorinated rubbers; isoprene-acrylonitrile polymers; chlorosulfinated polyethylenes; and homopolymers of polyvinyl acetate were found to be particularly useful. [See U.S. Patent No. 4,440,910 to O'Connor, the disclosures of each of which are hereby expressly incorporated herein by reference.] The elastomeric polymers are described in the '910 patent as either homopolymers of alkyl esters of acrylic acid; copolymers of another polymerizable monomer, such as lower alkenes, with an alkyl or alkoxy ester of acrylic acid; and copolymers of alkyl or alkoxy esters of acrylic acid. Other unsaturated monomers which may be copolymerized with the alkyl and alkoxy esters of acrylic include dienes, reactive halogen-containing unsaturated compounds and other acrylic monomers such as acrylamides.

[0062] For instance, one group of such elastomeric polymers are copolymers of methyl acrylate and ethylene, manufactured by DuPont, under the name of VAMAC, such as VAMAC N123 and VAMAC B-124. VAMAC N123 and VAMAC B-124 are reported by DuPont to be a master batch of ethylene/acrylic elastomer. The DuPont material VAMAC G is a similar copolymer, but contains no fillers to provide color or stabilizers. VAMAC VCS rubber appears to be the base rubber, from which the remaining members of the VAMAC product line are compounded. VAMAC VCS (also known as VAMAC MR) is a reaction product of the combination of ethylene, methyl

acrylate and monomers having carboxylic acid cure sites, which once formed is then substantially free of processing aids (such as the release agents octadecyl amine, complex organic phosphate esters and/or stearic acid), and anti-oxidants (such as substituted diphenyl amine).

[0063] DuPont provides to the market under the trade designation VAMAC VMX 1012 and VCD 6200, rubbers which are made from ethylene and methyl acrylate. It is believed that the VAMAC VMX 1012 rubber possesses little to no carboxylic acid in the polymer backbone. Like the VAMAC VCS rubber, the VAMAC VMX 1012 and VCD 6200 rubbers are substantially free of processing aids such as the release agents octadecyl amine, complex organic phosphate esters and/or stearic acid, and anti-oxidants, such as substituted diphenyl amine, noted above. All of these VAMAC elastomeric polymers are useful herein.

[0064] In addition, vinylidene chloride-acrylonitrile copolymers [see U.S. Patent No. 4,102,945 (Gleave)] and vinyl chloride/vinyl acetate copolymers [see U.S. Patent 4,444,933 (Columbus)] may be included in the Part A composition. Of course, the disclosures of each these U.S. patents are hereby incorporated herein by reference in their entirety.

[0065] Copolymers of polyethylene and polyvinyl acetate, available commercially under the trade name LEVAMELT by LANXESS Limited, are useful.

[0066] A range of LEVAMELT-branded copolymers are available and includes for example, LEVAMELT 400, LEVAMELT 600 and LEVAMELT 900. The LEVAMELT products differ in the amount of vinyl acetate present. For example, LEVAMELT 400 comprises an ethylene-vinyl acetate copolymer comprising 40 weight percent vinyl acetate. The LEVAMELT products are supplied in granular form. The granules are almost colourless and dusted with silica and talc. LEVAMELT consists of methylene units forming a

saturated main chain with pendant acetate groups. The presence of a fully saturated main chain is an indication that LEVAMELT-branded copolymers are particularly stable; they do not contain any reactive double bonds which make conventional rubbers prone to aging reactions, ozone and UV light. The saturated backbone is reported to make the polymer robust.

[0067] Interestingly, depending on the ratio of polyethylene/polyvinylacetate, the solubilities of these LEVAMELT-branded elastomers change in different monomers and also the ability to toughen changes as a result of the solubility.

[0068] The LEVAMELT-branded elastomers are available in pellet form and are easier to formulate than other known elastomeric toughening agents.

[0069] LEVAPREN-branded copolymers, also from Lanxess, may also be used.

[0070] VINNOL-branded surface coating resins available commercially from Wacker Chemie AG, Munich, Germany represent a broad range of vinyl chloride-derived copolymers and terpolymers that are promoted for use in different industrial applications. The main constituents of these polymers are different compositions of vinyl chloride and vinyl acetate. The terpolymers of the VINNOL product line additionally contain carboxyl or hydroxyl groups. These vinyl chloride/vinyl acetate copolymers and terpolymers may also be used.

[0071] VINNOL-branded surface coating resins with carboxyl groups are terpolymers of vinyl chloride, vinyl acetate and dicarboxylic acids, varying in terms of their molar composition and degree and process of polymerization. These terpolymers are reported to show excellent adhesion, particularly on metallic substrates.

[0072] VINNOL-branded surface coating resins with hydroxyl groups are copolymers and terpolymers of vinyl chloride, hydroxyacrylate and dicarboxylate, varying in terms of their composition and degree of polymerization.

[0073] VINNOL-branded surface coating resins without functional groups are copolymers of vinyl chloride and vinyl acetate of variable molar composition and degree of polymerization.

[0074] Rubber particles, especially rubber particles that have relatively small average particle size (e.g., less than about 500 nm or less than about 200 nm), may also be included, particularly in the Part B composition. The rubber particles may or may not have a shell common to known core-shell structures.

[0075] In the case of rubber particles having a core-shell structure, such particles generally have a core comprised of a polymeric material having elastomeric or rubbery properties (i.e., a glass transition temperature less than about 0°C, e.g., less than about -30°C) surrounded by a shell comprised of a non-elastomeric polymeric material (i.e., a thermoplastic or thermoset/crosslinked polymer having a glass transition temperature greater than ambient temperatures, e.g., greater than about 50°C). For example, the core may be comprised of a diene homopolymer or copolymer (for example, a homopolymer of butadiene or isoprene, a copolymer of butadiene or isoprene with one or more ethylenically unsaturated monomers such as vinyl aromatic monomers, (meth)acrylonitrile, (meth)acrylates, or the like) while the shell may be comprised of a polymer or copolymer of one or more monomers such as (meth)acrylates (e.g., methyl methacrylate), vinyl aromatic monomers (e.g., styrene), vinyl cyanides (e.g., acrylonitrile), unsaturated acids and anhydrides (e.g., acrylic acid), (meth)acrylamides, and the like having a

suitably high glass transition temperature. Other rubbery polymers may also be suitably be used for the core, including polybutylacrylate or polysiloxane elastomer (e.g., polydimethylsiloxane, particularly crosslinked polydimethylsiloxane).

[0076] Typically, the core will comprise from about 50 to about 95 weight percent of the rubber particles while the shell will comprise from about 5 to about 50 weight percent of the rubber particles.

[0077] Preferably, the rubber particles are relatively small in size. For example, the average particle size may be from about 0.03 to about 2 microns or from about 0.05 to about 1 micron. The rubber particles may have an average diameter of less than about 500 nm, such as less than about 200 nm. For example, the core-shell rubber particles may have an average diameter within the range of from about 25 to about 200 nm.

[0078] When used, these core shell rubbers allow for toughening to occur in the composition and oftentimes in a predictable manner -- in terms of temperature neutrality toward cure -- because of the substantial uniform dispersion, which is ordinarily observed in the core shell rubbers as they are offered for sale commercially.

[0079] In the case of those rubber particles that do not have such a shell, the rubber particles may be based on the core of such structures.

[0080] Desirably, the rubber particles are relatively small in size. For example, the average particle size may be from about 0.03 to about 2 μ or from about 0.05 to about 1 μ. In certain embodiments of the invention, the rubber particles have an average diameter of less than about 500 nm. In other embodiments, the average particle size is less than about 200 nm. For example, the rubber particles may have an average diameter

within the range of from about 25 to about 200 nm or from about 50 to about 150 nm.

[0081] The rubber particles may be used in a dry form or may be dispersed in a matrix, as noted above.

[0082] Typically, the composition may contain from about 5 to about 35 weight percent rubber particles.

[0083] Combinations of different rubber particles may advantageously be used in the present invention. The rubber particles may differ, for example, in particle size, the glass transition temperatures of their respective materials, whether, to what extent and by what the materials are functionalized, and whether and how their surfaces are treated.

[0084] Rubber particles that are suitable for use in the present invention are available from commercial sources. For example, rubber particles supplied by Eliokem, Inc. may be used, such as NEP R0401 and NEP R401S (both based on acrylonitrile/butadiene copolymer); NEP R0501 (based on carboxylated acrylonitrile/butadiene copolymer; CAS No. 9010-81-5); NEP R0601A (based on hydroxy-terminated polydimethylsiloxane; CAS No. 70131-67-8); and NEP R0701 and NEP 0701S (based on butadiene/styrene/2-vinylpyridine copolymer; CAS No. 25053-48-9). Also, those available under the PARALOID tradename, such as PARALOID 2314, PARALOID 2300, and PARALOID 2600, from Dow Chemical Co., Philadelphia, PA, and those available under the STAPHYLOID tradename, such as STAPHYLOID AC-3832, from Ganz Chemical Co., Ltd., Osaka, Japan.

[0085] Rubber particles that have been treated with a reactive gas or other reagent to modify the outer surfaces of the particles by, for instance, creating polar groups (e.g., hydroxyl groups, carboxylic acid groups) on the particle surface, are also suitable for use herein. Illustrative reactive gases include, for example, ozone, Cl_2, F_2, O_2, SO_3, and oxidative gases.

Methods of surface modifying rubber particles using such reagents are known in the art and are described, for example, in U.S. Patent Nos. 5,382,635; 5,506,283; 5,693,714; and 5,969,053, each of which being hereby expressly incorporated herein by reference in its entirety. Suitable surface modified rubber particles are also available from commercial sources, such as the rubbers sold under the tradename VISTAMER by Exousia Corporation.

[0086] Where the rubber particles are initially provided in dry form, it may be advantageous to ensure that such particles are well dispersed in the adhesive composition prior to curing the adhesive composition. That is, agglomerates of the rubber particles are preferably broken up so as to provide discrete individual rubber particles, which may be accomplished by intimate and thorough mixing of the dry rubber particles with other components of the adhesive composition.

[0087] Thickeners are also useful.

[0088] Stabilizers and inhibitors may also be employed to control and prevent premature peroxide decomposition and polymerization. The inhibitors may be selected from hydroquinones, benzoquinones, naphthoquinones, phenanthroquinones, anthraquinones, and substituted compounds thereof. Various phenols may also be used as inhibitors, such as 2,6-di-tertiary-butyl-4-methyl phenol. The inhibitors may be used in quantities of about 0.1% to about 1.0% by weight of the total composition without adverse effect on the curing rate of the polymerizable adhesive composition.

[0089] Toughеners may be used in the Part B composition. Those contemplated for use in the Part B composition include a (meth)acrylate-functionalized urethane resin having a backbone, at least a portion of which includes a urethane linkage formed from isophorane diisocyanate. An example of the (meth)acrylate-

functionalized urethane resin is a urethane (meth)acrylate resin made from an alkylane glycol (such as polypropylene glycol), isophorane diisocyanate and hydroxy alkyl(meth)acrylate (such as hydroxyl ethyl acrylate). Other examples include a polyester of hexanedioic acid, diethylene glycol, terminated with isophorone diisocyanate, capped with 2-hydroxyethyl acrylate; a polytetramethylene glycol ether terminated with isophorone diisocyanate, capped with 2-hydroxyethyl methacrylate; and a hydroxy terminated polybutadiene terminated with isophorone diisocyanate, capped with 2-hydroxyethyl acrylate.

[0090] Alkyl (meth)acrylates useful in making the (meth)acrylate-functionalized urethane resin includes isobornyl(meth)acrylate, isodecyl(meth)acrylate, lauryl(meth)acrylate, cyclic trimethylolpropane formal acrylate, octyldecyl acrylate, tetrahydrofurfuryl(meth)acrylate, tridecyl(meth)acrylate, and hydroxypropyl(meth)acrylate, among others.

[0091] Hydroxy alkyl(meth)acrylates include 2-hydroxyethyl(meth)acrylate, phenoxyethyl(meth)acrylate, N-vinyl caprolactam, N,N-dimethyl acrylamide, 2(2-ethoxyethoxy) ethyl acrylate, caprolactone acrylate, polypropylene glycol monomethacrylate, 1,3-butylene glycol dimethacrylate, 1,4-butanediol dimethacrylate, 1,6 hexanediol di(meth)acrylate, tricyclodecane dimethanol di(meth)acrylate, tripropylene glycol diacrylate, ethoxylated trimethylolpropane triacrylate, trimethylolpropane triacrylate, tris(2-hydroxy ethyl) isocyanurate triacrylate, and combinations thereof.

[0092] Instead of hydroxy ethyl(meth)acrylate, 1,4-butanediol dimethacrylate, 1,6 hexanediol di(meth)acrylate, tricyclodecane dimethanol di(meth)acrylate, tripropylene glycol diacrylate, ethoxylated trimethylolpropane triacrylate, trimethylolpropane

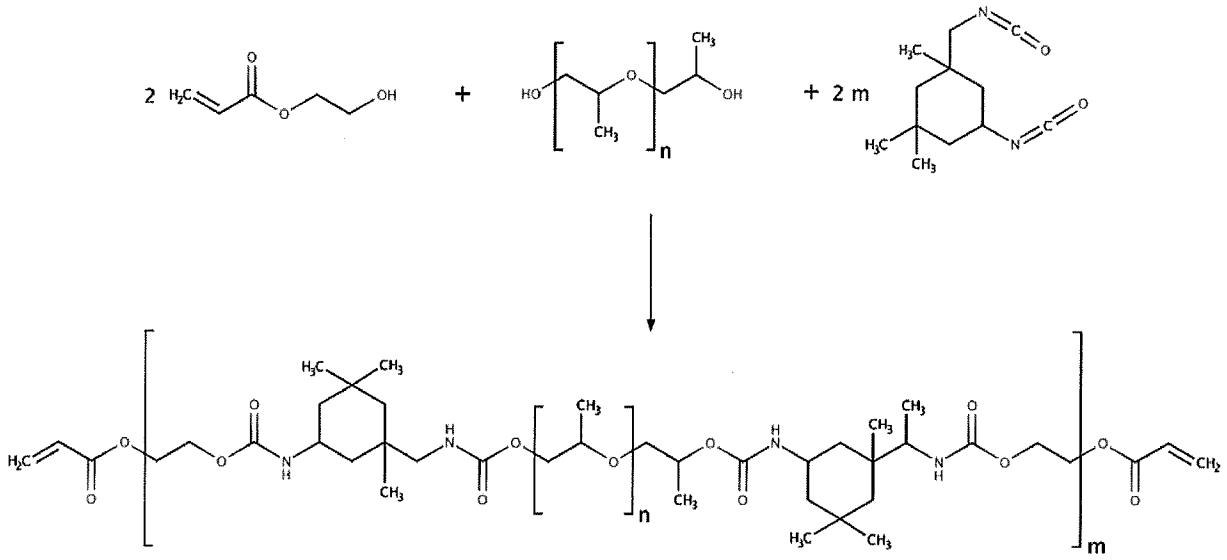
triacrylate, and tris(2-hydroxy ethyl) isocyanurate triacrylate may be used to cap the so-formed urethane (meth)acrylate resin.

[0093] Significant to the present invention is that the (meth)acrylate-functionalized urethane resins are made with an isophorane diisocyanate. For instance, a polyester of hexanedioic acid, diethylene glycol, terminated with isophorone diisocyanate, capped with 2-hydroxyethyl acrylate (CAS 72121-94-9) and a hydroxy terminated polybutadiene terminated with isophorone diisocyanate, capped with 2-hydroxyethyl acrylate are appropriate examples.

[0094] In addition, some of these (meth)acrylate-functionalized urethane resins may be commercially available. Examples of commercially available resins include those from Dymax Corporation, such as BR-345 (promoted by Dymax in its 2018 "BOMAR Oligomers Selected Guide," page 12 as a polyether urethane acrylate "[i]deal for 3D printing resins" with a nominal viscosity of 46,000 at 25°C and a Tg by DMA of -57°C), BR-302, BR 374-744B or BR-900. With respect to at least BR-345, see also A. Prabhakar et al., "Structural Investigations of Polypropylene glycol (PPG) and Isophorone diisocyanate (IPDI)-based Polyurethane Prepolymer by 1D and 2D NMR Spectroscopy", J. Polym. Sci.: Part A: Polym. Chem., 43, 1196-1209 (2005).

[0095] The BR-345 (meth)acrylate-functionalized urethane resin may be considered made according to the following reaction

scheme:



[0096] In one aspect of the invention, reaction products of the composition demonstrate a greater drop impact strength on substrates bonded together in a 1 mm spaced apart relationship than on substrates bonded together in a 0 mm spaced apart relationship.

[0097] The (meth)acrylate-functionalized urethane resin may be used in an amount of about 5 to about 60 percent by weight, such as about 15 to about 40 percent by weight of the free radical curable component of the Part B composition.

[0098] In practice, each of the Part A and the Part B compositions are housed in separate containment vessels in a device prior to use, where in use the two parts are expressed from the vessels mixed and applied onto a substrate surface. The vessels may be chambers of a dual chambered cartridge, where the separate parts are advanced through the chambers with plungers through an orifice (which may be a common one or adjacent ones) and then through a mixing dispense nozzle. Or the vessels may be coaxial or side-by-side pouches, which may be

cut or torn and the contents thereof mixed and applied onto a substrate surface.

[0099] The invention will be more readily appreciated by a review of the examples, which follow.

EXAMPLES

[00100] Reference to ECA means ethyl-2-cyanoacrylate.

[00101] With reference to Table 1, an adhesive system was prepared for control purposes where the Part A included ECA, mixed with LEVAPREN 900, t-BPB and a boron trifluoride/methane sulfonic acid combination, and the Part B included as the (meth)acrylate component the combination of an acrylated urethane ester, HPMA, and CN 2003 EU, to which was added a hydrated copper chlorate and a filler package as noted.

Table 1

Part A

Components		Sample/Amt (grams)
Type	**Identity**	**A1**
Cyanoacrylate	ECA	68.9
Toughener	LEVAPREN 900*	22.5
Peroxide	t-BPB	5.0
Stabilizer+	BF_3 / MSA	7.6

*Ethylene/vinyl acetate copolymer, available commercially from Lanxess Ltd.
+As a stock solution

Part B

Components		Sample/Amt (grams)
Type	**Identity**	**B1**
(Meth)acrylate	Acrylated Urethane Ester[1]	42.23
	HPMA	25
	CN 2003 EU[2]	22.5
Transition Metal	$Cu(ClO_4)_2 \cdot (H_2O)_6$	5
Filler	CAB-O-SIL TS 720	9
	HOMBINAN LW	7.5

[1] Made in sequential steps from the reaction of diols and dicarboxylic acids to form polyester diols, followed by reaction with toluene diisocyanate and finally capping with hydroxy propyl(meth)acrylate

[2] Epoxy acrylate, as reported by the manufacturer, Sartomer division of Arkema

[00102] For reference, the A1-B1 system was mixed and dispensed onto grit blasted mild steel lap shears in a 0 mm gap configuration and a 1 mm gap configuration with the noted substrates mated in an overlapped, off-set manner with the adhesive system disposed between the substrates in the overlapped, off-set portion. The substrates were of a thickness of 0.120 ± 0.005 inches. The A1-B1 system showed drop impact strength performance of 7.05 Joules at 0 mm gap and 1.77 Joules at 1 mm gap, based on an average of two replicates.

[00103] Here, the Part B composition from Table 1 was used in an amount progressively decreasing from 90 to 80 to 60 percent by weight with 10, 20 and 40 percent by weight of BOMAR BR 345 used in in its stead. These Part B compositions are noted as B2, B3 and B4, respectively, and are used together with the Part A composition from Table 1, namely A1.

[00104] As above, the A1-B2, A1-B3 and A1-B4 systems were mixed and dispensed onto grit blasted mild steel lap shears in a 0 mm gap configuration and a 1 mm gap configuration with the

noted substrates mated in an overlapped, off-set manner with the adhesive system disposed between the substrates in the overlapped, off-set portion. The substrates were of a thickness of 0.120 ± 0.005 inches.

[00105] In Table 2 below, the drop impact strength performance of these systems is recorded.

Table 2

Sample	Drop Impact Strength, Joules	
	0 mm	1 mm
A1-B2	5.48	3.98
A1-B3	11.56	28.50
A1-B4	1.59	6.33

[00106] At 0 mm gap, the A1-B2, A1-B3 and A1-B4 systems showed drop impact strength of 5.48, 11.56 and 1.59 Joules, respectively. At 1 mm gap, the A1-B2, A1-B3 and A1-B4 systems showed drop impact strength of 3.98, 28.50 and 6.33 Joules, respectively. (See FIGs. 1-2.)

[00107] Compared to the performance shown in the A1-B1 system, the A1-B2 system showed comparable performance at 0 mm. But the A1-B4 system showed significantly reduced performance at 0 mm gap. However, at 1 mm gap, the A1-B1 system showed drop impact strength performance of 1.77 Joules, whereas each of the systems shown in Table 2 have better performance than that. And the A1-B3 and A1-B4 systems showed improved drop impact strength performance in the 1 mm gap configuration, which was quite unexpected. Frankly, the A1-B3 system showed nearly three times improved impact strength at the 1 mm gap.

[00108] In Table 3 below, Part B compositions were prepared using a variety of (meth)acrylate-functionalized urethane resins. For instance, the following commercially available (meth)acrylate-functionalized urethane resins from Dymax Corporation, Torrington, Connecticut were evaluated at about 20 percent by weight with the remaining amount represented by the B1 Part B compositions: BOMAR BR-345 [described by the manufacturer as a polyether urethane acrylate that is flexible, with a nominal viscosity of 46,000 at 25°C and a T_g (°C) by DMA of -57. The manufacturer promotes BR-345 as having the following features for select applications: ideal for 3D printing resins; color stability; low moisture absorption; low T_g; soft surface hardness and provides impact resistance]; BR-930D [described by the manufacturer as a polyether urethane acrylate that is flexible and has weatherability, with a nominal viscosity of 7,700 at 60°C and a Tg (°C) by DMA of 95. The manufacturer promotes BR-930D as having the following features for select applications ideal for 3D printing resins; high heat-distortion temperature; provides good toughness and impact resistance; enhances weatherability and low skin irritation]; BR-374 [described by the manufacturer as a polyether urethane acrylate that is flexible and has weatherability, with a nominal viscosity of 35,000 at 25°C and a Tg (°C) by DMA of -48. The manufacturer promotes BR-374 as having the following features for select applications very low color; improves adhesion; chemical and oil resistant; non-yellowing and exhibits hydrolytic stability]; BR-302 [described by the manufacturer as a polyether urethane acrylate that is flexible and has flexibility and gloss with a nominal viscosity of 15,000 at 50°C and a Tg (°C) by DMA of 11. The manufacturer promotes BR-302 as having the following features for select applications excellent chemical resistance; exhibits hydrolytic stability; imparts

toughness; improves adhesion and low cost]; BR-744BT [described by the manufacturer as a polyether urethane acrylate that is flexible and has gloss and weatherability, with a nominal viscosity of, 44,500 at 60°C and a Tg (°C) by DMA of -18. The manufacturer promotes BR-744BT as having the following features for select applications improves adhesion; provides impact resistance; enhances flexibility; non-yellowing; weather resistant and low MEHQ levels]; BR 7432G130 [described by the manufacturer as a polyester urethane acrylate that is flexible and has weatherability, with a nominal viscosity of 80,000 at 25°C and a Tg (°C) by DMA of 28. The manufacturer promotes BR-7432G130 as having the following features for select applications: imparts toughness; high tensile strength; improves impact resistance; adheres to polymer films; elastomeric]; and BR-3741AJ [described by the manufacturer as a polyether urethane acrylate that is flexible and has weatherability, with a nominal viscosity of 25,000 at 60°C and a Tg (°C) by DMA of -50. The manufacturer promotes BR-3741AJ as having the following features for select applications: enhances softness and flexibility; improved optical clarity; non-yellowing; improves adhesion; adheres to a wide range of substrates; exhibits hydrolytic stability; oil and chemical resistant and ideal for PSAs].

Table 3

Components		Sample/Amt (weight percent)					
Type	**Identity**	**B5**	**B6**	**B7**	**B8**	**B9**	**B10**
(Meth)acrylate-functionalized urethane resin	BOMAR BR 930D	20.87					
	BOMAR BR 374		20.14				
	BOMAR BR 302			20.11			
	BOMAR BR 744BT				20.10		
	BOMAR BR 7432G130					19.97	
	BOMAR BR 3741AJ						20.34

[00109] In Table 3, the balance of the Part B composition is the B1 Part B composition.

[00110] The A1-B5, A1-B6, A1-B7, A1-B8, A1-B9 and A1-B10 systems were mixed and dispensed on grit blasted mild steel lap shears configured at 0 mm gap and 1 mm gap, which were mated in an overlapped, off-set manner with the adhesive system disposed between the substrates in the overlapped, off-set portion.

[00111] With reference to Table 3, each of these adhesive systems was applied to the noted substrate mated in an overlapped, off-set manner with the adhesive system disposed between the substrates in the overlapped, off-set portion, and allowed to cure for a period of time of about 24 hours at a temperature of about 40°C. When disposed between two substrates spaced apart by about 1 mm, reaction products of the inventive composition thus demonstrated a greater drop impact strength on the substrates bonded together in a 1 mm spaced apart relationship than on substrates bonded together in a 0 mm spaced

apart relationship, such as a drop impact strength of greater than twice that shown in a 0 mm spaced apart relationship.

[00112] The drop impact strength at 0 mm gap and 1 mm gap were observed in triplicate runs and captured as an average in Table 4 below. (See FIGs. 1-2.)

Table 4

Sample	Drop Impact Strength, Joules	
	0 mm	1 mm
A1-B5	4.25	2.03
A1-B6	12.89	16.5
A1-B7	5.25	2.17
A1-B8	13.67	4.37
A1-B9	4.03	2.93
A1-B10	6.23	6.57

[00113] In Tables 5A, 5B and 5C below, the following (meth)acrylate-functionalized urethane resins were evaluated in the amount recorded with the remaining amount represented by the B1 Part B compositions: GENOMER 4188 [reported by the manufacturer, Rahn AG, Switzerland, to be an aliphatic urethane acrylate having a viscosity of 120,000 mPas at 25°C and a Tg (°C) of -14 with high tack, high elongation and excellent adhesion], EBECRYL 242 [reported by the manufacturer, Allnex Netherlands BV, to be an aliphatic urethane diacrylate diluted with 30% isobornyl acrylate having a viscosity of 191,000 mPas at 25°C, a tensile strength of 4045 psi, a tensile elongation of 186% and a Tg (°C) of 46 with excellent flexibility, good adhesion to metal and good corrosion resistance], EBECRYL 246 [reported by the manufacturer, Allnex Netherlands BV, to be an aliphatic urethane diacrylate having a viscosity of 8,830,000 mPas at 25°C, a tensile strength of 8375 psi, a tensile elongation of 62% and a

Tg (˚C) of 54 with good abrasion resistance, excellent flexibility and exceptional toughness], EBECRYL 4491 [reported by the manufacturer, Allnex Netherlands BV, to be an aliphatic urethane diacrylate diluted with 20% isobornyl acrylate having a viscosity of 9,000 mPas at 25˚C, a tensile strength of 725 psi and a tensile elongation of 250% with very high flexibility and elongation], EBECRYL 4833 [reported by the manufacturer, Allnex Netherlands BV, to be an aliphatic urethane diacrylate diluted with 15% tripropylene glycol diacrylate having a viscosity of 161,000 mPas at 25˚C, a tensile strength of 2900 psi, a tensile elongation of 83% and a Tg (˚C) of 4 with good flexibility, abrasion resistance, exterior durability and adhesion], EBECRYL 8411 [reported by the manufacturer, Allnex Netherlands BV, to be an aliphatic urethane diacrylate diluted with 20% isobornyl acrylate having a viscosity of 149,500 mPas at 25˚C, a tensile strength of 1170 psi, a tensile elongation of 320% and a Tg (˚C) of -18 with outstanding extensibility and flexibility, good abrasion resistance and good exterior durability], and EBECRYL 8804 [reported by the manufacturer, Allnex Netherlands BV, to be an aliphatic urethane diacrylate having a viscosity of 3,200,000 mPas at 25˚C, a tensile strength of 3000 psi, a tensile elongation of 103% and a Tg (˚C) of 24 with extreme toughness, flexibility and abrasion resistance].

[00114] Part B compositions B2, B3 and B4 are reproduced from paragraph [0103] above and recorded below in Table 5C.

Table 5A

Components		Sample/Amt (weight percent)					
Type	Identity	B11	B12	B13	B14	B15	B16
(Meth)acrylate-functionalized urethane resin	GENOMER 4188	10	20				
	EBECRYL 242			10	20		
	EBECRYL 246					10	20

Table 5B

Components		Sample/Amt (weight percent)					
Type	Identity	B17	B18	B19	B20	B21	B22
(Meth)acrylate-functionalized urethane resin	EBECRYL 4491	10	20				
	EBECRYL 4833			10	20		
	EBECRYL 8411					10	20

Table 5C

Components		Sample/Amt (weight percent)				
Type	Identity	B23	B24	B2	B3	B4
(Meth)acrylate-functionalized urethane resin	EBECRYL 8804	10	20			
	BR-345			10	20	40

[00115] The A1-B11, A1-B12, A1-B13, A1-B14, A1-B15, A1-B16, A1-B17, A1-B18, A1-B19, A1-B20, A1-B21, A1-B22, A1-B23 and A1-B24 systems were mixed and dispensed on grit blasted mild steel lap shears configured at 0 mm gap and 1 mm gap, which were mated in an overlapped, off-set manner with the adhesive system disposed between the substrates in the overlapped, off-set portion. The A1-B2, A1-B3 and A1-B4 systems were evaluated above and provided here for illustrative purposes.

[00116] With reference to Tables 5A, 5B and 5C, each of these adhesive systems was applied to the noted substrate mated in an overlapped, off-set manner with the adhesive system disposed between the substrates in the overlapped, off-set portion, and allowed to cure for a period of time of about 24 hours at a temperature of about 40°C.

[00117] The drop impact strength at 0 and 1 mm gap were observed in triplicate runs and captured as an average in Table 6 below.

Table 6

Sample	Drop Impact Strength, J	
	0 mm	1 mm
A1-B11	7.57	3.02
A1-B12	5.48	2.83
A1-B13	7.93	1.97
A1-B14	6.41	2.70
A1-B15	6.90	1.73
A1-B16	6.12	1.46
A1-B17	4.69	2.44
A1-B18	12.77	2.82
A1-B19	4.14	2.21
A1-B20	5.09	2.12
A1-B21	10.96	2.74
A1-B22	8.30	3.67
A1-B23	5.00	2.25
A1-B24	7.04	1.85

[00118] None of these systems demonstrate the drop impact strength at 0 and 1 mm gap, as the A1-B3 and A1-B4 compositions, where the impact strength at a 1 mm gap is actually greater than that at a 0 mm gap. (See FIGs. 1-2.)

WHAT IS CLAIMED IS:

1. A two-part curable composition comprising:

(a) a first part comprising a cyanoacrylate component and a peroxide catalyst; and

(b) a second part comprising a free radical curable component and a transition metal, wherein at least one of the first part or the second part further comprises a (meth)acrylate-functionalized urethane resin having a backbone, at least a portion of which includes a urethane linkage formed from isophorane diisocyanate, and wherein when mixed together the peroxide catalyst initiates cure of the free radical curable component and the transition metal initiates cure of the cyanoacrylate component.

2. The composition of Claim 1, wherein the cyanoacrylate component comprises $H_2C=C(CN)-COOR$, wherein R is selected from alkyl, alkoxyalkyl, cycloalkyl, alkenyl, aralkyl, aryl, allyl and haloalkyl groups.

3. The composition of Claim 1, wherein the peroxide catalyst comprises perbenzoates.

4. The composition of Claim 1, wherein the peroxide catalyst is t-butyl perbenzoate.

5. The composition of Claim 1, wherein the (meth)acrylate-functionalized urethane resin is present in the second part.

6. The composition of Claim 1, wherein the peroxide catalyst is present in an amount from about 0.01 percent to about 10 percent by weight, based on the cyanoacrylate component.

7. The composition of Claim 1, wherein the free radical curable component is a (meth)acrylate component selected from the group consisting of polyethylene glycol di(meth)acrylates, tetrahydrofuran (meth)acrylates and di(meth)acrylates, hydroxypropyl (meth)acrylate, hexanediol di(meth)acrylate, trimethylol propane tri(meth)acrylate, diethylene glycol dimethacrylate, triethylene glycol dimethacrylate, benzylmethacrylate, tetraethylene glycol dimethacrylate, dipropylene glycol dimethacrylate, di-(pentamethylene glycol) dimethacrylate, tetraethylene diglycol diacrylate, diglycerol tetramethacrylate, tetramethylene dimethacrylate, ethylene dimethacrylate, neopentyl glycol diacrylate, trimethylol propane triacrylate, ethoxylated bisphenol-A (meth)acrylate, ethoxylated bisphenol-F (meth)acrylate, and methacrylate-functional urethanes.

8. The composition of Claim 1, wherein the transition metal comprises a member selected from the group consisting of copper, vanadium, cobalt and iron.

9. The composition of Claim 1, wherein the first part is housed in a first chamber of a dual chamber syringe and the second part is housed in a second chamber of the dual chamber syringe.

10. The composition of Claim 1, wherein the second part further comprises at least one of a plasticizer and a filler.

11. The composition of Claim 1, wherein the first part further comprises a toughener.

12. The composition of Claim 11, wherein the toughener is a member selected from the group consisting of (a) reaction products of the combination of ethylene, methyl acrylate and monomers having carboxylic acid cure sites, (b) dipolymers of ethylene and methyl acrylate, (c) combinations of (a) and (b), (4) vinylidene chloride-acrylonitrile copolymers, (5) and vinyl chloride/vinyl acetate copolymer, (6) copolymers of polyethylene and polyvinyl acetate, and combinations thereof.

13. The composition of Claim 1, wherein when disposed between two substrates spaced apart by about 1 mm, reaction products thereof demonstrating a drop impact strength of greater than twice that of reactions products thereof disposed between two substrates spaced apart by about 0 mm.

14. The composition of Claim 1, wherein the (meth)acrylate-functionalized urethane resin having a backbone, at least a portion of which includes a urethane linkage formed from isophorane diisocyanate is made from hydroxyethyl(meth)acrylate, polyethylene glycol and isophorane diisocyanate.

15. The composition of Claim 1, wherein the (meth)acrylate-functionalized urethane resin having a backbone, at least a portion of which includes a urethane linkage formed from isophorane diisocyanate is present in an amount of about 5 to about 60 percent by weight of the free radical curable component of the Part B composition.

16. The composition of Claim 1, wherein cured reaction products of the composition demonstrate a greater drop impact strength on substrates bonded together in a 1 mm spaced apart relationship

than on substrates bonded together in a 0 mm spaced apart relationship.

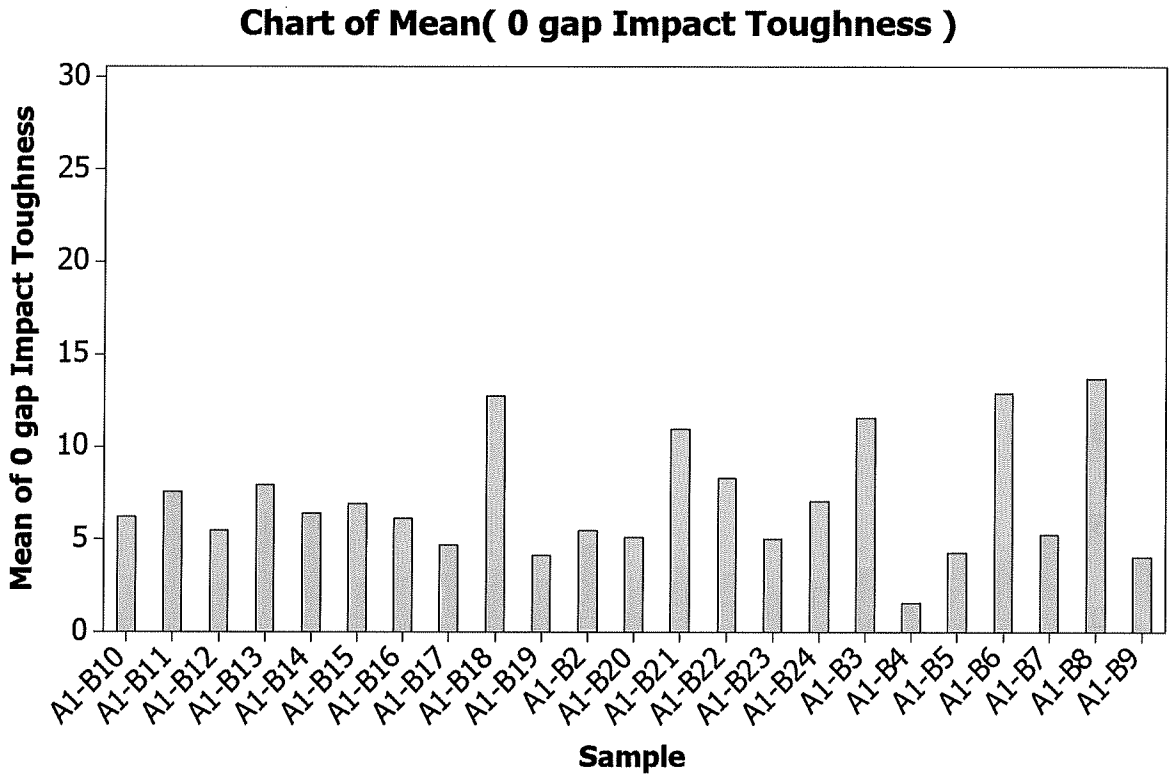

Chart of Mean(0 gap Impact Toughness)
Mean of 0 gap Impact Toughness
30
25
20
15
10
5
0
A1-B10
A1-B11
A1-B12
A1-B13
A1-B14
A1-B15
A1-B16
A1-B17
A1-B18
A1-B19
A1-B2
A1-B20
A1-B21
A1-B22
A1-B23
A1-B24
A1-B3
A1-B4
A1-B5
A1-B6
A1-B7
A1-B8
A1-B9
Sample

FIG. 1

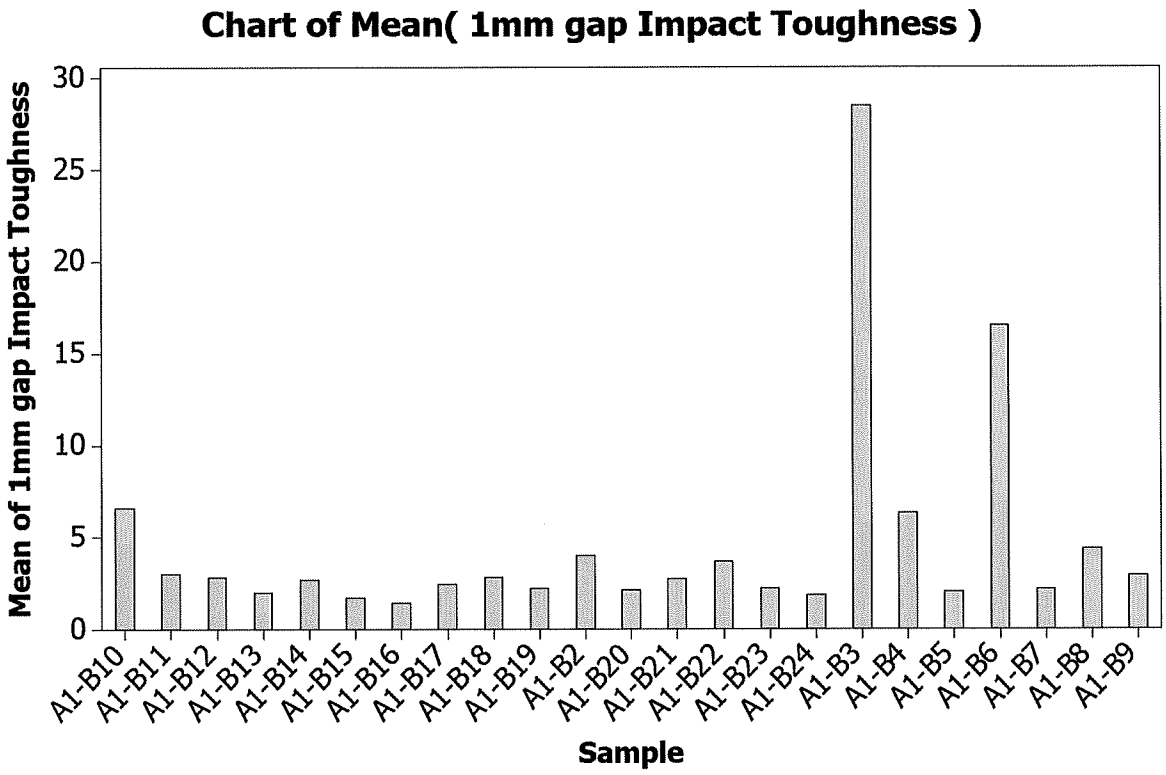

Chart of Mean(1mm gap Impact Toughness)
Mean of 1mm gap Impact Toughness
30
25
20
15
10
5
0
A1-B10
A1-B11
A1-B12
A1-B13
A1-B14
A1-B15
A1-B16
A1-B17
A1-B18
A1-B19
A1-B2
A1-B20
A1-B21
A1-B22
A1-B23
A1-B24
A1-B3
A1-B4
A1-B5
A1-B6
A1-B7
A1-B8
A1-B9
Sample

FIG. 2

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2019/057115

A. CLASSIFICATION OF SUBJECT MATTER

C09J 4/06(2006.01)i, C09J 11/00(2006.01)i, C09J 133/18(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C09J 4/06; C08F 2/50; C08F 220/20; C08G 18/36; C09J 111/00; C09J 3/14; C09J 4/00; C09J 4/04; C09J 5/00; C09J 11/00; C09J 133/18

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean utility models and applications for utility models
Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKOMPASS(KIPO internal) & Keywords: cyanoacrylate, radical, catalyst, metal, curable, adhesive, two-part, (meth)acrylate, urethane, isophorane diisocyanate

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2014-0329959 A1 (BARNES, R. B. et al.) 06 November 2014 See paragraph [0112]; and claims 1-4, 6, 8-12.	1-16
Y	US 2012-0302695 A1 (OSAE, S. B. et al.) 29 November 2012 See paragraphs [0090], [0138], [0158]; and claims 1-3.	1-16
Y	US 2003-0196753 A1 (RAINER SCHOENFELD et al.) 23 October 2003 See paragraphs [0004, [0022]-[0023], [0068]-[0075], [0095]; and claims 1, 4, 9-10, 13-15.	1-16
Y	US 2015-0005431 A1 (DAICEL-ALLNEX LTD.) 01 January 2015 See paragraphs [0014]-[0015], [0037]-[0039], [0070]-[0073], [0084]-[0085]; cl aim 1.	1-16
Y	JP 56-095966 A (MATSUMOTO SEIYAKU KOGYO KK) 03 August 1981 See examples 1-3; and claims 1-6.	1-16
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☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"D" document cited by the applicant in the international application
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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents,such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
10 March 2020 (10.03.2020)	**10 March 2020 (10.03.2020)**

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2019/057115

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