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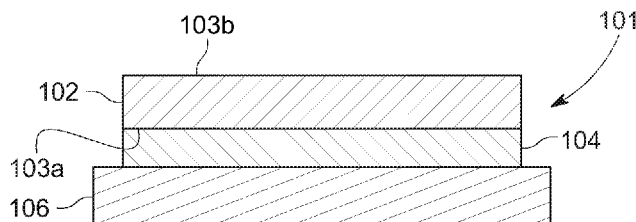


FIG. 1

(57) Abstract: A conductive curable adhesive composition is useful for electronic packages such as semiconductor packages that require high adhesion, low elastic modulus, and high electrical and/or thermal conductivity. The adhesive composition may therefore be employed as a conductive die attach or lid attach adhesive.



FLEXIBLE CONDUCTIVE ADHESIVE COMPOSITIONS

FIELD

[0001] The present invention relates to conductive adhesives generally, and more particularly to thermally and electrically conductive adhesives for electronic packages such as semiconductor packages. The conductive adhesives may be used as die attach or lid attach paste or film.

BACKGROUND

[0002] Conductive compositions are widely used in the fabrication and assembly of semiconductor packages and microelectronic devices. For example, metallic solder alloy (paste or preform) is used to bond electronic components to the circuit board. Limitations with the use of solder for affixation, such as the use of lead and flux agents, as well as high processing temperatures, has driven the use of conductive adhesives for component affixation in electronic packages. Attachment of electronic components, such as semiconductor dies, to a substrate in an electronic package is typically accomplished through the use of an adhesive that bonds the electronic component to the substrate surface. Numerous adhesives have been used over the years for this purpose, and are known as die attach adhesives or films to bond integrated circuit chips to substrates, lid attach adhesives or films to adhere metal lids to substrates, and assembly-conductive adhesives to bond circuit assemblies to the substrate board.

[0003] Typical conductive adhesives are sufficiently versatile to offer acceptable adhesion after cure, stable electrical resistance at high temperatures and humidity over time, and adequate thermal conductivity to ensure compliance with regulatory equipment. However, with increasing demand for high computing power and low-stress semiconductor packages, conventional conductive compositions are unable to simultaneously meet all the critical operating requirements. For example, metallic solder alloys exhibit high modulus values, such as >20 GPa at 25°C , which is not suitable for low-stress electronic packages. Many conductive adhesives require high modulus values, such as >1.6 GPa, to obtain sufficient adhesion strength. The limited post-cure flexibility of such conductive adhesives, however, limits their reliability in certain semiconductor package applications. Although certain adhesive compositions have

achieved useable post-cure flexibility characteristics, they have not to date exhibited both high adhesion qualities and good thermal and electrical conductivity.

[0004] It is therefore an aspect of the invention to provide a conductive adhesive composition that provides low post-cure modulus, while exhibiting high adhesion strength and good electrical and thermal conductivity properties.

[0005] It is another aspect of the invention to provide a conductive adhesive composition that provides a post cure modulus of less than 1.6 GPa at 25 °C, an adhesion strength of at least 3 MPa, a volume resistivity of less than $5 \times 10^{-4} \Omega \cdot \text{cm}$, and a thermal conductivity of at least 2 W/m·K.

SUMMARY

[0006] By means of the present invention, a curable composition may be formed into an adhesive layer that is positionable between, and adherent to a first body and a second body. In some embodiments, the adhesive layer may be positionable between a heat source and a heat sink, wherein the curable composition is thermally conductive to dissipate excess heat from the heat source to the heat sink. The curable composition may provide a conductive die attach film or a lid attach film with low modulus, yet high adhesion and conductivity characteristics.

[0007] In one embodiment, a conductive adhesive composition of the present invention includes a curable resin system having between 0.1 and 10 wt.% of a first resin material including one or more of a maleimide-functionalized resin, an itaconimide-functionalized resin, and a nadimide-functionalized resin, between 0.5 and 15 wt.% of a (meth)acrylate resin, and between 0.5 and 15 wt.% of a rubber or elastomer-modified epoxy resin. In addition to the curable resin system, the adhesive composition includes a filler being at least one of thermally and electrically conductive, and a curing agent. The composition, when cured, exhibits an elastic modulus of less than 1.6 GPa at 25 °C, a volume resistivity of less than $5 \times 10^{-4} \Omega \cdot \text{cm}$, and a thermal conductivity of at least 2 W/m·K.

[0008] In some embodiments, the first resin material includes a hydrocarbyl segment of least 20 carbon atoms. The first resin material may be monomeric or oligomeric, and may be free-radical curable to form a polymer network.

[0009] In some embodiments, the (meth)acrylate resin may include a hydrocarbyl segment of at least 20 carbon atoms. The (meth)acrylate resin may be selected from polybutadiene diacrylate, (meth)acrylated polyisoprene, and combinations thereof.

[0010] In some embodiments, the epoxy resin includes a hydrocarbyl segment of at least 20 carbon atoms.

[0011] In some embodiments, each of the first resin material, the (meth)acrylate resin, and the epoxy resin include a hydrocarbyl segment of at least 20 carbon atoms.

[0012] The conductive adhesive composition may include at least 75 wt.% of the filler. The filler may be particulate selected from silver, nickel, cobalt, copper, gold, palladium, platinum, carbon black, carbon fiber, graphite, carbon nanotubes, aluminum, indium tin oxide, silver coated copper, silver coated aluminum, silver coated graphite, nickel coated graphite, bismuth, tin, bismuth-tin alloy, metal coated glass spheres, silver coated fiber, silver coated spheres, antimony-doped tin oxide, alloys thereof, and combinations thereof.

[0013] In some embodiments, the curing agent may be selected from ureas, aliphatic and aromatic amines, polyamides, imidazoles, dicyandiamides, hydrazides, urea-amine hybrid curing systems, free radical initiators, organic bases, transition metal catalysts, phenols, acid anhydrides, Lewis acids, Lewis bases, peroxy esters, peroxy carbonates, hydroperoxides, alkylperoxides, arylperoxides, azo compounds, and combinations thereof.

[0014] In another embodiment, a conductive adhesive composition of the present invention includes a resin system having a first resin material selected from a maleimide-functionalized resin, a nadimide-functionalized resin, an itaconide-functionalized resin, and combinations thereof, the first resin material including a hydrocarbyl segment of at least 20 carbon atoms. The resin system further includes a (meth)acrylate resin including a hydrocarbyl segment of at least 20 carbon atoms, and an epoxy resin having a hydrocarbyl segment of at least 20 carbon atoms. The composition further includes a filler that is at least one of thermally and electrically conductive, and a curing agent.

[0015] In some embodiments, the (meth)acrylate resin is selected from polybutadiene diacrylate, (meth)acrylated polyisoprene, and combinations thereof. The epoxy resin may be curable into a three-dimensional network.

[0016] An electronic package of the present invention may include a silicon substrate, the conductive adhesive composition described above as applied to a surface of the silicon substrate,

and an electronic component connected to the silicon substrate by the conductive adhesive composition when in a cured condition.

[0017] In some embodiments, the conductive adhesive composition is disposed as a film onto the surface of the silicon substrate.

BRIEF DESCRIPTION OF THE DRAWINGS

[0018] Figure 1 is a schematic illustration of an assembly using the conductive adhesive compositions of the present invention.

[0019] Figure 2 is a schematic illustration of a semiconductor chip utilizing the conductive adhesive compositions of the present invention.

[0020] Figure 3 is a schematic illustration of an electronic package utilizing a die attach film formed from the conductive adhesive compositions of the present invention.

DETAILED DESCRIPTION

[0021] A composition, and in some embodiments, an adhesive composition, such as for use in die attach applications is provided. The adhesive composition includes a curable resin system, a curing agent, and conductive filler. The curing agent is effective to cure at least one resin of the curable resin system.

[0022] The conductive adhesive compositions of the present invention may be formed as a coating or film on a substrate, typically as an adherent along a thermal dissipation pathway, such as between a heat-generating electronic component and a substrate to which the component is attached. The conductive adhesive compositions of the present invention may be suitable as a die attach film, sometimes referred to as a Conductive Die Attach Film (“CDAF”), in electronic packages for securing “dies”, such as processors, power semiconductor devices, and the like, to a silicon wafer substrate. The compositions preferably exhibit sufficient wettability to coat the respective substrate surface prior to curing. When cured, the conductive film preferably exhibits a very low elastic modulus of less than 1.6 GPa when tested by dynamic mechanical analysis at 25 °C, a thermal conductivity of at least 2 W/m·K, and optionally a volume resistivity of less than $5 \times 10^{-4} \Omega\cdot\text{cm}$.

[0023] The curable adhesive compositions of the present invention may preferably be 1-part curable compositions that are activated at elevated temperatures. The curable compositions are therefore stable at room temperature, and are curable upon the application of sufficient heat. The curable compositions may be curable through an agent facilitated pathway, wherein the one or more curing agents present in the composition become active only above a minimum temperature threshold. Such curing agents are sometimes referred to as latent curing agents. In some embodiments, the one or more curing agents present in the composition may include those which act as a free radical initiator, usually activatable only at elevated temperature.

Resin Material

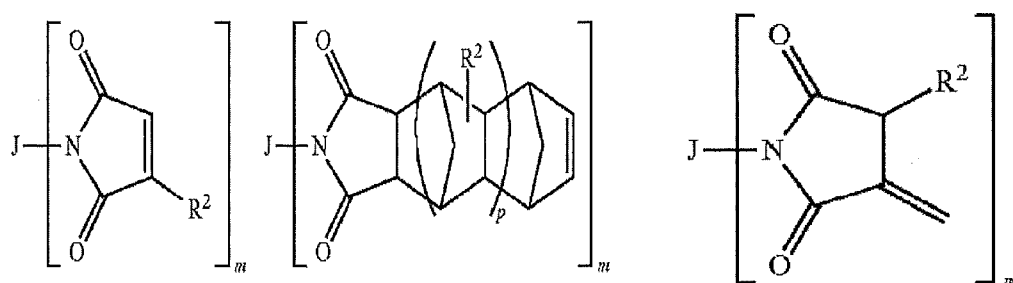
[0024] The conductive adhesives of the present invention comprise a matrix formed from at least a curable resin material and a chemical curing agent, wherein the term “resin” may include any natural or synthetic organic compound or mixture that is convertible into a polymer. Preferably, a cure reaction is initiated with exposure between the curable resin material and the curing agent, in some cases when in the presence of an environmental cure reaction facilitator, such as water, heat, pressure, electromagnetic radiation, and the like. In preferred embodiments, the cure reaction is initiated with exposure between the curable resin material and the curing agent in the presence of heat, and particularly temperatures above a minimum threshold.

[0025] Applicant has determined that, in order to obtain the desired physical properties of the curable resin material, a specific blend of resin materials is required. In particular, the adhesive, when cured, desirably exhibits an adhesion force of at least 3 MPa, and elastic modulus of less than 1.6 GPa, a volume resistivity of less than $5 \times 10^{-4} \Omega\text{-cm}$, and a thermal conductivity of at least 2 W/m·K. A specific blend of resins in a curable resin system has been surprisingly found by applicant to deliver such combination of physical properties, while conventional curable resin systems fall short, typically with one or both of the high adhesion force and the low elastic modulus properties.

[0026] The curable resin system may include at least one of a maleimide-functionalized resin, an itaconimide-functionalized resin, and a nadimide-functionalized resin as a first resin material. In some embodiments, one or more of the maleimide-functionalized resin, the itaconimide-functionalized resin, and the nadimide-functionalized resin includes a flexible aliphatic or aromatic/aliphatic backbone, wherein the backbone includes one or more straight or branched chain hydrocarbyl segments, wherein each hydrocarbyl segment has at least 20 carbon atoms. In

some embodiments, each of the maleimide-functionalized resin, the itaconimide-functionalized resin, and the nadimide-functionalized resin present in the first resin material includes a flexible aliphatic or aromatic/aliphatic backbone, wherein the backbone includes one or more straight or branched chain hydrocarbyl segments, wherein each hydrocarbyl segment has at least 20 carbon atoms. In some embodiments, the hydrocarbyl segments are straight chain segments with at least 20 carbon atoms.

[0027] In some embodiments, the maleimide-functionalized resins, itaconimide-functionalized resins, and the nadimide-functionalized resins contemplated for use herein have the following structure:



respectively, wherein:

m is 1-15,

p is 0-15,

each R² is independently selected from hydrogen or lower alkyl, and

J is a monovalent or a polyvalent radical selected from:

non-aromatic hydrocarbyl or substituted non-aromatic hydrocarbyl species having in the range of 20 up to 500 carbon atoms, where the non-aromatic hydrocarbyl species is selected from alkyl, alkenyl, alkynyl, cycloalkyl, or cycloalkenyl;

non-aromatic hydrocarbylene or substituted non-aromatic hydrocarbylene species having in the range of 20 up to 500 carbon atoms, where the non-aromatic hydrocarbylene species are selected from alkylene, alkenylene, alkynylene, cycloalkylene, or cycloalkenylene,

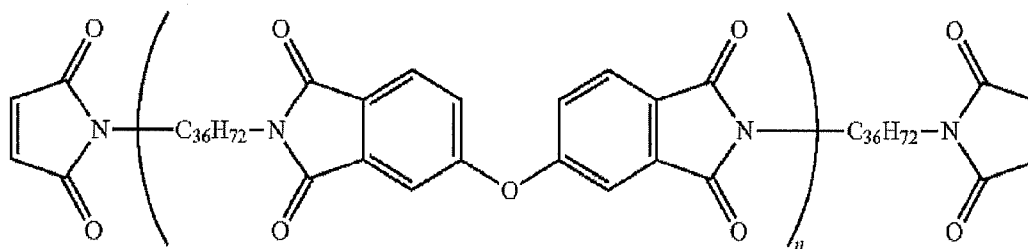
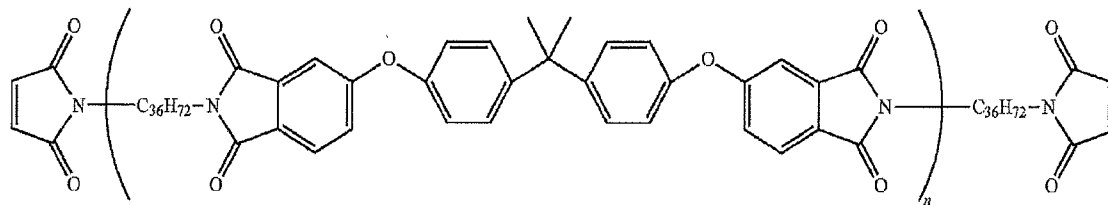
heterocyclic or substituted heterocyclic species having in the range of 20 up to 500 carbon atoms,

polysiloxane, or

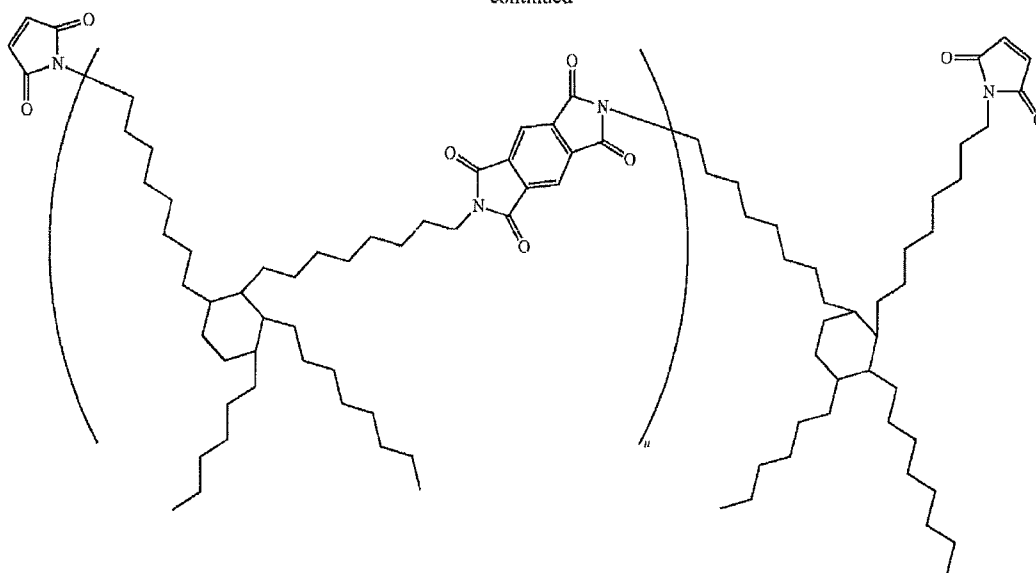
polysiloxane-polyurethane block copolymers, as well as combinations of one or more of the above with a linker selected from a covalent bond, - O- , - S-, - NR-, - NR-C(O)-, -NR-C(O)-O-, - NR- C(O)NR-, - S-C(O)-, - S-C(O)-O-, - S- C(O)NR-, -O- S(O)₂-, - O- S(O)₂- O-, -O- S(O)₂- NR-, -O- S(O)-, -O- S(O)- 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)-, -ONR-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-, -NRC(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-NRS(O)-NR-, -O- NR-S(O)₂-O-, -O- NRS(O)₂-NR-, -O-NR-S(O)₂-, -O-P(O)R₂-, -S-P(O)R₂-, or -NR-P(O)R₂-; where each R is independently hydrogen, alkyl or substituted alkyl.

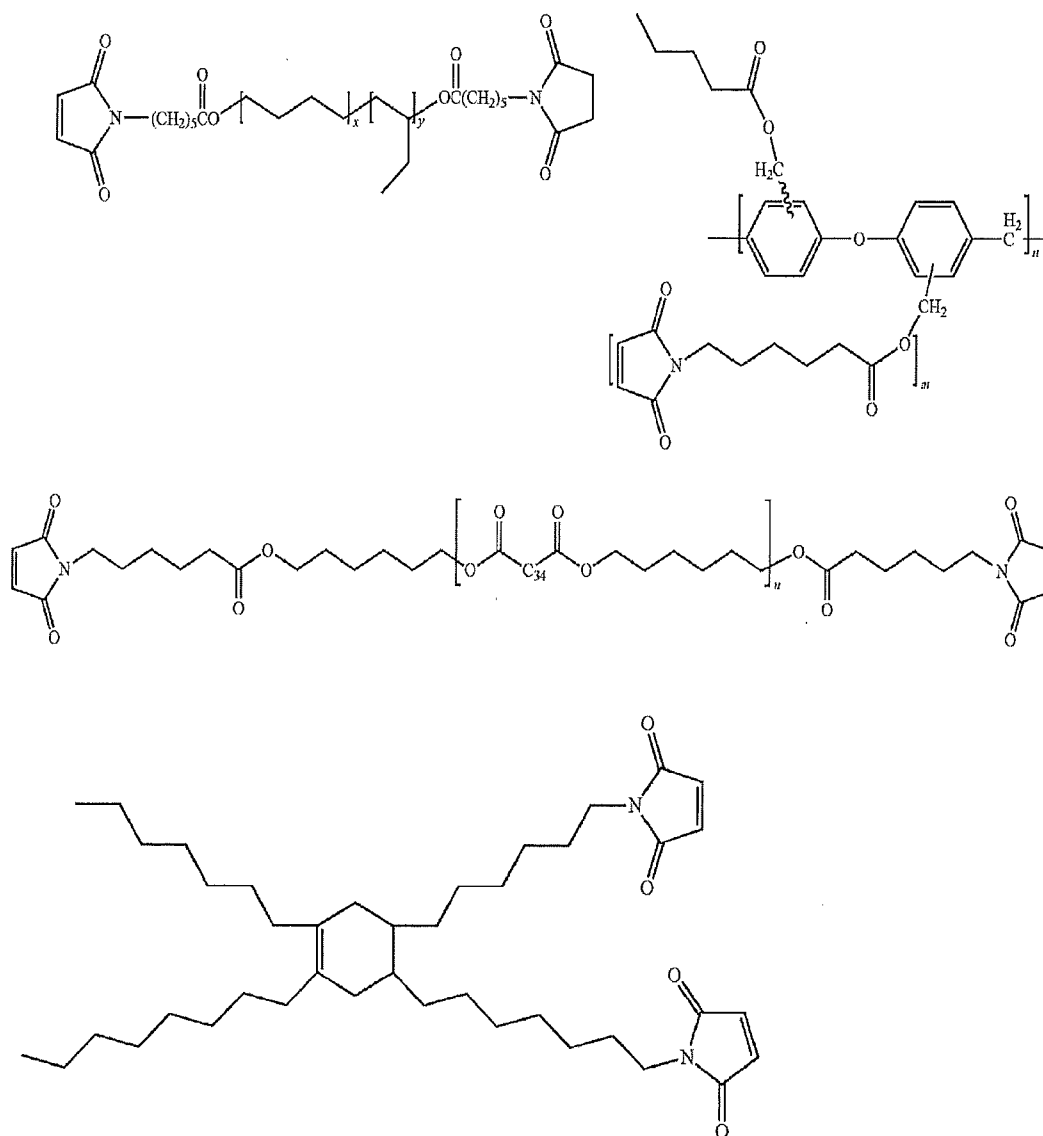
[0028] In certain embodiments, J of the above-described maleimide, nadimide or itaconimide is oxyalkyl, thioalkyl, aminoalkyl, carboxylalkyl, oxyalkenyl, thioalkenyl, aminoalkenyl, carboxyalkenyl, oxyalkynyl, thioalkynyl, aminoalkynyl, carboxyalkynyl, oxycycloalkyl, thiocycloalkyl, aminocycloalkyl, carboxycycloalkyl, oxycycloalkenyl, thiocycloalkenyl, aminocycloalkenyl, carboxycycloalkenyl, heterocyclic, oxyheterocyclic, thioheterocyclic, aminoheterocyclic, carboxyheterocyclic, oxyalkylene, thioalkylene, aminoalkylene, carboxyalkylene, oxyalkenylene, thioalkenylene, aminoalkenylene, carboxyalkenylene, oxyalkynylene, thioalkynylene, aminoalkynylene, carboxyalkynylene, oxycycloalkylene, thiocycloalkylene, aminocycloalkylene, carboxycycloalkylene, oxycycloalkenylene, thiocycloalkenylene, aminocycloalkenylene, carboxycycloalkenylene, 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, or a carboxyheteroatom-containing di- or polyvalent cyclic moiety.

[0029] Further example structures of the maleimide-functionalized resin, the nadimide-functionalized resin, and the itaconamide-functionalized resin include:



-continued





[0030] In some embodiments, the first resin material is present in the compositions of the invention in a range of between 0 and 10 wt.%. In some embodiments, the first resin material is present in the compositions of the invention in a range of between 0.1 and 10 wt.%. In some embodiments, the first resin material is present in the compositions of the invention in a range of between 0.2 and 9 wt.%. In some embodiments, the first resin material is present in the compositions of the invention in a range of between 0.2 and 5 wt.%. In some embodiments, the first resin material is present in the compositions of the invention in a range of between 0.5 and 2

wt.%. In some embodiments, the first resin material is present in the compositions of the invention in a range of between 0.5 and 1 wt.%.

[0031] The first resin material may include any one or more of the maleimide-functionalized resins, the itaconimide-functionalized resins, and the nadimide-functionalized resins as described herein. In some embodiments, the first resin material includes only the one or more maleimide-functionalized resins, the itaconimide-functionalized resins, and the nadimide-functionalized resins described herein. The maleimide-functionalized resins, the itaconimide-functionalized resins, and the nadimide-functionalized resins may be any of monomeric or oligomeric, and may be free-radical curable to form a polymer network.

[0032] The curable resin system preferably includes a (meth)acrylate resin. Acrylates useful in the curable resin material may be selected from a host of different compounds. Acrylates contemplated for use in the practice of the present invention are well known in the art. See, for example, U.S. Pat. No. 5,717,034, the entire contents of which are hereby incorporated by reference herein. Exemplary acrylates contemplated for use herein include monofunctional (meth)acrylates, difunctional (meth)acrylates, trifunctional (meth)acrylates, polyfunctional (meth) acrylates, and the like.

[0033] Exemplary monofunctional (meth)acrylates include phenylphenol acrylate, methoxypolyethylenc acrylate, acryloyloxyethyl succinate, fatty acid acrylate, methacryloyloxy ethylphthalic acid, phenoxyethylene glycol methacrylate, fatty acid methacrylate, B-carboxyethyl acrylate, isobomyl acrylate, isobutyl acrylate, t-butyl acrylate, hydroxyethyl acrylate, hydroxypropyl acrylate, dihydrocyclopentadiethyl acrylate, cyclohexyl methacrylate, t-butyl methacrylate, dimethylaminoethyl methacrylate, diethylaminoethyl methacrylate, t-butylaminoethyl methacrylate, 4-hydroxybutyl acrylate, tetrahydrofurfuryl acrylate, benzyl acrylate, ethyl carbitol acrylate, phenoxyethyl acrylate, methoxytriethylene glycol acrylate, monopentaerythritol acrylate, dipentaerythritol acrylate, tripentaerythritol acrylate, polypentaerythritol acrylate, and the like.

[0034] Exemplary difunctional (meth)acrylates include hexane diol dimethacrylate, hydroxyacryloyloxypropyl methacrylate, hexanediol diacrylate, urethane acrylate, epoxyacrylate, bisphenol A-type epoxyacrylate, modified epoxyacrylate, fatty acid-modified epoxyacrylate, amine-modified bisphenol A-type epoxyacrylate, allyl methacrylate, ethylene glycol dimethacrylate, diethylene glycol dimethacrylate, ethoxylated bisphenol A dimethacrylate,

tricyclodecanedi methanol dimethacrylate, glycerin dimethacrylate, polypropylene glycol diacrylate, propoxylated ethoxylated bisphenol A diacrylate, 9,9-bis(4-(2-acryloyloxyethoxy)phenyl) fluorene, tricyclodecane diacrylate, dipropylene glycol diacrylate, polypropylene glycol diacrylate, PO-modified neopentyl glycol diacrylate, tricyclodecanedimethanol diacrylate, 1,12-dodecanediol dimethacrylate, and the like.

[0035] Exemplary trifunctional (meth)acrylates include trimethylolpropane trimethacrylate, trimethylolpropane triacrylate, trimethylolpropaneethoxy triacrylate, polyether triacrylate, glycerin propoxy triacrylate, and the like.

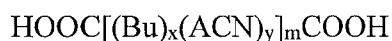
[0036] Exemplary polyfunctional (meth)acrylates include dipentaerythritol polyacrylate, dipentaerythritol hexaacrylate, pentaerythritol tetraacrylate, pentaerythritolethoxy tetraacrylate, ditrimethylolpropane tetraacrylate, and the like.

[0037] In some embodiments, the (meth)acrylate resin has a flexible aliphatic or aliphatic/aromatic backbone, wherein the backbone includes one or more straight or branched chain hydrocarbyl segments, wherein each hydrocarbyl segment has at least 20 carbon atoms. In some embodiments, the hydrocarbyl segments are straight chain segments with at least 20 carbon atoms. Examples of these (meth)acrylate resins include polybutadiene diacrylate, (meth)acrylated polyisoprene, and combinations thereof. In some embodiments, the (meth)acrylate resin is monomeric or oligomeric, and is free-radical curable to form a polymer network.

[0038] In some embodiments, the (meth)acrylate resin is present in the compositions of the invention in a range of between 0.5 and 25 wt.%. In some embodiments, the (meth)acrylate resin is present in the compositions of the invention in a range of between 0.5 and 15 wt.%. In some embodiments, the (meth)acrylate resin is present in the compositions of the invention in a range of between 1 and 10 wt.%. In some embodiments, the (meth)acrylate resin is present in the compositions of the invention in a range of between 5 and 10 wt.%.

[0039] The curable resin system preferably further includes an epoxy resin. In some embodiments, the epoxy resin is rubber or elastomer-modified epoxy. In some embodiments, the epoxy resin has a flexible aliphatic or aliphatic/aromatic backbone, wherein the backbone includes straight or branched chain hydrocarbyl segments, wherein each hydrocarbyl segment has at least 20 carbon atoms.

[0040] In some embodiments, the epoxy resin contemplated for use herein is an epoxidized carboxyl-terminated butadiene-acrylonitrile (CTBN) oligomer or polymer. In some embodiments, the epoxidized CTBN oligomer or polymer is an epoxy-containing derivative of an oligomeric or polymeric precursor having the structure:



wherein:

each Bu is a butylene moiety (e.g. 1,2-butadienyl or 1,4-butadienyl),

each ACN is an acrylonitrile moiety,

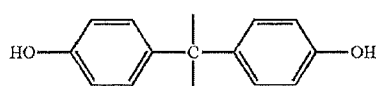
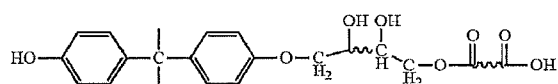
the Bu units and the ACN units can be arranged randomly or in blocks,

each of x and y are greater than zero, provided the total of $x+y=1$,

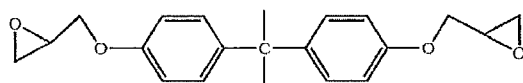
the ratio of x:y falls in the range of about 10:1 – 1:10, and

m falls in the range of about 20 to about 100.

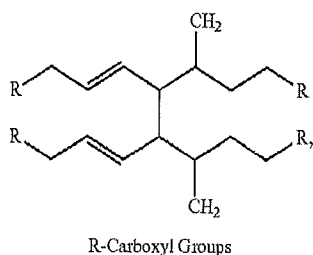
As readily recognized by those of skill in the art, epoxidized CTBN oligomers or polymers can be made in a variety of ways, e.g., from (1) a carboxyl terminated butadiene/acrylonitrile copolymer, (2) an epoxy resin and (3) bisphenol A:



Bisphenol A Chain Extender



Reactive Epoxy



by reaction between the carboxylic acid group of CTBN and epoxies (via chain-extension reactions), and the like.

[0041] Examples of the epoxy resin (i.e., rubber or elastomer-modified epoxy) include epoxidized CTBN oligomers or polymers made from (1) a carboxyl terminated butadiene/acrylonitrile copolymer, (2) an epoxy resin and (3) bisphenol A as described above; Hypro™ Epoxy-Functional Butadiene-Acrylonitrile Polymers (formerly Hycar® ETBN), and the like.

[0042] Rubber or elastomer-modified epoxies include epoxidized derivatives of:

(a) homopolymers or copolymers of conjugated dienes having a weight average molecular weight (M_w) of 30,000 to 400,000 or higher as described in U.S. Pat. No. 4,020,036 (the entire contents of which are hereby incorporated by reference herein), in which conjugated dienes contain from 4-11 carbon atoms per molecule (such as 1,3-butadiene, isoprene, and the like);

(b) epihalohydrin homopolymers, a copolymer of two or more epihalohydrin monomers, or a copolymer of an epihalohydrin monomer(s) with an oxide monomer(s) having a number average molecular weight (M_n) which varies from about 800 to about 50,000, as described in U.S. Pat. No. 4,101,604 (the entire contents of which are hereby incorporated by reference herein);

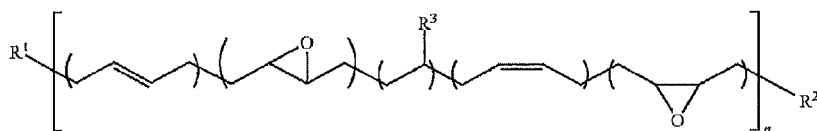
(c) hydrocarbon polymers including ethylene/propylene copolymers and copolymers of ethylene/propylene and at least one nonconjugated diene, such as ethylene/propylene/hexadiene/norbornadiene, as described in U.S. Pat. No. 4,161,471; or

(d) conjugated diene butyl elastomers, such as copolymers consisting of from 85 to 99.5% by weight of a C4-C5 olefin combined with about 0.5 to about 15% by weight of a conjugated multi-olefin having 4 to 14 carbon atoms, copolymers of isobutylene and isoprene where a major portion of the isoprene units combined therein have conjugated diene unsaturation

(see, for example, U.S. Pat. No. 4,160,759; the entire contents of which are hereby incorporated by reference herein).

[0043] In certain embodiments, the epoxy resin is an epoxidized polybutadiene diglycidylether oligomer or polymer.

[0044] In certain embodiments, epoxidized polybutadiene diglycidylether oligomers contemplated for use herein have the structure:



wherein:

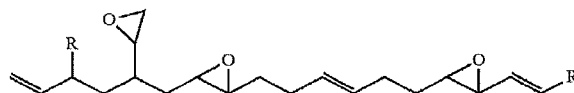
R^1 and R^2 are each independently H or lower alkyl,

R^3 is H, saturated or unsaturated hydrocarbyl, or epoxy,

at least 1 epoxy-containing repeating unit set forth above, and at least one olefinic repeating unit set forth above are present in each oligomer, and, when present, in the range of 1-10 of each repeating unit is present, and

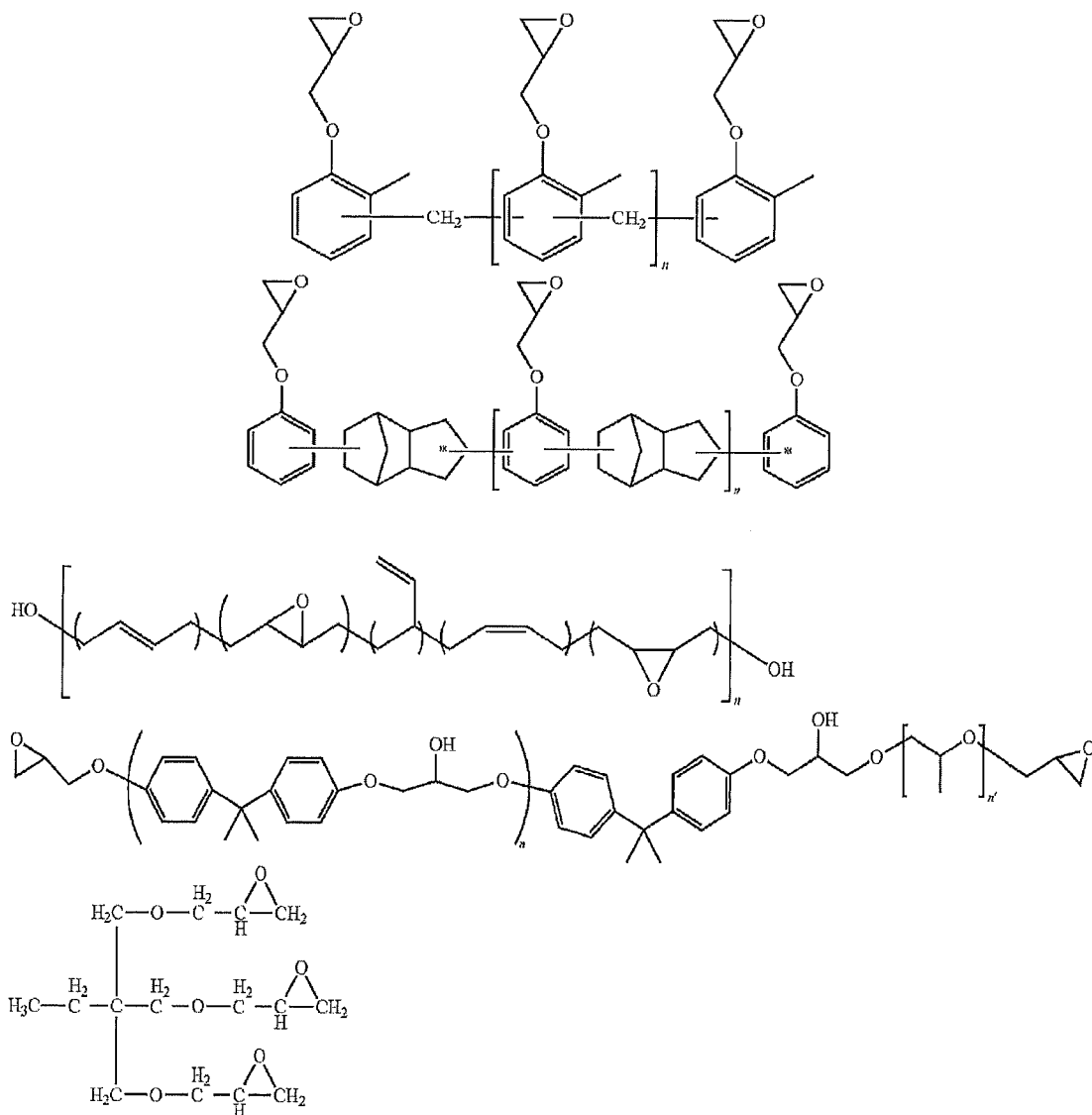
n falls in the range of 2-150.

[0045] In certain embodiments, epoxidized polybutadiene diglycidylether oligomer or polymer contemplated for use in the practice of the present invention has the structure:



wherein R is H, OH, lower alkyl, epoxy, oxirane-substituted lower alkyl, aryl, alkaryl, and the like.

[0046] Examples of epoxy resin contemplated for use herein (i.e., epoxy having a flexible backbone) include:



[0047] A wide variety of epoxy-functionalized resins are contemplated for use in the curable compositions of the present invention. For example, liquid-type epoxy resins based on bisphenol A, liquid-type epoxy resins based on bisphenol F, multifunctional epoxy resins based on phenol novolac resin, dicyclopentadiene-type epoxy resins, naphthalene-type epoxy resins, and the like. Other example epoxy-functionalized resins contemplated for use herein include the diepoxide of the cycloaliphatic alcohol, hydrogenated bisphenol A (commercially available as Epalloy 5000), a difunctional cycloaliphatic glycidyl ester of hexahydrophthalic anhydride (commercially available as Epalloy 5200), Epiclon EXA-835LV, Epiclon HP-7200L, and the like, as well as mixtures of any two or more thereof.

[0048] In some embodiments, the curable composition may include a combination of two or more different epoxy-functionalized resins, including two or more different bisphenol-based epoxies. The bisphenol-based epoxies may be selected from bisphenol A, bisphenol F, or bisphenol S epoxies, and combinations thereof. In addition, two or more different bisphenol epoxies within the same type of resin (such A, F, or S) may be used.

[0049] Commercially available examples of the bisphenol epoxies contemplated for use herein include bisphenol-F-type epoxies (such as RE-404-S from Nippon Kayaku, Japan, and EPICLON 830 (RE1801), 830S (RE1815), 830A (RE1826) and 830W from Dai Nippon Ink & Chemicals, Inc., and RSL 1738 and YL-983U from Resolution) and bisphenol-A-type epoxies (such as YL-979 and 980 from Resolution). Further examples of commercially available epoxy resins include Epon 828, Epon 826, Epon 862 (all from Hexion Co., Ltd.), DER 331, DER 383, DER 332, DER 330-EL, DER 331-EL, DER 354, DER 321, DER 324, DER 29, DER 353 (all from Dow Chemical Co.), JER YX8000, JER RXE21, JER YL 6753, JER YL6800, JER YL980, JER 825, and JER 630 (all from Japan Epoxy Resins Co).

[0050] The bisphenol epoxies available commercially from Dai Nippon and noted above are promoted as liquid undiluted epichlorohydrin-bisphenol F epoxies having much lower viscosities than conventional epoxies based on bisphenol A epoxies and have physical properties similar to liquid bisphenol A epoxies. Bisphenol F epoxy has lower viscosity than bisphenol A epoxies, all else being the same between the two types of epoxies, which affords a lower viscosity and thus a fast flow underfill sealant material. The Epoxy Equivalent Weight (EEW), which is the molecular weight divided by the number of epoxy groups of these four bisphenol F epoxies is between 165 and 180. The viscosity at 25°C is between 3,000 and 4,500 cps (except for RE1801 whose upper viscosity limit is 4,000 cps). The hydrolyzable chloride content is reported as 200 ppm for RE1815 and 830W, and that for RE1826 as 100 ppm.

[0051] The bisphenol epoxies available commercially from Resolution and noted above are promoted as low chloride containing liquid epoxies. The bisphenol A epoxies have an EEW (g/eq) of between 180 and 195 and a viscosity at 25°C of between 100 and 250 cP. The total chloride content for YL-979 is reported as between 500 and 700 ppm, and that for YL-980 as between 100 and 300 ppm. The bisphenol F epoxies have an EEW (g/eq) of between 165 and 180 and a viscosity at 25°C of between 30 and 60. The total chloride content for RSL-1738 is reported as between 500 and 700 ppm, and that for YL-983U as between 150 and 350 ppm.

[0052] In addition to the bisphenol epoxies, other epoxy compounds are contemplated for use as the epoxy component of invention formulations. For instance, cycloaliphatic epoxies, such as 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexylcarbonate, can be used. Also, monofunctional, difunctional or multifunctional reactive diluents may be used to adjust the viscosity and/or lower the glass transition temperature (T_g) of the resulting resin material. Exemplary reactive diluents include butyl glycidyl ether, cresyl glycidyl ether, o-cresyl glycidyl ether, polyethylene glycol glycidyl ether, polypropylene glycol glycidyl ether, and the like.

[0053] Other epoxies suitable for use herein include polyglycidyl derivatives of phenolic compounds, such as those available commercially under the tradename EPON, such as EPON 828, EPON 1001, EPON 1009, and EPON 1031 from Resolution; DER 331, DER 332, DER 334, and DER 542 from Dow Chemical Co.; and BREN-S from Nippon Kayaku. Other suitable epoxies include polyepoxides prepared from polyols and the like and polyglycidyl derivatives of phenol-formaldehyde novolacs, the latter of such as DEN 431, DEN 438, and DEN 439 from Dow Chemical. Cresol analogs are also available commercially under the tradename ARALDITE, such as ARALDITE ECN 1235, ARALDITE ECN 1273, and ARALDITE ECN 1299 from Ciba Specialty Chemicals Corporation. SU-8 is a bisphenol-A-type epoxy novolac available from Resolution. Polyglycidyl adducts of amines, aminoalcohols and polycarboxylic acids are also useful in this invention, commercially available resins of which include GLYAMINE 135, GLYAMINE 125, and GLYAMINE 115 from F.I.C. Corporation; ARALDITE MY-720, ARALDITE 0500, and ARALDITE 0510 from Ciba Specialty Chemicals and PGA-X and PGA-C from the Sherwin-Williams Co.

[0054] In some embodiments, the epoxy resin is present in the compositions of the invention in a range of between 0.5 and 15 wt.%. In some embodiments the epoxy resin is present in the compositions of the invention in a range of between 0.5 and 10 wt.%. In some embodiments, the epoxy resin is present in the compositions of the invention in a range of between 1 and 10 wt.%. In some embodiments, the epoxy resin is present in the compositions of the invention in a range of between 1 and 5 wt.%. In some embodiments, the epoxy resin is present in the compositions of the invention in a range of between 1 and 2 wt.%.

[0055] In some embodiments, alpha, beta-ethylenically unsaturated dicarboxylic acids and derivatives, for example maleic anhydride, may be adducted to unsaturated polymers as polybutadiene or styrene butadiene resins. The rubberized polymers have been determined to

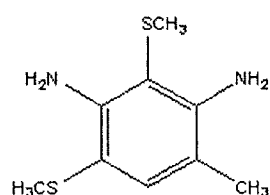
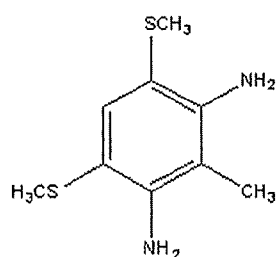
improve adhesion and act as a flexibilizer. The conductive compositions of the present invention may include a polybutadiene in a range of between 0 and 10 wt.%. In some embodiments, the polybutadiene is present in the compositions of the invention in a range of between 0.5 and 10 wt.%. In some embodiments, the polybutadiene is present in the compositions of the invention in a range of between 1 and 10 wt.%. In some embodiments, the polybutadiene is present in the compositions of the invention in a range of between 1 and 5 wt.%. The polybutadiene component may, in some embodiments, be a maleated polybutadiene or a carboxyl polybutadiene, and may be present in addition to the first resin material described above.

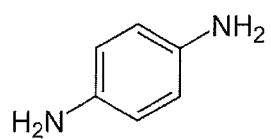
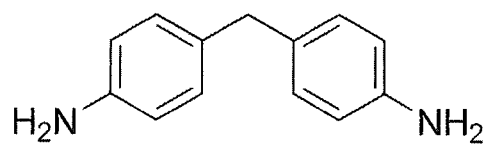
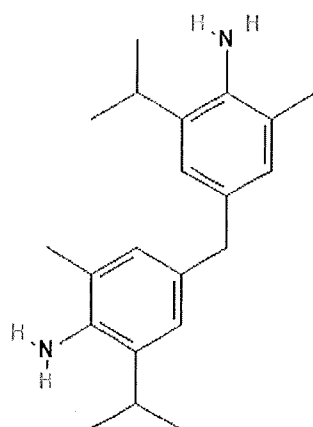
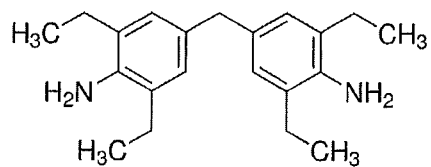
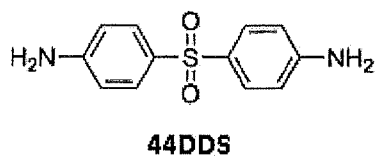
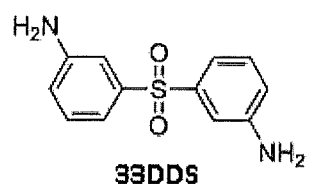
Curing Agent

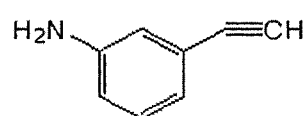
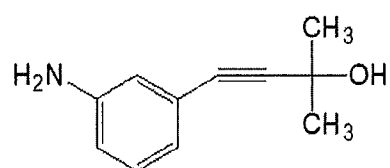
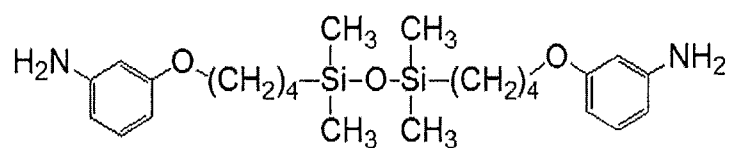
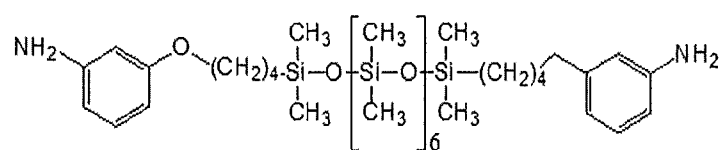
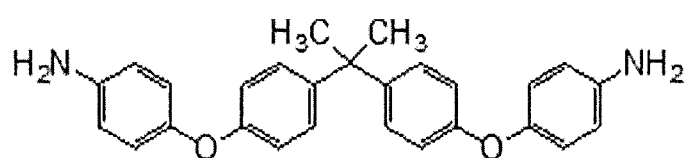
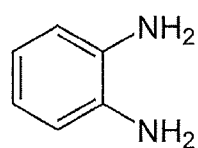
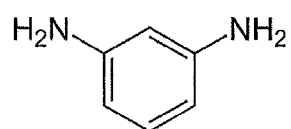
[0056] Curing agents contemplated for use in the practice of the present invention include ureas, aliphatic and aromatic amines, polyamides, imidazoles, dicyandiamides, hydrazides, urea-amine hybrid curing systems, free radical initiators, organic bases, transition metal catalysts, phenols, acid anhydrides, Lewis acids, Lewis bases, and the like. See, for example, U.S. Pat. No. 5,397,618, the entire contents of which are hereby incorporated by reference herein.

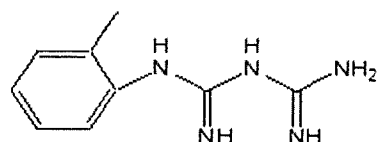
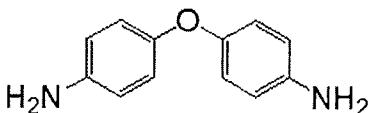
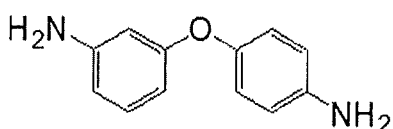
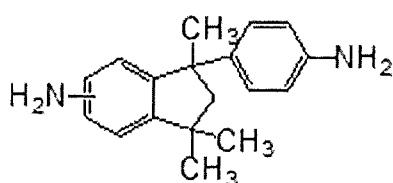
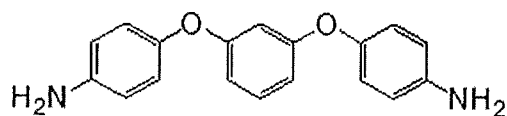
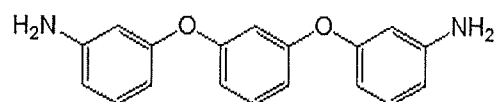
[0057] Exemplary free radical initiators include peroxy esters, peroxy carbonates, hydroperoxides, alkylperoxides, arylperoxides, azo compounds, and the like.

[0058] Example cure agents in the compositions of the present invention include the following structures:









[0059] Cure agents may be present in the compositions of the invention in a range of between 0.1 and 10 wt.%. In some embodiments, the cure agents may be present in the compositions of the invention in a range of between 0.1 and 5 wt.%. In some embodiments, the cure agents may be present in the compositions of the invention in a range of between 0.2 and 3 wt.%.

[0060] In some embodiments, the cure agents may include an epoxy hardener, such as an amine-based curing agent, a phenol novoloac hardener, and the like. The epoxy hardener may be present in the compositions of the invention in a range of between 0.1 and 5 wt.%. In some

embodiments, the epoxy hardener may be present in the compositions of the invention in a range of between 0.1 and 3 wt.%. In some embodiments, the epoxy hardener may be present in the compositions of the invention in a range of between 0.2 and 2 wt.%.

[0061] In some embodiments, the cure agents may include a free-radical initiator. The free-radical initiator may be present in the compositions of the present invention in a range of between 0.1 and 5 wt.%. In some embodiments, the free-radical initiator may be present in a range of between 0.1 and 3 wt.%. In some embodiments, the free-radical initiator may be present in a range of between 0.1 and 1 wt.%.

Conductive Filler

[0062] In order to enhance the electrical and/or thermal conductivity, the conductive compositions of the present invention include conductive filler dispersed therein. The conductive filler may be in particulate form, and may be both thermally conductive and electrically conductive. In some embodiments, the filler may be thermally conductive and electrically insulating.

[0063] Conductive fillers contemplated for use in the present compositions include silver, nickel, cobalt, copper, gold, palladium, platinum, carbon black, carbon fiber, graphite, carbon nanotubes, aluminum, indium-tin oxide, silver-coated copper, silver-coated aluminum, silver-coated graphite, nickel-coated graphite, bismuth, tin, bismuth-tin alloy, metal-coated glass spheres, silver-coated fiber, silver-coated spheres, antimony-doped tin oxide, conductive nanofillers, alloys, and combinations thereof.

[0064] In some embodiments, the conductive filler may be substantially spherical, plate-like, rod-like, or combinations thereof. It is contemplated that a particle size distribution may be employed to fit the parameters of any particular application, although certain particle size distributions may be found to be more effective than others.

[0065] Conductive fillers may be present in the compositions of the invention in a range of between 75 and 95 wt.%. In some embodiments, the conductive fillers are present in the compositions of the invention in a range of between 80 and 90 wt.%.

[0066] In some embodiments, the conductive filler may comprise a multi-modal particle size distribution, having discrete concentrations of particles with different average particle sizes. In some embodiments, a first portion of the conductive filler may have an average particle size (d_{50}) of less than 1 micrometer, and a second portion of the conductive filler may have an average

particle size (d_{50}) of greater than 1 micrometer. In some embodiments, the first portion of the conductive filler may comprise between 25 and 40 percent by weight of the total conductive filler. In some embodiments, the first portion of the conductive filler may comprise between 25 and 35 wt.% of the total conductive filler. Applicant has found that such particle size distributions can promote high conductivity values without detracting from the desired physical properties of the composition.

[0067] It is desirable that the curable compositions of the present invention, when cured, exhibit a thermal conductivity of at least 2 W/m·K, and more preferably at least 7 W/m·K.

Other Additives

[0068] In some embodiments, optionally, suitable flow additives, adhesion promoters, conductivity additives, toughening agents, and rheology modifiers may be added as desired. Optional flow additives include silicone polymers, ethyl acrylate/2-ethylhexyl acrylate copolymers, alkylol ammonium salt of acid, phosphoric acid esters of ketoxime or mixtures thereof.

[0069] Suitable adhesion promoters include various forms of silane.

[0070] Suitable conductivity additives include anhydride, glutaric acid, citric acid, phosphoric acid and other acid catalysts.

[0071] Suitable toughening agents include additives which enhance the impact resistance of the formulation to which they are introduced.

[0072] Suitable rheology modifiers include fumed silica and the like.

Cured Composition

[0073] The curable compositions of the present invention, when cured, may form a film-like adhesive. For the purposes hereof, the term “film” means a thin film having a thickness of less than 250 micrometers. In some embodiments, the film formed from the curable compositions of the present invention, alone or in combination, may be disposed at a surface of a substrate, such as a silicon substrate of an electronic package. The film may also be applied only a surface of a release-treated substrate liner for ease of handling and application to the package substrate. Example release-treated films include release-treated polypropylene, release-treated polyethylene, and release-treated polyethylene terephthalate.

[0074] The compositions of the present invention exhibit good flowability at relatively low temperatures, such as below 80 °C. This facilitates processing of the compositions into die attach films or lid attach films, including the step of laminating the compositions to a substrate. In some embodiments, compositions as described herein may be applied to a suitable substrate, then B-staged at elevated temperature to remove substantially all of the solvent therefrom.

[0075] Conductive adhesives according to the present invention may be characterized, upon cure, with reference to an elastic modulus thereof. For the purposes hereof, the term “elastic modulus” is intended to be equivalent to “tensile modulus” and “Young’s modulus”. In some embodiments, the elastic modulus of the cured adhesive, as measured by dynamic mechanical analysis (DMA) at 25 °C, is less than 1.6 GPa. In some embodiments, the elastic modulus of the cured adhesive is less than 1.0 GPa. In some embodiments, the elastic modulus of the cured adhesive is less than 500 MPa.

[0076] Conductive adhesives of the present invention may also be characterized, upon cure, with reference to the hot die shear strength thereof. In some embodiments, the hot die shear strength of the cured adhesive at 260 °C is at least 3 MPa. In some embodiments, the hot die shear strength of the cured adhesive at 260 °C is at least 5 MPa. In some embodiments, the hot die shear strength of the cured adhesive at 260 °C is between 5 and 10 MPa.

[0077] The conductive adhesives of the present invention, when cured, may have a volume resistivity of less than $5 \times 10^{-4} \Omega \cdot \text{cm}$. In some embodiments, the conductive adhesives of the present invention, when cured, may exhibit a volume resistivity of less than $3 \times 10^{-4} \Omega \cdot \text{cm}$. Additionally, the conductive adhesives of the present invention, when cured, may have a thermal conductivity of at least 2 W/m·K. In some embodiments, the conductive adhesives of the present invention, when cured, may have a thermal conductivity of at least 5 W/m·K. In some embodiments, the conductive adhesives of the present invention, when cured, may exhibit a thermal conductivity of at least 7 W/m·K.

[0078] In some embodiments, an assembly 101 as illustrated in Figure 1 may be prepared by applying the curable resin composition to a semiconductor substrate or silicon wafer 102, such as by ink jet printing, stencil printing, screen printing, or spray coating. Conductive adhesives of the present invention may also be applied to substrates through dispensing tools, such as time pressure dispensing valves, auger pumps, positive displacement pumps, and jetting valves. The application preferably uniformly coats an application surface of the substrate, and may be

partially cured, or B-staged, into an adhesive layer 104. Alternatively, the curable composition may first be applied to a support layer 106, such as a dicing tape, and then thermocompression bonded onto the application surface 103a of substrate 102. Support layer 106 may, in some embodiments, be a polyolefin film, such as one or more layers of polyethylene, polyvinyl chloride, polybutadiene, polybutene, polyurethane, polyester, polyamide, and copolymers thereof.

[0079] Examples of substrate 102 include a semiconductor wafer in which a circuit surface 103b may support a semiconductor circuit, with the wafer substrate being formed from silicon, SiC, or GaN. In some embodiments, adhesive layer 104 may be formed by a single layer of curable composition, or two or more layers may be laminated to substrate 102. One or more layers of curable composition may be laminated to one or both of substrate 102 and support layer 106 to a desired thickness under laminating conditions, such as temperature of between 50 °C and 150 °C along with the application of pressure to, for example, circuit surface 103b of substrate 102. During lamination, the curable composition softens and wets application surface 103a to adhere substrate 102 to support layer 106.

[0080] Following lamination, substrate 102 and adhesive layer 104 are diced using a dicing saw to form a semiconductor chip 108 having the semiconductor substrate 102 and adhesive layer 104 separated into distinct regions or dies 110 on support layer 106. After dicing is complete, the chip dies 110 may be removed from support layer 106 by a process known as die pickup or die pick and place. Die pickup is typically accomplished through the use of pick and place equipment to lift the individual dies from support layer 106 with suction force. The pick and place equipment then mounts the die 110 to a wiring board 112, typically through thermocompression, with adhesive layer 104 serving as the die attach medium. Example die attach conditions include temperatures of between 100 °C and 150 °C with about 10 N applied pressure. Wiring board 112 may be used to form semiconductor circuits with one or more wires 114 bonded between circuit surface 103b of substrate 102 and wiring board 112. The completed wire connection to wiring board 112 forms electronic package 116.

[0081] To fully secure die 110 to wiring board 112, adhesive layer 104 is preferably cured through a thermal cure, optionally including applied pressure to one or more of die 110 and wiring board 112. The thermal cure may include increasing the temperature of adhesive layer 104 to at least 140 °C, and preferably at least 150 °C. The cure conditions may be established in

a cure oven with a temperature of between 140 °C and 180 °C, and preferably between 150 °C and 175 °C for a time period sufficient to bring the temperature of adhesive layer 104 to or above the thresholds described above. In some embodiments, the time period is between 10 and 120 minutes.

[0082] In some embodiments, wiring board 112 and die 110 may be sealed with a sealing resin in the form of a mold. Sealing electronic package 116 may be performed by methods known by those of ordinary skill in the art.

EXAMPLES

[0083] The following examples are intended to assist one skilled in the art to better understand and practice the present invention. The scope of the invention is not limited by the examples, but is defined in the appended claims. All parts and percentages are based on weight of solids unless otherwise stated, and do not include solvents or other liquid materials which may be present to facilitate storage and dispensation of the curable compositions.

[0084] Solid resins were mixed in a container and subjected to mixing, initially with a high-speed mechanical mixer at 1000-2500 rpm for 60 seconds. Other ingredients, such as the conductive filler, were then added to the resin mixture, followed by mixing at room temperature, initially by hand, and subsequently by high-speed mechanical mixer at 500-1000 rpm for 30 seconds. Conductive adhesive films were prepared by pouring the slurry onto a prepared substrate using a coating machine. A snap, or B-stage cure was performed by exposing the adhesive to a temperature of 150 °C for 300 seconds. Full cure was achieved by placing the B-stage cured samples in an oven at 160 °C for one hour.

Table 1

<u>Constituents</u>	<u>Comp. Ex. A (wt.%)</u>	<u>Comp. Ex. B (wt.%)</u>	<u>Comp. Ex. C (wt.%)</u>	<u>Comp. Ex. D (wt.%)</u>	<u>Ex. 1 (wt.%)</u>	<u>Ex. 2 (wt.%)</u>	<u>Ex. 3 (wt.%)</u>
Maleimide, Nadimide, and/or Itaconimide functionalized resin	1.3	7.5	7.0	7.7	0.7	0.9	1.0
(Meth)Acrylate resin	11.6	3.8	3.5	6.0	6.2	9.0	10
Epoxy resin	2.7	6.0	5.0	0	1.5	1.9	2.1
Maleated Polybutadiene	7.0	0	0	1.2	4.3	4.1	4.9
Silane Adhesion Promoter	0.5	0.4	0.3	0.6	0.3	0.3	0.4
Conductivity Promoter	0.3	0.2	0.2	0.2	0.1	0.2	0.3
Epoxy Hardener	1.1	0.8	0.7	0	0.6	0.8	0.9
Free-Radical Initiator	0.4	0.4	0.3	0.3	0.2	0.3	0.3
Silver filler, 0.8 m ² /g, flake, d ₅₀ = 2.4 μm	75	81	83	84	86	83	80

[0085] The Example formulations were evaluated by a die-shear test using a silicon die (size: 3.0mm x 3.0mm x 0.7mm), wherein the die is attached on a nickel substrate. The Example formulations were dispensed onto the nickel substrate and the silicon dies were placed onto the adhesive bead to produce a bond line of approximately 0.05mm. The prepared samples were snap cured at 150 °C for 300 seconds, followed by oven cure at 160 °C for one hour. Die-shear strength was tested at 260 °C using a TA Instruments, TA-Q800 with a flat edge tension film fixture.

Table 2

<u>Physical Property</u>	<u>Comp. Ex. A (MPa)</u>	<u>Comp. Ex. B (MPa)</u>	<u>Comp. Ex. C (MPa)</u>	<u>Comp. Ex. D (MPa)</u>	<u>Ex. 1 (MPa)</u>	<u>Ex. 2 (MPa)</u>	<u>Ex. 3 (MPa)</u>
Die Shear Strength at 260 °C	4.5	4.6	4.7	5.5	5.8	6.5	6.1

[0086] The die-shear strength for the Example 1-3 formulations demonstrates high utility in semiconductor packages, and exhibited superior results in comparison to the Comparison Examples A-D. The die-shear strength results exhibit benefits of the Example 1-3 compositions

within specific concentration ranges of the BMI resins, the (meth)acrylate resins, the epoxy resins, and the polybutadiene resin.

[0087] The Example compositions were further tested for elastic/tensile modulus by DMA. The Example compositions were dispensed onto a nickel substrate to a film thickness of 200 μm using a drawdown bar. The films were snap-cured for 300 seconds at 150 °C on a hot plate, followed by full oven cure at 160 °C for one hour.

Table 3

Physical Property	<u>Comp.</u> <u>Ex. A</u> <u>(MPa)</u>	<u>Comp.</u> <u>Ex. B</u> <u>(MPa)</u>	<u>Comp.</u> <u>Ex. C</u> <u>(MPa)</u>	<u>Comp.</u> <u>Ex. D</u> <u>(MPa)</u>	<u>Ex. 1</u> <u>(MPa)</u>	<u>Ex. 2</u> <u>(MPa)</u>	<u>Ex. 3</u> <u>(MPa)</u>
Elastic/Tensile Modulus at 25 °C	1110	2052	2270	3179	306	1277	1271
Elastic/Tensile Modulus at 250 °C	95	106	149	396	112	187	141

[0088] The elastic/tensile modulus of each of the Example 1-3 formulations of the present invention were within the desired range of less than 1.6 GPa. By contrast, the Comparative Examples B-D exhibited undesirably high elastic/tensile modulus values. Comparative Examples B and C lacked the maleated polybutadiene component that has been found by Applicant to assist in both high adhesion and low elastic/tensile modulus. Comparative Example D lacked the epoxy resins that have been found to interact with the resin blend within concentration ranges to provide the desired physical properties of high adhesion with low modulus.

[0089] The Example compositions were evaluated for electrical conductivity by dispensing each Example composition onto a glass slide and cured as above. Once cured, the sample was measured first for its thickness, and then volume resistance by an ohmmeter. The volume resistivity was then calculated.

Table 4

Physical Property	<u>Comp.</u> <u>Ex. A</u> ($\Omega^*\text{cm}$)	<u>Comp.</u> <u>Ex. B</u> ($\Omega^*\text{cm}$)	<u>Comp.</u> <u>Ex. C</u> ($\Omega^*\text{cm}$)	<u>Comp.</u> <u>Ex. D</u> ($\Omega^*\text{cm}$)	<u>Ex. 1</u> ($\Omega^*\text{cm}$)	<u>Ex. 2</u> ($\Omega^*\text{cm}$)	<u>Ex. 3</u> ($\Omega^*\text{cm}$)
Volume Resistivity at 25 °C	7.3×10^{-3}	3.4×10^{-3}	2.4×10^{-3}	1.0×10^{-5}	1.5×10^{-4}	1.4×10^{-4}	2.9×10^{-4}

[0090] The Comparative Examples A-C did not exhibit sufficient electrical conductivity, with the desired threshold being less than $5 \times 10^{-4} \Omega\bullet\text{cm}$.

[0091] The Example compositions were further evaluated for thermal conductivity by laser flash method (ASTM E1461) using NETZSCH LFA Systems. The samples were prepared by curing the pre-dispensed films having a thickness of 0.5mm using the cure process as described above.

Table 5

Physical Property	<u>Comp.</u> <u>Ex. A</u>	<u>Comp.</u> <u>Ex. B</u>	<u>Comp.</u> <u>Ex. C</u>	<u>Comp.</u> <u>Ex. D</u>	<u>Ex. 1</u>	<u>Ex. 2</u>	<u>Ex. 3</u>
Thermal Conductivity (W/m·K)	1.4	0.8	0.9	4.0	2.5	5.0	2.7

[0092] Review of the results above reveals that the Example 1-3 compositions of the present invention exhibit low modulus at room temperature and at high temperature, while maintaining high die-shear adhesion, as well as electrical and thermal conductivity. The Example 1-3 compositions therefore reduce stress formation in typical electronic packages.

[0093] Various modifications of the present invention, in addition to those shown and described herein, will be apparent to those skilled in the art of the above description. Such modifications are also intended to fall within the scope of the appended claims.

Claims

1. A conductive adhesive composition, comprising:
 - (a) a curable resin system having:
 - (i) 0.1-10 wt.% of a first resin material including one or more of a maleimide-functionalized resin, an itaconimide-functionalized resin, and a nadimide-functionalized resin;
 - (ii) 0.5-15 wt.% of a (meth)acrylate resin;
 - (iii) 0.5-15 wt.% of an epoxy resin; and
 - (iv) 1 – 10 wt.% of a maleated polybutadiene;
 - (b) a filler being at least one of thermally and electrically conductive; and
 - (c) a curing agent,wherein the composition, when cured, exhibits an elastic modulus of less than 1.6 GPa at 25 °C, a volume resistivity of less than $5 \times 10^{-4} \Omega \cdot \text{cm}$, and a thermal conductivity of at least 2 W/m·K.
2. The conductive adhesive composition as in Claim 1 wherein the first resin material includes a hydrocarbyl segment of at least 20 carbon atoms.
3. The conductive adhesive composition as in Claim 2 wherein the first resin material is monomeric or oligomeric, and is free-radical curable to form a polymer network.
4. The conductive adhesive composition as in Claim 1 wherein the (meth)acrylate resin includes a hydrocarbyl segment of at least 20 carbon atoms.
5. The conductive adhesive composition as in Claim 4 wherein the (meth)acrylate resin is selected from polybutadiene diacrylate, (meth)acrylated polyisoprene, and combinations thereof.
6. The conductive adhesive composition as in Claim 1 wherein the epoxy resin includes a hydrocarbyl segment of at least 20 carbon atoms.

7. The conductive adhesive composition as in Claim 1 wherein each of the first resin material, the (meth)acrylate resin, and the epoxy resin include a hydrocarbyl segment of at least 20 carbon atoms.

8. The conductive adhesive composition as in Claim 1, including at least 75 wt.% of the filler.

9. The conductive adhesive composition as in Claim 1 wherein the filler is selected from silver, nickel, cobalt, copper, gold, palladium, platinum, carbon black, carbon fiber, graphite, carbon nanotubes, aluminum, indium tin oxide, silver coated copper, silver-coated aluminum, silver-coated graphite, nickel-coated graphite, bismuth, tin, bismuth-tin alloy, metal coated glass spheres, silver-coated fiber, silver-coated spheres, antimony-doped tin oxide, alloys thereof, and combinations thereof.

10. The conductive adhesive composition as in Claim 1 wherein the curing agent is selected from ureas, aliphatic and aromatic amines, polyamides, imidazoles, dicyandiamides, hydrazides, urea-amine hybrid curing systems, free radical initiators, organic bases, transition metal catalysts, phenols, acid anhydrides, Lewis acids, Lewis bases, peroxy esters, peroxy carbonates, hydroperoxides, alkylperoxides, arylperoxides, azo compounds, and combinations thereof.

11. The conductive adhesive composition as in Claim 1, including between 1 and 5 wt.% of the maleated polybutadiene.

12. A conductive adhesive composition, comprising:

(a) a resin system, including:

(i) a first resin material selected from a maleimide functionalized resin, a nadimide functionalized resin, an itaconide functionalized resin, and combinations thereof, the first resin material including a hydrocarbyl segment of at least 20 carbon atoms;

(ii) a (meth)acrylate resin including a hydrocarbyl segment of at least 20 carbon atoms;

- (iii) an epoxy resin having a hydrocarbyl segment of at least 20 carbon atoms;
- (b) a filler being at least one of thermally and electrically conductive; and
- (c) a curing agent.

13. The conductive adhesive composition as in Claim 12 wherein the (meth)acrylate resin is selected from polybutadiene diacrylate, (meth)acrylated polyisoprene, and combinations thereof.

14. The conductive adhesive composition as in Claim 12 wherein the epoxy resin is curable into a three-dimensional network.

15. The conductive adhesive composition as in Claim 12 wherein the resin system includes maleated polybutadiene.

16. An electronic package, comprising,
a silicon substrate;
the conductive adhesive composition of Claim 15 applied to a surface of the silicon substrate; and
an electronic component connected to the silicon substrate by the conductive adhesive composition when in a cured condition.

17. The electronic package as in Claim 16 wherein the conductive adhesive composition is disposed as a film onto the surface of the silicon substrate.

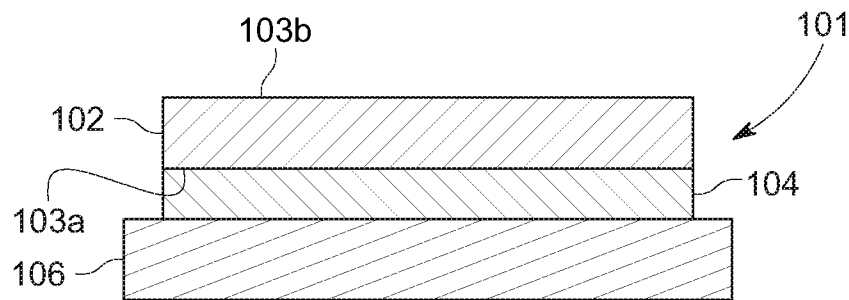


FIG. 1

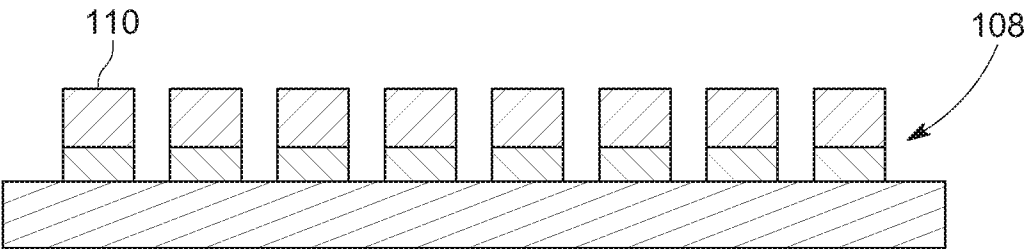


FIG. 2

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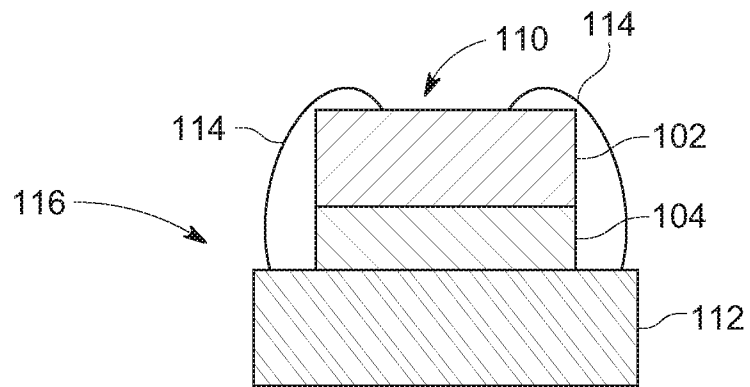


FIG. 3

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US2024/056312

A. CLASSIFICATION OF SUBJECT MATTER C09J 9/02(2006.01)i; C09J 133/04(2006.01)i; C08L 33/04(2006.01)i; C08L 63/00(2006.01)i; C08L 9/00(2006.01)i; C08K 3/08(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 9/02(2006.01); C09J 201/00(2006.01); C09J 7/00(2006.01); H01B 1/22(2006.01); H01L 21/58(2006.01); H01L 21/60(2006.01); H01L 23/00(2006.01); H01L 23/482(2006.01); H01L 23/52(2006.01) 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: package, conductive adhesive, maleimide, itaconimide, nadimide		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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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 “E” earlier application or patent but published on or after the international filing date “L” document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) “O” document referring to an oral disclosure, use, exhibition or other means “P” document published prior to the international filing date but later than the priority date claimed “T” later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention “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 05 March 2025		Date of mailing of the international search report 05 March 2025
Name and mailing address of the ISA/KR Korean Intellectual Property Office 189 Cheongsa-ro, Seo-gu, Daejeon 35208, Republic of Korea Facsimile No. +82-42-481-8578		Authorized officer HEO, Joo Hyung Telephone No. +82-42-481-5373

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