

A CURABLE COMPOSITION

Technical Field

5 The present invention generally relates to a curable composition. The present invention also relates to a curable composition that is substantially free of conventional flame retardants such as those containing halogen and/or phosphorous.

10 Background

Curable resin compositions such as epoxy resin compositions are plastics, which are commonly used to encapsulate a variety of electronic components, ranging from capacitors and transistors to central processing
15 units and memory devices. Epoxy resin compositions have gradually evolved into a complex formulation containing as many as 20 different raw materials, which are added in multiple processing steps, each statistically controlled to yield a uniform and predictable end product.

20 Typically, epoxy resin compositions contain at least five classes of raw materials, namely organic resins, fillers, catalysts, releasing agents and pigments or colorants. Fillers are non-melting inorganic materials. Catalysts are compounds that are included to accelerate
25 the cure reaction. Releasing agents enhance the ease of retrieval of the epoxy resin, which has an adhesive nature, from the mold. Pigments or colorants are added to give the final composition the desired color. Other raw materials, such as flame-retardants, adhesion promoters,
30 ion traps and stress-relief agents may also be added to the epoxy resin composition as appropriate.

In recent times, industrial requirements of larger dies, thinner packages, new package designs, smaller device feature sizes and reliability of packaging have

also resulted in the continuous evolvement of epoxy resin compositions. For example, low stress, anti-popcorn and high thermal conductivity epoxy resin compositions are subsequently developed to meet the specific requirements of the device sizes and superior packaging properties.

In addition, the industrial need for encapsulated devices to meet increasingly stringent mechanical requirements, has led to a push for the formulation of new epoxy resin compositions. Typically, the temperature cycle test (T/C), which involves exposing a device to alternating temperature extremes, determines the ability of a device to withstand mechanical stresses and is used as a benchmark for testing suitable epoxy resin composition candidates. Other favorable factors inherent in a epoxy resin composition such as low coefficient of thermal expansion (CTE) as well as low modulus (which contributes to low stress), are also determinative of the composition's suitability to be used for certain industrial applications. The importance of a low stress epoxy resin composition is accentuated when the chip size of the device to be packaged increases. In such instances, reducing the CTE of the epoxy resin composition becomes particularly significant in minimizing internal stresses.

At present, known epoxy resin compositions are typically filled with fused silica at 80 to 90 percent w/w loading. Since the CTE of fused silica is about 10% that of epoxy resin, an increase in the filler loading will reduce CTE. The tradeoff, however, is that increasing filler content also degrades the flowability and modulus of the material. To overcome this dilemma, stress-relief additives are usually added into an epoxy resin composition to lower the thermo-mechanical shrinkage stresses by lowering the modulus of epoxy resin composition.

In known epoxy resin compositions, one of the most commonly used stress-relief agents used includes acrylonitrile-butadiene rubbers. Although butadiene rubber is known to be effective for modulus reduction, the
5 resultant epoxy resin composition tends to exhibit drawbacks such as high dissipation factor (more signal loss of the encapsulated device) and poor electrical performance (circuitry corrosion) in an environment of high temperature and high relative humidity with
10 electrical biased voltage.

Moreover, known epoxy resin compositions that utilize other elastomeric stress-relief agents as a substitute for butadiene rubber in an attempt to reduce the problems of high dissipation and poor electrical performance, do not
15 exhibit effective stress relieving properties due to poor compatibility of the elastomeric stress-relief agents with the resins, which usually forms the main component of the epoxy resin composition.

In view of the apparent conflicting needs of low
20 dissipation, good electrical performance as well as the superior stress relieving properties, there is a need to provide a curable composition that exhibits all of these properties at the same time without compromising any one of these properties at the expense of satisfying another.

25 Furthermore, in order to meet the requirements of flame retardancy, some known epoxy resin compositions incorporate halogenated epoxy resins. The incorporation of halogenated epoxy resins in some epoxy resin compositions results in disposal problems due to the toxicity of
30 halogenated epoxy resin. As a substantial amount of preparations have to be carried out in order to ensure the safe disposal of any unwanted or excess halogenated epoxy resins, increased operating costs are incurred.

There is a need to provide a curable composition that overcomes or at least ameliorates one or more of the disadvantages described above.

5

Summary

According to a first aspect, there is provided a curable composition comprising an epoxy resin in admixture with a plurality of particles having an elastomeric inner core and an epoxy-functional organic polymer outer shell.

10 Advantageously, the particles provided in the curable composition may function as stress relief agents.

Advantageously, the particles may aid in substantially improving the thermal cycling resistance of the curable composition. Advantageously, the particles
15 can be used at a higher temperature than conventional stress-relief agents. For example, the particles may be used in the disclosed curable composition at a temperature less than about 150°C, or about 110°C to about 120°C.

According to a second aspect, there is provided use
20 of the curable composition as claimed in claim 1 as a sealant for a semiconductor device.

According to a third aspect, there is provided a curable composition comprising an epoxy resin in admixture with a plurality of particles having an elastomeric inner
25 core and an organic polymer outer shell, wherein said composition does not substantially comprise at least one of a halogen-containing flame retardant, a phosphorous-containing flame retardant or antimony hydroxide.

Advantageously, the composition of the third aspect
30 may not require a halogenated epoxy resin compound or a halogenated phenolic resin compound to be provided therein.

According to a fourth aspect, there is provided use of the curable composition of the third aspect as a sealant for a semiconductor device.

5

Definitions

The following words and terms used herein shall have the meaning indicated:

The term 'elastomeric' is to be interpreted broadly to include any material that is capable of undergoing deformation or elongation when a stress is applied, and to substantially return to its previous configuration when the stress is removed.

The term 'epoxy-functional' is to be interpreted broadly to include any organic functional groups that are capable of forming covalent bonds with an epoxy resin compound. The epoxy-functional organic polymer shell disclosed herein may have epoxy groups that are grafted or attached to a polymeric backbone such that the epoxy-groups are disposed at the terminal ends of the polymer or form the pendant groups of the polymer.

The term 'nano-scale' is to be interpreted to include any dimensions that are below about 1 μm , preferably about 50 nm to about 150 nm or about 100 nm.

The term 'micro-size' is to be interpreted to include any particle size that is between about 1 μm to about 1 mm. The term 'micro-size' further includes any particle size that is about 20 μm to about 150 μm , about 20 μm to about 100 μm , about 40 μm to about 150 μm or about 40 μm to about 100 μm .

The term 'C₁-C₄' is to be interpreted broadly to include any organic functional group that has 1, 2, 3 or 4 carbon atoms. The term 'C₁-C₄ alkyl' is to be interpreted broadly to include any alkyl radical that has 1, 2, 3 or 4

carbon atoms. The 'C₁-C₄ alkyl' includes any straight-chained or branched methyl, ethyl, propyl, butyl, or isomeric forms thereof.

5 The word "substantially" does not exclude "completely" e.g. a composition which is "substantially free" from Y may be completely free from Y. Where necessary, the word "substantially" may be omitted from the definition of the invention.

10 Unless specified otherwise, the terms "comprising" and "comprise", and grammatical variants thereof, are intended to represent "open" or "inclusive" language such that they include recited elements but also permit inclusion of additional, unrecited elements.

15 As used herein, the term "about", in the context of concentrations of components of the formulations, typically means +/- 5% of the stated value, more typically +/- 4% of the stated value, more typically +/- 3% of the stated value, more typically, +/- 2% of the stated value, even more typically +/- 1% of the stated value, and even 20 more typically +/- 0.5% of the stated value.

Throughout this disclosure, certain embodiments may be disclosed in a range format. It should be understood that the description in range format is merely for convenience and brevity and should not be construed as an inflexible limitation on the scope of the disclosed 25 ranges. Accordingly, the description of a range should be considered to have specifically disclosed all the possible sub-ranges as well as individual numerical values within that range. For example, description of a range such as 30 from 1 to 6 should be considered to have specifically disclosed sub-ranges such as from 1 to 3, from 1 to 4, from 1 to 5, from 2 to 4, from 2 to 6, from 3 to 6 etc., as well as individual numbers within that range, for

example, 1, 2, 3, 4, 5, and 6. This applies regardless of the breadth of the range.

Disclosure of Optional Embodiments

5 Exemplary, non-limiting embodiments of a curable composition comprising an epoxy resin in admixture with a plurality of particles having an elastomeric inner core and an epoxy-functional organic polymer outer shell will now be disclosed.

10 The particles having an elastomeric inner core and an epoxy-functional organic polymer outer shell may be provided in the curable composition as stress relief agents.

The particles may be in the nano-scale range. The
15 particles may be substantially spherical in shape. The substantially spherical particles may have a diameter in the range selected from the group consisting of about 50 nm to about 150 nm, about 50 nm to about 120nm, about 50 nm to about 100 nm, about 50 nm to about 80 nm, about 80
20 nm to about 150 nm, about 100 nm to about 150 nm and about 120 nm to about 150 nm. In one embodiment, the diameter of the substantially spherical particles may be about 100 nm.

The particles may be provided in powder form.

25 The elastomeric inner core may be a material selected from the group consisting of silicone, an ethylene propylene diene monomer rubber, an isoprene rubber, a nitrile rubber, natural rubber, butadiene-styrene rubber, and ethylene-propylene rubber.

30 In one embodiment, the elastomeric inner core is a silicone inner core. The silicone inner core may be at least partially crosslinked. Types of cross-linkable silicone composition are disclosed in US Patent No.

7,276,556, the disclosure of which is herein incorporated by reference.

The epoxy-functional organic polymer may comprise at least one epoxy-functional group selected from the group
5 such as, but not limited to, glycidoxyalkyl, glycidyl acrylate, epoxyalkyl and epoxycylcoalkyl.

The epoxy-functional group may be selected from the group such as, but not limited to, 2-glycidoxyethyl, 3-glycidoxypropyl, 4-glycidoxybutyl, 5-glycidoxypentyl,
10 glycidyl methacrylate, 2-(3,4-epoxycyclohexyl)ethyl, 3-(3,4-epoxycyclohexyl)propyl and 4-(3,4-epoxycyclohexyl)butyl.

The epoxy-functional group may be grafted onto the organic polymer backbone or may be a monomer that co-
15 polymerizes with another monomer to form the epoxy-functional organic polymer.

The organic polymer may be a vinyl polymer. The vinyl polymer may be selected from the group consisting of polyethylene, polypropylene, polybutadiene, polystyrene,
20 polyvinyl acetate, polyvinyl alcohol, polyacrylonitrile, polyvinyl toluene, polymethyl methacrylate, polyethyl methacrylate, polybutyl methacrylate, polyvinyl propionate, polyvinyl cyanides and polymethacrylonitrile.

The inner core may comprise at least about 90 wt% of
25 an elastomeric material, at least about 95 wt% of an elastomeric material or about 100 wt% of an elastomeric material.

The elastomeric inner core may comprise at least about 55 wt% of the total weight of the particle, at least
30 about 60 wt% of the total weight of the particle, at least about 65 wt% of the total weight of the particle, or at least about 70 wt% of the total weight of the particle.

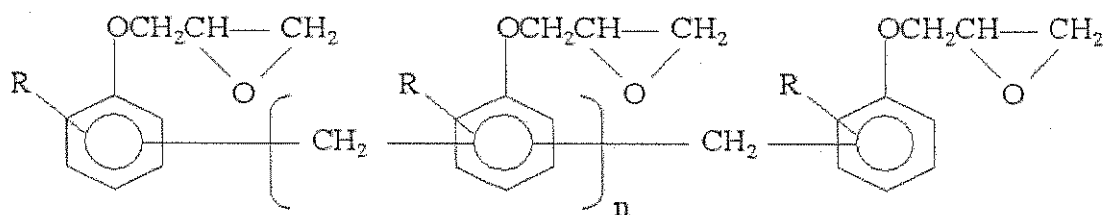
The nano-scale particles may agglomerate to form a micro-size agglomerated particle that may have a particle

size of about 20 μm to about 150 μm , about 40 μm to about 150 μm , about 60 μm to about 150 μm , about 80 μm to about 150 μm , about 100 μm to about 150 μm , about 120 μm to about 150 μm , about 20 μm to about 120 μm , about 20 μm to about 100 μm , about 20 μm to about 80 μm , about 20 μm to about 60 μm , about 20 μm to about 40 μm or about 40 μm to about 100 μm .

The amount of particles present in the curable composition may be in the range of about 4 wt% to about 20 wt%, about 8 wt% to about 20 wt%, about 12 wt% to about 20 wt%, about 16 wt% to about 20 wt%, about 4 wt% to about 16 wt%, about 4 wt% to about 12 wt%, about 4 wt% to about 8 wt% or about 6 wt% to about 12 wt%, relative to the unfilled curable composition.

The epoxy resin may be a compound comprising at least two epoxide groups in its molecular form. The epoxy resin may be selected from the group consisting of:

a phenol novolac or ortho-cresol novolac type epoxy resin of Formula I

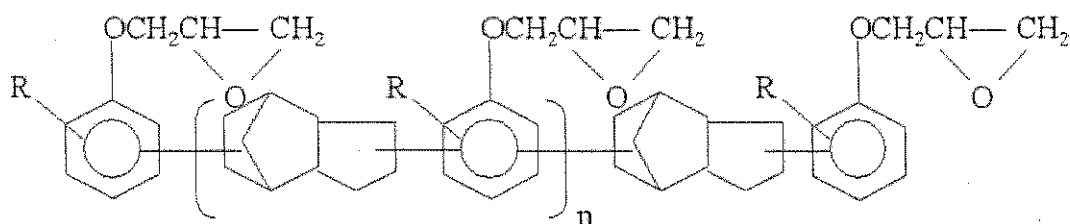


Formula I

wherein n is an integer selected from 0 to 10, or n may be 0, 1, 2, 3, 4, 5, 6, 7, 8, 9, or 10, and

each R may be independently a hydrogen atom, or a C₁-C₄ alkyl group;

a dicyclopentadiene type epoxy resin of Formula II

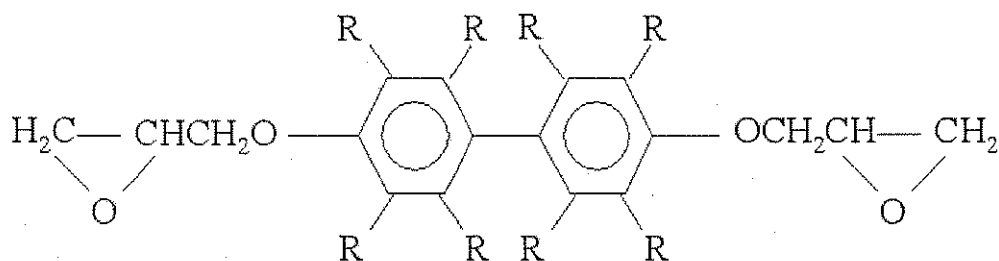


Formula II

wherein n is an integer selected from 0 to 10, or n may be 0, 1, 2, 3, 4, 5, 6, 7, 8, 9, or 10, and

5 each R may be independently a hydrogen atom or a C₁-C₄ alkyl group;

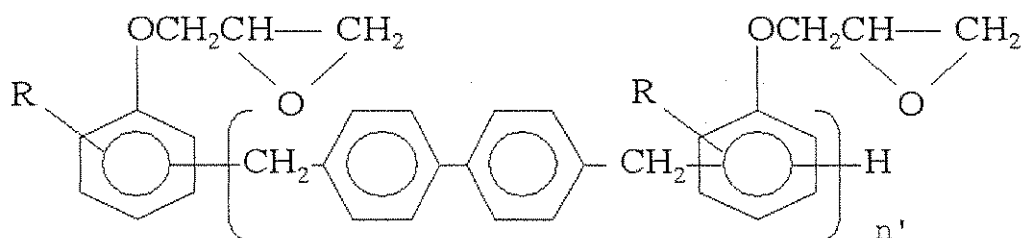
a biphenyl type epoxy resin of Formula III



Formula III

10 wherein each R may be independently a hydrogen atom or a C₁-C₄ alkyl group;

a biphenyl alkyl modified epoxy resin of Formula IV



Formula IV

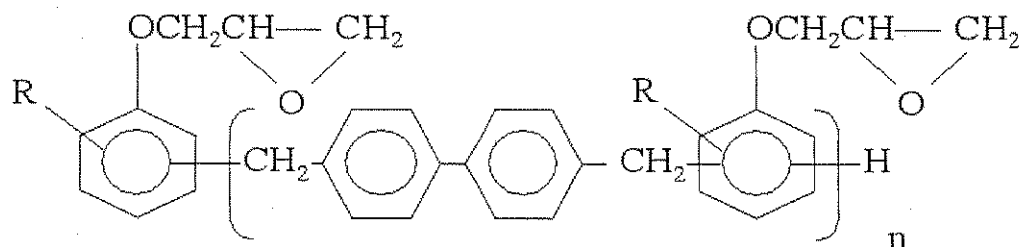
15 wherein n' is an integer selected from 1 to 11, or n' may be 1, 2, 3, 4, 5, 6, 7, 8, 9, 10 or 11, and

each R may be independently a hydrogen atom or a C₁-C₄ alkyl group;

an epoxy resin of bisphenol type; a paraxylene-
20 modified epoxy resin; a multi-functional type epoxy resin;

a naphthalene type epoxy resin; a triazine nucleus type epoxy resin; and mixtures thereof.

In one embodiment, the epoxy resin is a compound of Formula IV



Formula IV

wherein n' is an integer selected from 1 to 11, or n' may be 1, 2, 3, 4, 5, 6, 7, 8, 9, 10 or 11, and

each R may be independently a hydrogen atom or a $\text{C}_1\text{-C}_4$ alkyl group.

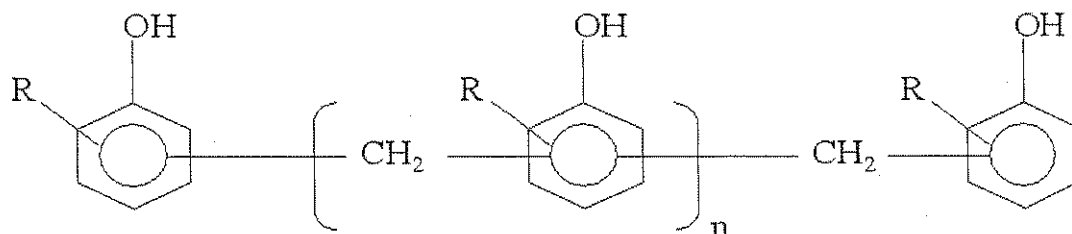
The resultant curable composition comprising one or more of the above epoxy resin compounds may have self-extinguishing properties such that the curable composition may be capable of removing heat from a fire in order to substantially prevent the spread of the fire. Furthermore, due to the high aromatic content of one or more of the epoxy resin compounds mentioned above, the resultant curable composition comprising one or more of the above epoxy resin compounds may be capable of inhibiting the spread of fire. When the curable composition is burnt, a carbonized layer is first formed at the surface such that further burnings may be substantially inhibited. In this embodiment, the curable composition may not require flame retardants such as those containing halogen and/or phosphorous to be provided therein. The curable composition may also not require antimony hydroxide to be provided therein.

The curable composition may further comprise a resin curing agent. The resin curing agent may be a phenolic

resin curing agent having at least two phenolic groups per molecule.

The phenolic resin curing agent may be selected from the group consisting of:

- 5 a phenol novolac type resin of Formula VI

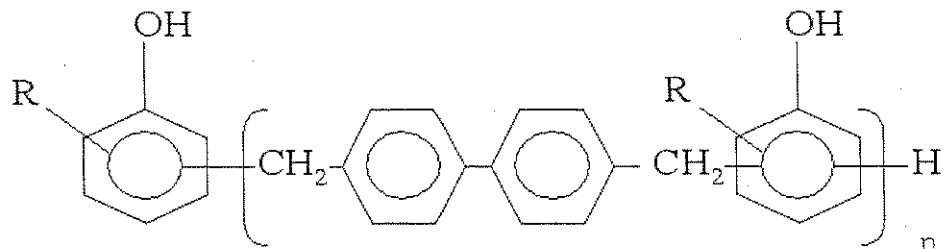


Formula VI

- wherein n is an integer selected from 0 to 10, or n
- 10 may be 0, 1, 2, 3, 4, 5, 6, 7, 8, 9, or 10, and

each R may be independently a hydrogen atom or a C₁-C₄ alkyl group;

- a biphenyl alkyl modified phenolic resin of Formula VII



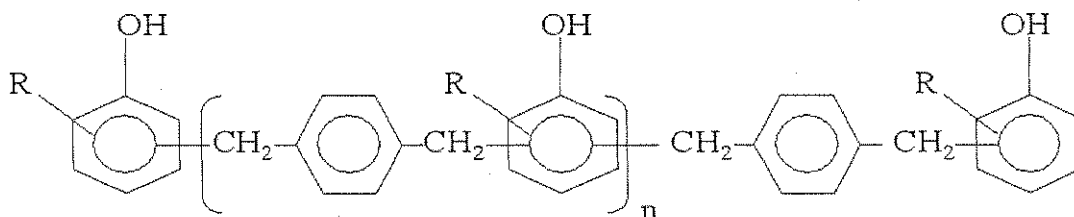
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Formula VII

- wherein n' is an integer selected from 1 to 11, or n'
- may be 1, 2, 3, 4, 5, 6, 7, 8, 9, 10 or 11, and

- each R may be independently a hydrogen atom or a
- 20 C₁-C₄ alkyl group;

- a paraxylene-modified phenolic resin of Formula VIII



Formula VIII

wherein n is an integer selected from 0 to 10, or n may be 0, 1, 2, 3, 4, 5, 6, 7, 8, 9, or 10, and

each R may be independently a hydrogen atom or a C₁-C₄ alkyl group;

a dicyclopentadiene-modified phenolic resin; a multifunctional phenolic resin; a naphthalene type phenolic resin; a triazine nucleus type phenolic resin; and mixtures thereof.

In the above compounds of Formula I, II, III, IV, V, VI, VII or VIII, in embodiments where the R group is a C₁-C₄ alkyl group, it is to be appreciated that the C₁-C₄ alkyl group may be selected from a methyl, an ethyl, a propyl, a butyl, or isomeric forms thereof.

The equivalent ratio of the epoxy resin to the phenolic resin curing agent, that is, the number of epoxy groups of the epoxy resin per hydroxyl group of the phenolic resin curing agent is not particularly limited and may be in the range of about 0.6 to about 1.4 or about 0.8 to about 1.2.

The curable composition may further comprise an inorganic filler selected from the group consisting of fused silica powder, substantially spherical silica powder, crystalline silica powder, secondary agglomerated silica powder, porous silica powder, silica powder obtained from grinding secondary agglomerated silica powder or porous silica powder, alumina, and mixtures thereof.

The amount of the inorganic filler in the curable composition may be about 60 wt% to about 95 wt%, about 60 wt% to about 90 wt%, about 60 wt% to about 80 wt%, about 60 wt% to about 70 wt%, about 70 wt% to about 95 wt%, about 80 wt% to about 95 wt%, about 90 wt% to about 95 wt% or about 70 wt% to about 90 wt%. A person

skilled in the art may be able to determine the amount of inorganic filler to add to the curable composition in order to achieve a desired soldering stress resistance and moldability of the curable composition.

5 The curable composition may further comprise a curing accelerator selected from the group consisting of diazabicycloundecene (DBU), triphenylphosphine (TPP), benzyldimethylamine (BDMA), 2-methylimidazole (2-MZ), and mixtures thereof.

10 The amount of curing accelerator in the curable composition may be about 0.1 wt% to about 0.4 wt%, about 0.2 wt% to about 0.4 wt%, about 0.3 wt% to about 0.4 wt%, about 0.1 wt% to about 0.3 wt% or about 0.1 wt% to about 0.2 wt%. If the amount of curing accelerator is less than
15 0.1 wt%, the hardness of the resulting cured composition decreases and mold release characteristics tend to deteriorate. If the amount of curing accelerator is more than 0.4 wt%, the curing reaction proceeds undesirably fast such that fluidity of the resultant cured composition
20 decreases.

 The curable composition may further comprise additives such as a silane coupling agent such as an epoxysilane, an aminosilane, an alkylsilane, a vinylsilane; a pigment or a colouring agent such as carbon
25 black or red iron oxide; a releasing agent such as a fatty acid, a metallic salt of a fatty acid, an ester wax, natural wax or synthetic wax.

 In some embodiments, the curable composition may comprise a flame retardant material that does not
30 substantially pollute the environment. The flame retardant material may be a metal hydroxide. The metal hydroxide may be aluminium hydroxide. The metal hydroxide may be magnesium hydroxide.

The curable composition may be used to seal, coat or insulate electronic parts of a semiconductor device such as a capacitor, a transistor, a central processing unit, a memory device, etc.

5 The curable composition may be made by sufficiently mixing or blending a mixture containing formulated amounts of the above-described components using a mixer or the like to obtain blended matter. The blended matter is subsequently melted and kneaded using hot rolls, a
10 kneader, an extruder or the like to obtain kneaded product. The kneaded product is cooled and grounded into powder form to obtain molding material. The molding material obtained can be used to seal, coat or insulate electronic parts of a semiconductor device as described
15 above.

Brief Description Of Drawings

The accompanying drawings illustrate a disclosed embodiment and serves to explain the principles of the
20 disclosed embodiment. It is to be understood, however, that the drawings are designed for purposes of illustration only, and not as a definition of the limits of the invention.

Fig. 1 is an exemplary graph showing the
25 determination of α_1 and α_2 using a Thermal Mechanical Analyzer as will be described further below.

Fig. 2 is an exemplary graph showing the
determination of storage modulus and glass transition temperature using a Dynamic Mechanical Analyzer as will be
30 described further below.

Examples

Non-limiting examples of the invention and comparative examples will be further described in greater detail by reference to specific Examples and Comparative
5 Examples, which should not be construed as in any way limiting the scope of the invention.

Details regarding the experimental tests used in characterizing the curable compositions of Examples 1 to 3 and Comparative Examples 1 to 6 are as follows.

10

Determination of Spiral Flow

A certain amount of molding material that gives a cull thickness of 3 ± 0.3 cm was weighed. A spiral flow mold die was placed in a molding machine (from Kohtaki)
15 and was heated up to 175°C. When the temperature reaches 175°C, the molding material was poured into a transfer pot and a plunger was lowered. The material was molded for 120s. Following which, the mold press was opened and the spiral flow length (up to the lustrous tip) was measured
20 after the mold die was taken out from the molding machine.

Determination of Flexural Modulus

The molding material was molded into 60mm(L) x 10mm(W) x 4mm(t) test pieces under the conditions of
25 175°C, 150kg/cm² and 120s using a 37 ton transfer molding machine. The molded test pieces were subjected to 4 hours post-mold-cure at 175°C. Each of the test pieces was subsequently placed into a Tensilon machine (from Orientec Co. Ltd) and 3 point bending stress was applied on the
30 test pieces until fracture. The Tensilon machine can calculate and give readings of flexural modulus at room temperature (25°C) and at elevated temperatures (e.g. 260°C) when set to test at the respective temperature.

Determination of Coefficients of Thermal Expansion

The molding material was molded into 15.0mm(L) x 4.7mm(W) x 3.0mm(t) test pieces under the conditions of 175°C, 150kg/cm² and 120s using a 37-ton transfer-molding machine. The molded test pieces were subjected to 4 hours post-mold-cure at 175°C. Each of the test pieces was subsequently placed into a Thermal Mechanical Analyzer (TMA) (from Seiko Instruments USA Inc.) and its thermal expansion over a range of temperature from 25°C to 300°C was tested. The coefficients of thermal expansion below and above the glass transition temperature (T_g), known as α_1 and α_2 respectively, were obtained as the slope of the curve below and above the inflection point, as shown in Fig. 1.

Determination of Storage Modulus and Glass Transition Temperature

The molding material was molded into 20mm(L) x 10mm(W) x 1.6mm(t) test pieces under the conditions of 175°C, 150kg/cm² and 120s using a 37-ton transfer-molding machine. The molded test pieces were subjected to 4 hours post-mold-cure at 175°C. Each of the test pieces was subsequently placed into a Dynamic Mechanical Analyzer (DMA) (from Seiko Instruments USA Inc.) and tested for their storage modulus over a range of temperature from 25°C to 300°C at a frequency of 10Hz. The storage modulus at 25°C and 260°C were analyzed. T_g of the material was obtained as the temperature where the two tangent lines intersect, as shown in Fig. 2.

Determination of Dissipation Factor

The molding material was molded into a circular disc of 50mm in diameter and 3mm thickness under the conditions of 175°C, 150kg/cm² and 120s using a 75-ton transfer-

molding machine. The molded test pieces were subjected to 4 hours post-mold-cure at 175°C. Thin foils of 38mm in diameter and 0.0275mm thickness were adhered to both sides of the test piece using a thin layer of grease.

5 Measurement was done using Precision LCR Meter at a fixed frequency of 1M-Hz. The following equations were used to calculate Dissipation Factor ($\tan \delta$)

$$\text{Dissipation Factor } (\tan \delta) = \frac{(Q_1 - Q_2)}{Q_1 \times Q_2} \times C_1 \times T_0$$

Where, Q_1 = Q value of Dielectric Tester Adapter (16451A) without test piece

10

Q_2 = Q value of Dielectric Tester Adapter (16451A) with specimen

C_1 = Turning Capacitance (pF)

T_0 = Electrode Spacing of Dielectric Tester Adapter (16451A) (cm)

15

Flammability Test (Underwriters Laboratory Flammability Rating; UL-94 V-0, UL-94 V-1)

The molding material was molded into five specimens, each with dimension of about 127.0mm(L) x 13.0mm(W) x 3.2mm(t) using a 37-ton transfer-molding machine. Before the test was conducted, all specimens were treated at the following conditions: temperature of about $23 \pm 2^\circ\text{C}$ with about $50 \pm 5\%$ relative humidity for at least 48 hours.

20

Each specimen was clamped vertically and burnt for about 10 ± 0.5 seconds. A record was taken of the flaming time and of any burnt residue dropping off each specimen. After the flames of the specimens died out, the burner was immediately placed under the specimen again. The burner

25

was removed after about 10 seconds and a record was taken of the flaming time, the glowing time and of any burnt residue dropping off each specimen. The same procedure was repeated for all specimens.

30

The test specimen was classified as V-1 or V-0 standard according to criteria summarized in Table 1 below.

5

Table 1

(Underwriters Laboratory Flammability Rating; UL-94: V-0, V-1) Criteria	Classification	
	V-1	V-0
Number of specimens	5	5
Number of Ignitions	2	2
Maximum flaming time per specimen per flame application (seconds)	30	10
Total flaming time, five specimens, 2 ignitions (seconds)	250	50
Flaming drips ignite cotton	No	No
Maximum afterglow time, per specimen (seconds)	60	30
Burn to holding clamp	No	No

Determination of Stress Index

Stress created from the sealing of semiconductor devices may be estimated by the Stress Index. Stress Index at various temperatures (-65°C, 150°C and 260°C) was calculated using the following formulas:

For T_g smaller or equal to 175°C,

when $T < T_g$,

$$\text{Stress Index} = (\alpha_1 - \alpha_{\text{chip}}) \times (T - T_g) \times E_1 + (\alpha_2 - \alpha_{\text{chip}}) \times (T_g - 175) \times E_2 \text{ ---- Eqn. (1)}$$

when $T \geq T_g$,

$$\text{Stress Index} = (\alpha_2 - \alpha_{\text{chip}}) \times (T - 175) \times E_2 \text{ ---- Eqn. (2)}$$

whereby,

T_g = glass transition temperature

α_1 = coefficient of thermal expansion below T_g

α_2 = coefficient of thermal expansion above T_g

α_{chip} = coefficient of thermal expansion of chip

E_1 = modulus @ 25°C

E2 = modulus @ 260°C

T = stress calculation temperature

Assumptions:

- a. stress index = 0 at 175°C (molding temperature)
- b. stress = K x Stress Index wherein K is a constant
- c. E = Flexural Modulus or Storage Modulus
- d. $\alpha_{chip} = 0.3 \times 10^{-5} / ^\circ\text{C}$

Temperature Cycle (T/C) Test

For performance testing at the semiconductor package level, similar pellets were prepared into various sizes. Depending on test requirements, it can then be molded into (i) 100L-QFP packages 14mm x 20mm x 2.7mm, encapsulating SiN (Silicon Nitride) coated chips of size 5.0mm x 5.0mm or (ii) 208L-QFP packages 28mm x 28mm x 3.2mm, encapsulating SiN coated chips of size 9.5mm x 9.5mm at a temperature of 175°C, transfer pressure in the range of 80-120 kgf/cm² and in-mold cure time of 90 sec. Subsequently the packages were sent for post mold cure at 175°C for 4 hrs before T/C test between -65°C to 150°C according to JEDEC testing standard.

The packages were taken out after every 100 cycles and packages were scanned using CSAM (C-mode Scanning Acoustic Microscope) for delaminated interfaces with focus on the chip top, top pad and the bottom.

Pressure Cooker Biased Test (PCBT)

Preformed tablets were prepared from the Examples described further below, each having a diameter of about 48mm and weighing about 75g. The tablets were used to seal gold wire-bonded Test Electric Grid (TEG) die (without passivation for protection) for 16-pin Plastic Dual Inline Package (16p PDIP). These assembled units were then subjected to PCBT (Pressure Cooker Biased Test).

Sealed 16p PDIP were stored in saturated steam (100% relative humidity or RH), at a temperature of 121°C (corresponding to about two times atmospheric pressure) and wired up in order for a voltage of 20 volts to be applied, in a sealed autoclave containing deionised water. The packages were suspended at a minimum height of about 1 cm above the initial water level in the chamber. Interval electrical measurements were made and the devices were stored for up to about 24 hours.

Using a sample size of 5 packages with each encapsulated die having 6 circuits on it yields a total of 30 parallel circuits per curable composition. Failure of each circuit is decided when open circuit was detected due to internal device corrosion at the wired bonded lead, circuitry on the die or the formation of conducting matter between the leads. The time taken for 20% or 6 circuits to failure is termed the Time-to-Failure.

Determination of Acetone Insoluble Content (wt%)

300g of blended matter were collected after the components of the epoxy composition were mixed together in a process described further below. 500g of acetone was added into a bottle together with the blended matter. The bottle was shaken for 20 minutes with a Shaker. After shaking, the mixture was poured through a 212µm sieve to retain any insoluble particles that did not pass through the pores of the sieve. The sieve was subsequently rinsed with acetone until only the insoluble particles remain and dried in an oven at 80°C to 100°C for 5 minutes. The dried insoluble particles were then weighed. The acetone insoluble content as calculated as follows:

$$\text{Acetone Insoluble Content (wt\%)} = \frac{\text{Weight of dried insoluble particles}}{300\text{g}} \times 100\%$$

Examples 1 and 2 and Comparative Examples 1 to 5

The weight ratios of the components making up the respective curable compositions of Examples 1 and 2 and Comparative Examples 1 to 5 are seen in Table 2 below.

The ortho-Cresol novolac type of epoxy resin (Formula I) was obtained from Nippon Kayaku Co., Ltd of Tokyo, Japan. The phenol novolac resin (Formula VI) was obtained from Sumitomo Durez Co., Ltd of Detroit of Michigan of the United States of America. The elastomeric core-shell particles comprising a silicone inner core and an epoxy-functional PMMA shell (Genioperl® P53) were obtained from Wacker-Chemie AG of München of Germany.

Table 2

Formulation	Example		Comparative Example				
	1	2	1	2	3	4	5
	parts by weight						
Ortho-Cresol novolac type of epoxy resin (Formula I) Softening point: 55°C, Epoxy group equivalent: 196g/eq	11.4	11.1	12.4	11.4	11.1	11.4	11.1
Phenol novolac resin (Formula VI) Softening point: 81°C, Hydroxyl group equivalent: 105g/eq	4.8	4.7	5.2	4.8	4.7	4.8	4.7
Fused silica powders	72.2	72.2	72.2	72.2	72.2	72.2	72.2
Aluminium hydroxide	8.5	8.5	8.5	8.5	8.5	8.5	8.5
Carbon black	0.3	0.3	0.3	0.3	0.3	0.3	0.3
Silane coupling agent	0.4	0.4	0.4	0.4	0.4	0.4	0.4
Triphenylphosphine (TPP)	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Releasing agent: Carnauba wax	0.2	0.2	0.2	0.2	0.2	0.2	0.8
Polyethylene wax	0.6	0.6	0.6	0.6	0.6	0.6	-
Stress-relief agent:							
Silicone core and an epoxy-functional PMMA shell	1.4	1.8					
Silicone core and a PMMA shell						1.4	1.8
Acrylic-butadiene-acrylonitrile copolymer				1.4	1.8		

The components were sufficiently and uniformly mixed using a high speed mixer for about 10 minutes at about 20°C to obtain blended matter. The blended matter was subsequently melted and kneaded at 70°C to 100°C using a bi-axial roll, cooled and grounded to obtain the resin composition.

Examples 1 and 2 and Comparative Examples 1 to 5 represent curable compositions comprising a flame-retardant. Examples 1 and 2 and Comparative Examples 1 to 5 were subjected to the experimental tests detailed above and the results of these experimental tests are shown in Table 3 below.

Table 3

Properties	Example		Comparative Example				
	1	2	1	2	3	4	5
Spiral flow (cm)	60	51	65	52	44	59	56
Water absorption (%)	0.30	0.31	0.30	0.31	0.32	0.30	0.31
α_1 , $\times 10^{-5}/^{\circ}\text{C}$ (Coefficient of thermal expansion below T_g)	1.2	1.2	1.3	1.3	1.4	1.2	1.2
α_2 , $\times 10^{-5}/^{\circ}\text{C}$ (Coefficient of thermal expansion above T_g)	6.2	6.3	6.1	6.0	6.0	6.3	6.3
T_g ($^{\circ}\text{C}$)	155	154	156	157	159	155	156
Flexural Modulus @25°C, kgf/mm ²	1940	1935	2200	1880	1830	1945	1960
Flexural Modulus @260°C, kgf/mm ²	105	115	150	120	120	115	115
Storage Modulus @25°C (kgf/mm ²)	1714	1714	1850	1748	1619	1708	1712
Storage Modulus @260°C (kgf/mm ²)	164	165	190	173	171	165	165
UL-94 Flammability Test (3.2mm thickness)	V-0	V-0	V-0	V-0	V-0	V-0	V-0

Temperature Cycle Test

The results of the temperature cycle test as outlined above for Examples 1 and 2 and Comparative Examples 1 to 5 are seen in Table 4 below.

5

Table 4

Temperature Cycle Test @ -65°C to 150°C	Example		Comparative Example				
	1	2	1	2	3	4	5
14mm x 20mm 100pin QFP, 5mm x 5mm SiN die	# cycles before full die paddle delamination						
a) Cu leadframe (Ag-plated Pad)	300	300	50	100	100	200	200
b) Pre-plated leadframe	400	400	100	300	300	400	400

Table 4 indicates that the curable compositions comprising the silicone core-epoxy functional PMMA shell particles performed better than curable compositions that do not comprise the silicone core-epoxy functional PMMA shell particles. Furthermore, curable compositions that comprise silicone core-epoxy functional PMMA shell particles (Examples 1 and 2) have slightly better temperature cycle performance as compared to curable compositions comprising silicone core-PMMA shell particles (Comparative Examples 4 and 5) due to improved compatibility of the silicone core-epoxy functional PMMA shell particles with the epoxy resin matrix as epoxy-functionality on the shell can link the particles with the resin matrix covalently.

Stress Index Calculation

Stress created from the sealing of semiconductor devices was estimated by the Stress Index procedure as outlined above. Stress Index at various temperatures (-65°C, 150°C and 260°C) was calculated using Equations 1 and 2 above. From the Stress Indexes calculated, curable

compositions comprising silicone core-epoxy functional PMMA shell particles (Examples 1 and 2) have lower Stress Indexes as compared to curable compositions comprising no stress relief agent (Comparative Example 1) or curable compositions comprising Acrylic-Butadiene-Acrylonitrile copolymer (Comparative Examples 2 and 3), in particular, at low temperatures such as -65°C. Details are seen in Table 5 below.

10

Table 5

Stress Index Calculation	Example		Comparative Example				
	1	2	1	2	3	4	5
Stress Index at -65°C (Flexural Modulus), kgf/mm ²	-3.97	-3.96	-5.03	-4.30	-4.62	-3.99	-4.03
Stress Index at 150°C (Flexural Modulus), kgf/mm ²	-0.21	-0.21	-0.30	-0.26	-0.29	-0.23	-0.24
Stress Index at 260°C (Flexural Modulus), kgf/mm ²	0.53	0.59	0.74	0.58	0.58	0.59	0.59
Stress Index at -65°C (Storage Modulus), kgf/mm ²	-3.59	-3.59	-4.30	-4.05	-4.15	-3.58	-3.59
Stress Index at 150°C (Storage Modulus), kgf/mm ²	-0.27	-0.27	-0.32	-0.29	-0.32	-0.28	-0.28
Stress Index at 260°C (Storage Modulus), kgf/mm ²	0.82	0.84	0.94	0.84	0.83	0.84	0.84

Pressure Cooker Biased Test (PCBT)

Devices for test purposes were prepared using the molding materials obtained from the curable compositions of Example 1 and Comparative Examples 1 and 2, and subjected to pressure cooker biased test as outlined above. The results are shown in Table 6.

Table 6

	Example	Comparative Example	
	1	1	2
Stress Relief Agents	1.4% silicone core-epoxy functional PMMA shell particles	No stress relief agent	1.4% Acrylic- butadiene- acrylonitrile copolymer
Pressure Cooker Biased Test @ 121°C / 100% RH / 20volt- biased (On Cu L/F) # of hrs till 20% units failed by open circuit	200	180	90

When 20 volts of biased voltage was applied to the device at high temperature (121°C) and high relative humidity (100%) conditions, the circuitry corrosion would be accelerated as compared to actual operating conditions. As depicted for Example 1, the presence of 1.4% of silicone core-epoxy functional PMMA shell particles exhibits the longest time among the test devices for 20% of the units to fail. Although the test device from Comparative Example 1 showed just about 10% (180 hrs vs. 200 hrs) earlier time-to-failure, this curable composition does not possess the desirable low modulus properties. Finally, in Comparative Example 2, the curable compositions with 1.4% of Acrylic-Butadiene-Acrylonitrile copolymer displayed a much shorter time-to-failure of 90hrs. Therefore, curable compositions comprising silicone core-epoxy functional PMMA shell particles result in superior PCBT performance when compared to curable compositions without any stress relief agents or to curable compositions comprising Acrylic-Butadiene-Acrylonitrile copolymer as stress relief agents.

Dissipation Factor Test

Mold discs for dissipation factor test as outlined above were prepared using the molding materials obtained from curable compositions of Example 1 and Comparative Examples 1 and 2. The results are shown in Table 7.

Table 7

	Example	Comparative Example	
	1	1	2
Stress Relief Agents	1.4% silicone core-epoxy functional PMMA shell	No stress relief agents	1.4% Acrylic- butadiene- acrylonitrile copolymer
Dissipation Factor (1M-HZ)	0.007	0.006	0.014

Higher dissipation factor denotes higher electrical signal loss when the encapsulated device is in operation and is hence undesirable.

As seen in Table 7, the dissipation factor for Example 1 is comparable to that of Comparative Example 1. However, the curable composition of Example 1 is superior to that of Comparative Example 1 due to its lower modulus value at both room and high temperatures as seen in Table 2. Accordingly, the low modulus value of the curable composition of Example 1 indicates that it is capable of relieving stress better than that of Comparative Example 1.

On the other hand, in comparing between the dissipation factors of Example 1 and Comparative Example 2, the use of 1.4% acrylic-butadiene-acrylonitrile copolymer as the stress relief agent in the curable composition of Comparative Example 2 results in an undesirable increase in the dissipation factor of Comparative Example 2 to 0.014. Therefore, the use of

silicone core-epoxy functional PMMA shell particles results in a curable composition with a lower dissipation factor and modulus value.

5 Spiral Flow

Molding materials obtained from curable compositions of Example 2 and Comparative Examples 1 and 3 were tested to determine the spiral flow values using the procedure outlined above. The spiral flow values are further
10 tabulated relative to the spiral flow value of Comparative Example 1, whereby no stress-relief agent was added. The results are shown in Table 8.

Table 8

	Example	Comparative Example	
	2	1	3
Stress Relief Agents	1.8% silicone core-epoxy functional PMMA shell	No stress relief agents	1.8% Acrylic- butadiene- acrylonitrile copolymer
Spiral flow (cm)	51	65	44
Relative Spiral flow (%) (with respect to Spiral flow of Comparative Example 1)	78	100	68

15 In comparing the relative spiral flow of Example 2 to that of Comparative Example 3, the use of silicone core-epoxy functional PMMA shell particles in the curable composition of Example 2 causes lower degradation in
20 spiral flow as compared to that of Comparative Example 3 which uses Acrylic-Butadiene-Acrylonitrile copolymer in the curable composition by a magnitude of 10% or more. Hence, better flowability can be achieved using silicone

core-epoxy functional PMMA shell particles as stress-relief agents instead of butadiene rubber.

Acetone Insoluble Content of Blended Matter

The acetone insoluble contents of the blended matter obtained from Example 2 and Comparative Example 3 according to the procedure outlined above are tabulated in Table 9 below.

Table 9

	Example	Comparative Example
	2	3
Stress Relief Agents	1.8% silicone core-epoxy functional PMMA shell	1.8% Acrylic- butadiene- acrylonitrile copolymer
Acetone Insoluble Content of blended matter (wt%)	2.3	4.4

Comparing the acetone insoluble content of blended matter of Example 2 to that of Comparative Example 3, the blended matter of Comparative Example 3 contains about twice as much acetone insoluble content than that of Example 2. Generally, high acetone insoluble content in the blended matter can lead to higher occurrence of incomplete fill during the transfer molding process of the final molding material and is hence undesirable. Therefore, the use of silicone core-epoxy functional PMMA shell particles as a stress relief agent aids in decreasing the acetone insoluble content of the curable composition.

Example 3 and Comparative Example 6

The weight ratios of the components making up the respective curable compositions of Example 3 and Comparative Example 6 are seen in Table 10 below.

5 The ortho-Cresol novolac type of epoxy resin (Formula I), novolac epoxy resin of biphenyl type (Formula IV) and paraxylene-modified phenolic resin (Formula VIII) were obtained from Nippon Kayaku Co., Ltd of Tokyo, Japan. The novolac phenolic resin of biphenyl type (Formula VII) was
10 obtained from Matsui Chemicals Company Ltd of Kyoto, Japan. The elastomeric core-shell particles comprising a silicone inner core and an epoxy-functional PMMA shell (Genioperl® P53) were obtained from Wacker-Chemie AG of München of Germany.

15

Table 10

	Example	Comparative Example
Formulation	3	6
Ortho-Cresol novolac type of epoxy resin (Formula I) Softening point: 55°C, epoxy group equivalent: 196g/eq	3.2	3.5
Novolac epoxy resin of biphenyl type (Formula IV) Softening point: 60°C, epoxy group equivalent: 272 g/eq	3.2	3.5
Novolac phenolic resin of biphenyl type (Formula VII) Softening point: 107°C, hydroxyl group equivalent: 199 g/eq	2.5	2.7
Paraxylene-modified phenolic resin (Formula VIII) Softening point: 62°C, hydroxyl group equivalent: 174 g/eq	2.4	2.6
Fused silica powders	86.5	86.5
Carbon black	0.3	0.3

Coupling agent	0.2	0.2
Gamma-mercaptopropyl trimethoxysilane	0.1	0.1
3-Glycidoxypropyltrimethoxysilane	0.1	0.1
Phenylaminopropyltrimethoxysilane		
Curing accelerator:		
Triphenylphosphine (TPP)	0.2	0.2
Releasing agent:		
Montanic acid ester wax	0.15	0.15
Oxidized Polyethylene wax	0.15	0.15
Stress-relief agent:		
Silicone core and an epoxy-functional PMMA shall	1.0	

The components were sufficiently and uniformly mixed using a high speed mixer for about 10 minutes at about 20°C to obtain blended matter. The blended matter was subsequently melted and kneaded at 70°C to 100°C using a bi-axial roll, cooled and grounded to obtain the resin composition.

Example 3 and Comparative Example 6 represent curable compositions free from flame-retardants, as they comprise of self-extinguishing multi-aromatic-type resin to achieve flame retardancy. Example 3 and Comparative Example 6 were subjected to the experimental tests detailed above and the results of these experimental tests are shown in Table 11 below.

15

Table 11

	Example	Comparative Example
Properties	3	6
Spiral flow (cm)	72	80
Water absorption (%)	0.15	0.14
$\alpha 1$, $\times 10^{-5}/^{\circ}\text{C}$ (Coefficient of thermal expansion below T_g)	0.8	0.9
$\alpha 2$, $\times 10^{-5}/^{\circ}\text{C}$ (Coefficient of thermal expansion above T_g)	3.5	3.6
T_g ($^{\circ}\text{C}$)	146	147
Flexural Modulus @25 $^{\circ}\text{C}$, kgf/mm ²	2142	2420
Flexural Modulus @260 $^{\circ}\text{C}$, kgf/mm ²	85	100
Storage Modulus @25 $^{\circ}\text{C}$ (kgf/mm ²)	2085	2250
Storage Modulus @260 $^{\circ}\text{C}$ (kgf/mm ²)	135	158
UL-94 Flammability Test (3.2mm thickness)	V-0	V-0

Temperature Cycle Test

The results of the temperature cycle test as outlined above for Example 3 and Comparative Example 6 are seen in Table 12 below.

Table 12

	Example	Comparative Example
Temperature Cycle Test at -65$^{\circ}\text{C}$ to 150$^{\circ}\text{C}$	3	6
28mm x 28mm 208pin QFP, 9.5mm x 9.5mm SiN die	# cycles before onset of die corner delamination	
Cu leadframe (Ag-plated Pad)	300	150

Table 12 indicates that the curable composition of Example 3 comprising the silicone core-epoxy functional PMMA shell particles performed better than the curable composition of Comparative Example 6 which does not comprise the silicone core-epoxy functional PMMA shell.

particles. There is a two-fold increase in the number of cycles when stress relief agents such as silicone core-epoxy functional PMMA shell particles were used in the curable composition.

5

Stress Index Calculation

Stress created from the sealing of semiconductor devices was estimated by the Stress Index procedure as outlined above. Stress Index at various temperatures (-
10 65°C, 150°C and 260°C) was calculated using Equations 1 and 2 above. From the Stress Indexes calculated, the curable composition of Example 3 comprising silicone core-epoxy functional PMMA shell particles had a lower Stress Index as compared to that of Comparative Example 6 which
15 does not have any stress relief agents therein. Details are seen in Table 13 below. Therefore, the use of silicone core-epoxy functional PMMA shell particles as stress relief agents aided in decreasing the stress of the curable composition.

Table 13

	Example	Comparative Example
Stress Index Calculation	3	6
Stress Index at -65°C (Flexural Modulus), kgf/mm ²	-2.34	-3.17
Stress Index at 150°C (Flexural Modulus), kgf/mm ²	-0.07	-0.08
Stress Index at 260°C (Flexural Modulus), kgf/mm ²	0.23	0.28
Stress Index at -65°C (Storage Modulus), kgf/mm ²	-2.32	-3.01
Stress Index at 150°C (Storage Modulus), kgf/mm ²	-0.11	-0.13
Stress Index at 260°C (Storage Modulus), kgf/mm ²	0.37	0.44

5

Applications

The disclosed curable composition is a epoxy resin composition suitable for use in sealing semiconductor devices and also one which can improve the thermal cycling resistance of the epoxy resin composition while maintaining good flowability at high filler loadings.

The disclosed curable composition exhibit a variety of desirable properties such as low dissipation, good electrical performance and enhanced stress relieving properties together at the same time, which is not possible in known compositions due to the conflicting nature of the desirable properties. Advantageously, the dissipation and electrical performance of the disclosed composition will not be undesirably compromised in an environment of high temperature and high relative humidity with electrical biased voltage. More advantageously, the

disclosed curable may be used effectively to encapsulate or package electrical, electronic devices and semiconductor devices such as capacitors and transistors.

As the disclosed curable composition also comprises a plurality of particles having an elastomeric inner core, the curable composition possess lower thermo-mechanical shrinkage stresses due to the lowering of the modulus of composition, without degrading the flowability and of the whole composition. Advantageously, the lower shrinkage stresses translate into lower CTE and the disclosed composition is able to pass the T/C tests required by various industries. More advantageously, the filler loading does not have to be increased to minimize internal stresses. Even more advantageously, the particles used in the disclosed composition cause less degradation in spiral flow as compared to epoxy resin compositions comprising butadiene rubber of the same loading. In addition, the blended matter of the disclosed epoxy resin compositions comprising silicone core-shell particles contain less insoluble content in acetone as compared to blended matter obtained from epoxy resin compositions comprising butadiene rubber as stress-relief agent.

Due to the fact that the particles of the disclosed composition comprises an epoxy-functional organic polymer outer shell, the compatibility of particles with the resin matrix is enhanced which in turns improves the effectiveness of particles as stress-relief agents. While not being bound by theory, it is believed that the epoxy-functionality on the shell can link the particles with the resin matrix covalently resulting in better temperature cycle performance of the disclosed composition as compared to one which does not have particles comprising an epoxy-functional organic polymer outer shell.

The disclosed composition is also suitable for use in large scale packaging of devices with large chip sizes, as the internal stresses inherent in the disclosed composition is minimal.

5 Advantageously, the elastomeric core of the particles use in the disclosed composition has high-purity and high temperature properties and are effective as stress-relief agents. More advantageously, the elastomeric core of the particles used in the disclosed composition has low
10 temperature flexibility (due to low glass transition temperature, T_g of about -120°C relative to -35°C for acrylonitrile-butadiene systems) and is able to withstand harsh weather conditions and is moisture resistant.

 The disclosed composition may also be substantially
15 free of a flame retardant material containing a halogen and/or a phosphorous. The disclosed composition may not comprise antimony hydroxide. Advantageously, since the composition does not comprise a halogenated epoxy resin, additional disposal costs associated with the disposing of
20 the toxic halogenated epoxy resin would not be incurred. More advantageously, the constituents of the disclosed curable composition may not contribute to environmental pollution.

 While reasonable efforts have been employed to
25 describe equivalent embodiments of the present invention, it will be apparent to the person skilled in the art after reading the foregoing disclosure, that various other modifications and adaptations of the invention may be made therein without departing from the spirit and scope of the
30 invention and it is intended that all such modifications and adaptations come within the scope of the appended claims.

Claims

1. A curable composition comprising an epoxy resin in admixture with a plurality of particles having an elastomeric inner core and an epoxy-functional organic polymer outer shell.

2. The curable composition as claimed in claim 1, wherein said epoxy-functional organic polymer comprises at least one epoxy-functional group selected from the group consisting of glycidoxyalkyl, glycidyl acrylate, epoxyalkyl and epoxycycloalkyl.

3. The curable composition as claimed in claim 2, wherein said epoxy-functional group is selected from the group consisting of 2-glycidoxyethyl, 3-glycidoxypropyl, 4-glycidoxybutyl, 5-glycidoxypentyl, glycidyl methacrylate, 2-(3,4-epoxycyclohexyl)ethyl, 3-(3,4-epoxycyclohexyl)propyl and 4-(3,4-epoxycyclohexyl)butyl.

4. The curable composition as claimed in claim 1, wherein said organic polymer is a vinyl polymer.

5. The curable composition as claimed in claim 4, wherein said vinyl polymer is selected from the group consisting of polyethylene, polypropylene, polybutadiene, polystyrene, polyvinyl acetate, polyvinyl alcohol, polyacrylonitrile, polyvinyl toluene, polymethyl methacrylate, polyethyl methacrylate, polybutyl methacrylate, polyvinyl propionate, polyvinyl cyanides and polymethacrylonitrile.

6. The curable composition as claimed in claim 1, wherein said elastomeric inner core comprises a material selected from the group consisting of silicone, an

ethylene propylene diene monomer rubber, an isoprene rubber, a nitrile rubber, natural rubber, butadiene-styrene rubber, and ethylene-propylene rubber.

5. 7. The curable composition as claimed in claim 6, wherein said silicone inner core is at least partially crosslinked.

8. The curable composition as claimed in claim 1,
10 comprising 5 wt% to 20 wt% of said particles therein.

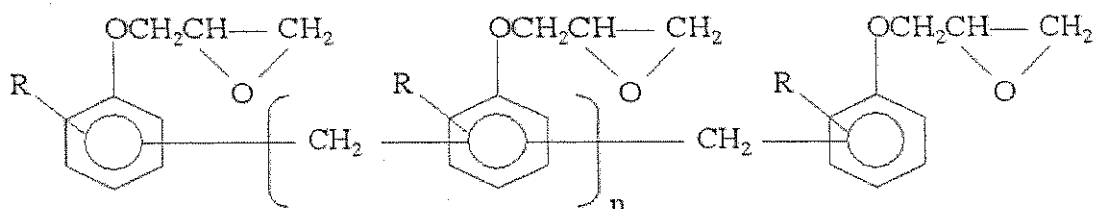
9. The curable composition as claimed in claim 1, wherein said particle has a size in the nano-scale range.

15 10. The curable composition as claimed in claim 10, wherein said particle size is in the range of 50 nm to 150 nm.

11. The curable composition as claimed in claim 1,
20 wherein said epoxy resin is a compound having at least two epoxide groups per molecule.

12. The curable composition as claimed in claim 11,
wherein said epoxy resin is selected from the group
25 consisting of:

i. a phenol novolac or ortho-cresol novolac type epoxy resin of Formula I

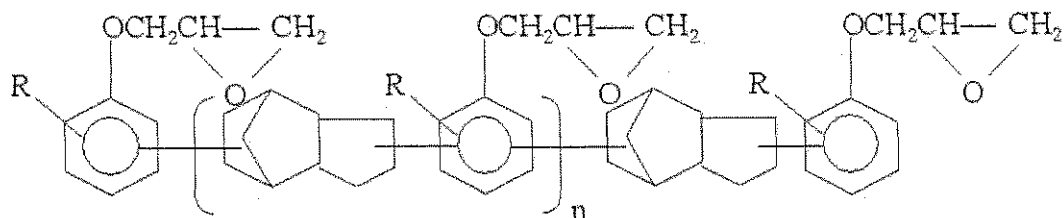


Formula I

wherein n is an integer selected from 0 to 10 and

each R is independently a hydrogen atom, or a C₁-C₄ alkyl group;

ii. a dicyclopentadiene type epoxy resin of Formula II



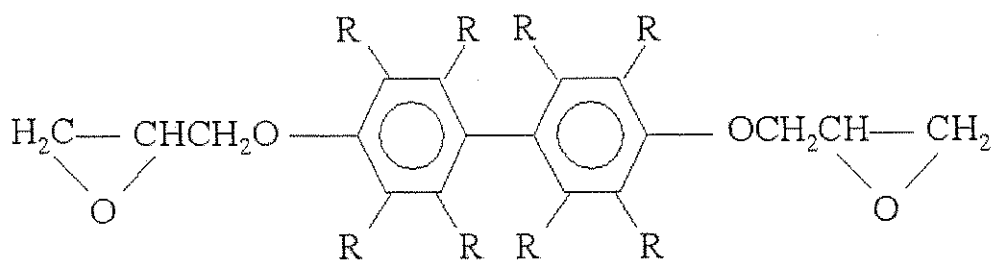
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Formula II

wherein n is an integer selected from 0 to 10, and

each R is independently a hydrogen atom or a C₁-C₄ alkyl group;

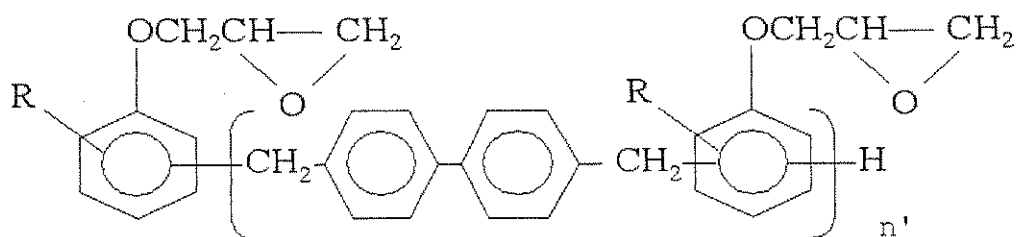
10 iii. a biphenyl type epoxy resin of Formula III



Formula III

wherein each R is independently a hydrogen atom or a C₁-C₄ alkyl group;

15 iv. a biphenyl alkyl modified epoxy resin of Formula IV



Formula IV

wherein n' is an integer selected from 1 to 11, and

20 each R is independently a hydrogen atom or a C₁-C₄ alkyl group;

- v. an epoxy resin of bisphenol type;
 - vi. a paraxylene-modified epoxy resin;
 - vii. a multi-functional type epoxy resin;
 - viii. a naphthalene type epoxy resin;
- 5 ix. a triazine nucleus type epoxy resin; and mixtures thereof.

13. The curable composition as claimed in claim 1, further comprising a resin curing agent.

10

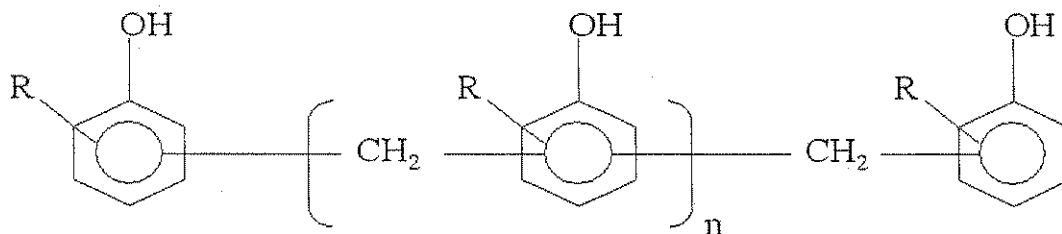
14. The curable composition as claimed in claim 13, wherein said resin curing agent is a phenolic resin curing agent having at least two phenolic groups per molecule.

15

15. The curable composition as claimed in claim 14, wherein said phenolic resin curing agent is selected from the group consisting of:

- i. a phenol novolac type resin of Formula VI

20



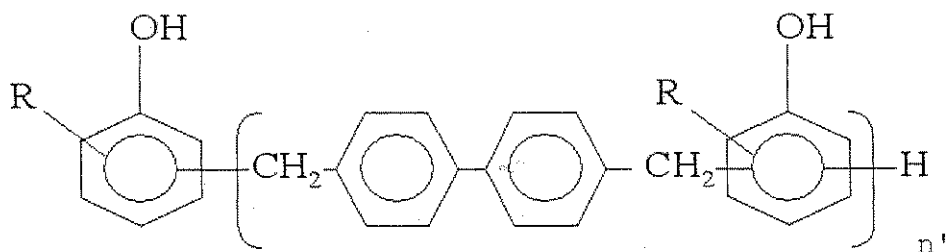
Formula VI

wherein n is an integer selected from 0 to 10, and

each R is independently a hydrogen atom or a C₁-C₄

25 alkyl group;

- ii. a biphenyl alkyl modified phenolic resin of Formula VII

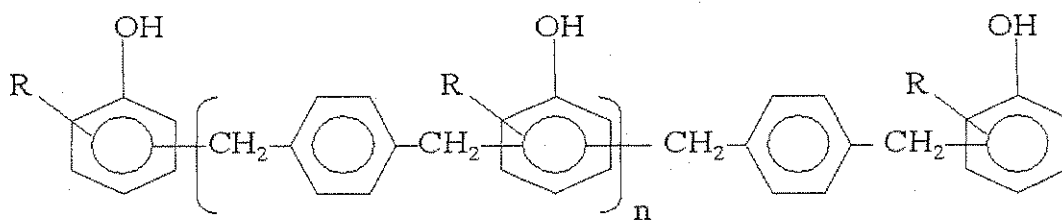


Formula VII

wherein n' is an integer selected from 1 to 11, and
each R is independently a hydrogen atom or a C_1 -

5 C_4 alkyl group;

iii. a paraxylene-modified phenolic resin of Formula VIII



Formula VIII

10 wherein n is an integer selected from 0 to 10, and
each R is independently a hydrogen atom or a C_1 - C_4
alkyl group;

iv. a dicyclopentadiene-modified phenolic resin;

v. a multifunctional phenolic resin;

15 vi. a naphthalene type phenolic resin;

vii. a triazine nucleus type phenolic resin; and
mixtures thereof.

16. The curable composition as claimed in claim 1,
20 further comprising an inorganic filler selected from the
group consisting of fused silica powder, substantially
spherical silica powder, crystalline silica powder,
secondary agglomerated silica powder, porous silica
powder, silica powder obtained from grinding secondary
25 agglomerated silica powder or porous silica powder,
alumina, and mixtures thereof.

17. The curable composition as claimed in claim 1,
further comprising a curing accelerator selected from the
group consisting of diazabicycloundecene (DBU),
5 triphenylphosphine (TPP), benzyldimethylamine (BDMA), 2-
methylimidazole (2-MZ), and mixtures thereof.

18. The curable composition as claimed in claim 1,
further comprising a flame retardant selected from a
10 metal hydroxide.

19. The curable composition as claimed in claim 1,
wherein said metal hydroxide is at least one of aluminium
hydroxide and magnesium hydroxide.

15

20. Use of the curable composition as claimed in
claim 1 as a sealant for a semiconductor device.

21. A curable composition comprising an epoxy resin
20 in admixture with a plurality of particles having an
elastomeric inner core and an organic polymer outer
shell, wherein said composition does not substantially
comprise at least one of a halogen-containing flame
retardant; a phosphorous-containing flame retardant or
25 antimony hydroxide.

22. The curable composition as claimed in claim 21,
wherein said organic polymer is an epoxy-functional
organic polymer.

30

23. The curable composition as claimed in claim 22,
wherein said epoxy-functional organic polymer comprises
at least one epoxy-functional group selected from the

group consisting of glycidoxyalkyl, glycidyl acrylate, epoxyalkyl and epoxycylcoalkyl.

24. The curable composition as claimed in claim 23,
5 wherein said epoxy-functional group is selected from the group consisting of 2-glycidoxyethyl, 3-glycidoxypropyl, 4-glycidoxybutyl, 5-glycidoxypentyl, glycidyl methacrylate, 2-(3,4-epoxycyclohexyl)ethyl, 3-(3,4-epoxycyclohexyl)propyl and 4-(3,4-epoxycyclohexyl)butyl.

10

25. The curable composition as claimed in claim 21, wherein said organic polymer is a vinyl polymer.

26. The curable composition as claimed in claim 25,
15 wherein said vinyl polymer is selected from the group consisting of polyethylene, polypropylene, polybutadiene, polystyrene, polyvinyl acetate, polyvinyl alcohol, polyacrylonitrile, polyvinyl toluene, polymethyl methacrylate, polyethyl methacrylate, polybutyl
20 methacrylate, polyvinyl propionate, polyvinyl cyanides and polymethacrylonitrile.

27. The curable composition as claimed in claim 21, wherein said elastomeric inner core comprises a material
25 selected from the group consisting of silicone, an ethylene propylene diene monomer rubber, an isoprene rubber, a nitrile rubber, atural rubber, butadiene-styrene rubber, and ethylene-propylene rubber.

30 28. The curable composition as claimed in claim 27, wherein said silicone inner core is at least partially crosslinked.

29. The curable composition as claimed in claim 21, comprising 5 wt% to 20 wt% of said particles therein.

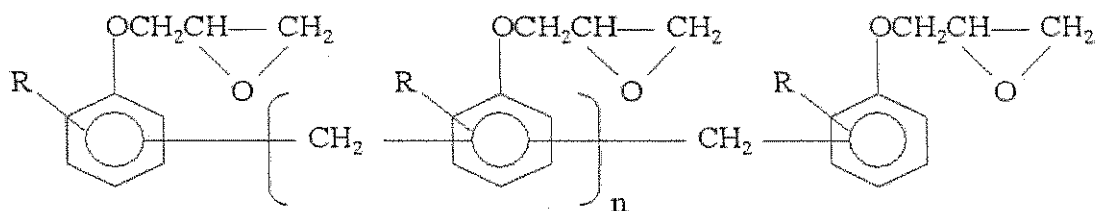
30. The curable composition as claimed in claim 21, wherein said particle has a size in the nano-scale range.

31. The curable composition as claimed in claim 21, wherein said particle size is in the range of 50 nm to 150 nm.

10

32. The curable composition as claimed in claim 21, wherein said epoxy resin is selected from the group consisting of:

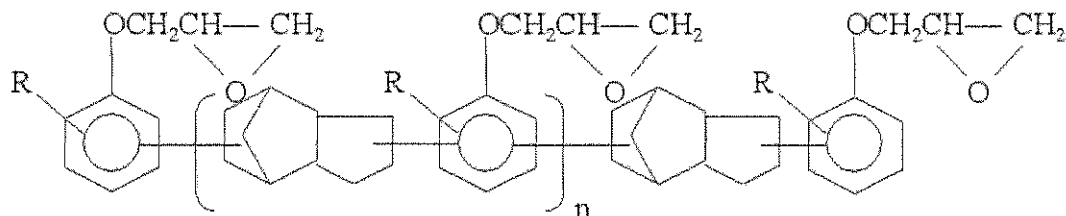
15 i. a phenol novolac or ortho-cresol novolac type epoxy resin of Formula I



Formula I

20 wherein n is an integer selected from 0 to 10, and each R is independently a hydrogen atom, or a C₁-C₄ alkyl group;

ii. a dicyclopentadiene type epoxy resin of Formula II



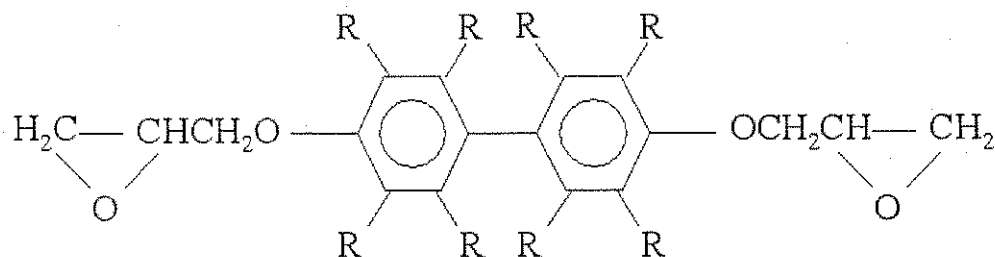
25

Formula II

wherein n is an integer selected from 0 to 10, and

each R is independently a hydrogen atom or a C₁-C₄ alkyl group;

iii. a biphenyl type epoxy resin of Formula III

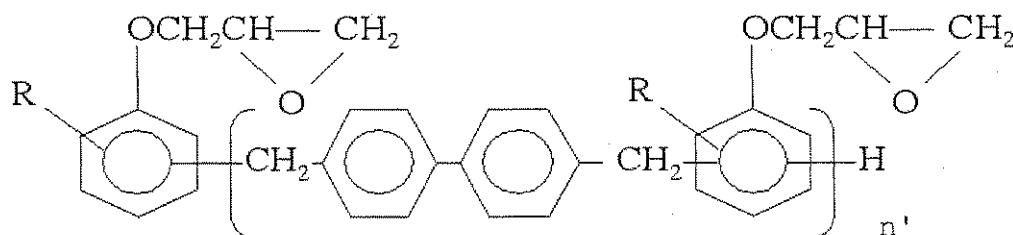


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Formula III

wherein each R is independently a hydrogen atom or a C₁-C₄ alkyl group;

iv. a biphenyl alkyl modified epoxy resin of Formula IV



10

Formula IV

wherein n' is an integer selected from 1 to 11, and

each R is independently a hydrogen atom or a C₁-C₄ alkyl group;

15

v. an epoxy resin of bisphenol type;

vi. a paraxylene-modified epoxy resin;

vii. a multi-functional type epoxy resin;

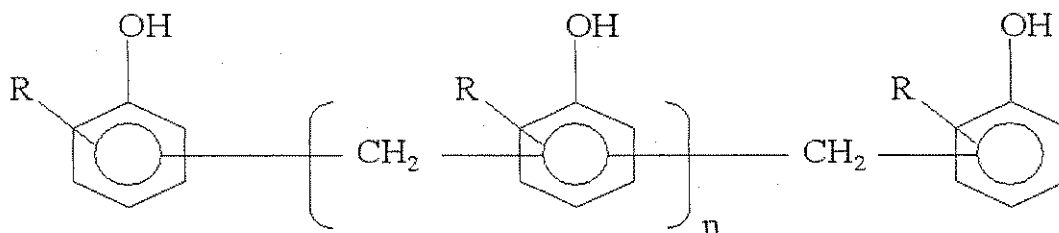
viii. a naphthalene type epoxy resin;

ix. a triazine nucleus type epoxy resin; and
20 mixtures thereof.

33. The curable composition as claimed in claim 21, further comprising a phenolic resin curing agent selected from the group consisting of:

25

i. a phenol novolac type resin of Formula VI

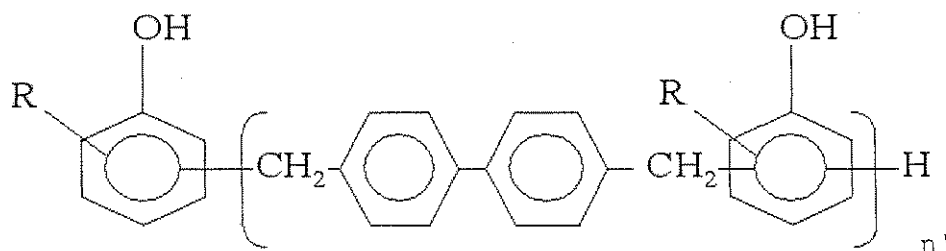


Formula VI

wherein n is an integer selected from 0 to 10, and

5 each R is independently a hydrogen atom or a C_1 - C_4 alkyl group;

ii. a biphenyl alkyl modified phenolic resin of Formula VII

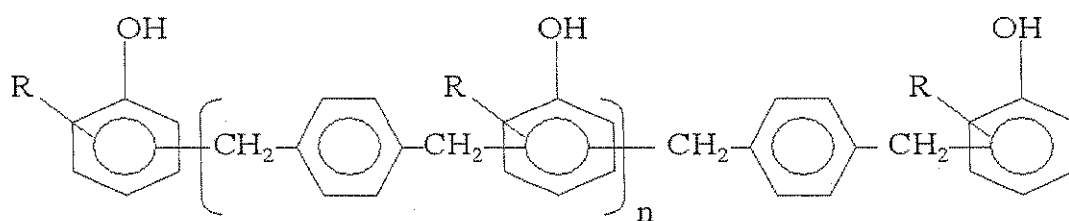


Formula VII

wherein n' is an integer selected from 1 to 11, and

each R is independently a hydrogen atom or a C_1 - C_4 alkyl group;

15 iii. a paraxylene-modified phenolic resin of Formula VIII



Formula VIII

wherein n is an integer selected from 0 to 10, and

20 each R is independently a hydrogen atom or a C_1 - C_4 alkyl group;

iv. a dicyclopentadiene-modified phenolic resin;

v. a multifunctional phenolic resin;

vi. a naphthalene type phenolic resin;
vii. a triazine nucleus type phenolic resin; and
mixtures thereof.

5 34. The curable composition as claimed in claim 21,
further comprising a flame retardant selected from a
metal hydroxide.

10 35. The curable composition as claimed in claim 21,
wherein said metal hydroxide is at least one of aluminium
hydroxide and magnesium hydroxide.

15 36. Use of the curable composition as claimed in
claim 21 as a sealant for a semiconductor device.