

THERMOSETTING RESIN COMPOSITION FOR SEMICONDUCTOR DEVICE ENCAPSULATION AND SEMICONDUCTOR DEVICES

5 FIELD OF INVENTION

The present invention relates to a thermosetting resin composition for semiconductor device encapsulation. In particular, the present invention relates to a thermosetting resin composition comprising amine catalyzed hardeners. The epoxy resin compositions of the present invention are also able to maintain good moldability and reliability after storage at room temperature for an extended period of time.

10 BACKGROUND OF THE INVENTION

Electrical parts such as capacitors, resistance diodes, transistors, as well as integrated circuits (IC) and the like have been sealed with a thermosetting resin. In particular, there has been used in integrated circuits a thermosetting resin such as an epoxy resin having excellent heat resistance and moisture resistance, obtained by curing an o-cresol novolac type epoxy resin with a novolac type phenolic resin.

Presently, an integrated circuit sealed in a thermosetting resin is used widely in commercial electronic products and telecommunications electronics and, thus, offers a large manufacturing base. The thermosetting resin encapsulated integrated circuits offer some major benefits in terms of cost, size, weight, performance and availability. The capability of manufacturing the thermosetting resin encapsulated integrated circuits in large volumes and at a low cost is the major driving force for wide industrial usage of thermosetting resin encapsulated integrated circuits. Consequently, it is desirable by IC manufacturers to obtain a faster production cycle together with a low or reduced operating cost to provide a cost-effective and efficient production environment.

The thermosetting resin encapsulated integrated circuits are known to be sensitive to temperature and thus require cold room storage to prevent degradation of the thermosetting resin composition before usage. The cold room storage temperature required for storage is usually in the range of 0°C to 10°C, and thus it can be seen that considerable energy is expended to maintain this low temperature range. Consequently, the cold room storage requirement increases the operating cost for integrated circuit manufacturers. Thus, it would be desirable and beneficial to eliminate or reduce this cold room storage requirement so as to lead to considerable cost savings and facilitate faster production for integrated circuit manufacturers.

The invention disclosed in Singapore Patent Application No. 200202092-3 filed on 9 April 2002 (Sumitomo Bakelite Singapore Pte Ltd) discloses a thermosetting resin composition such as an epoxy resin composition, which is able to be stored at normal molding room temperatures of from about 20°C to about 30°C, with minimal effect on its physical properties. The contents of Singapore Patent Application No. 200202092-3 are incorporated herein by cross-reference.

The thermosetting resin composition such as an epoxy resin composition disclosed in this application is useful for sealing electrical parts such as integrated circuits. However, the thermosetting resin composition disclosed in Singapore Patent Application No. 200202092-3 typically contains flame retardants which contain halogen and phosphorous.

These halogen and phosphorous containing flame retardants are usually considered to be not environmentally friendly and a useful guide for determining whether electronic parts meet the requirements of consumers is set out in the Waste Electrical and Electronic Equipment (WEEE) and Restriction of Hazardous Substances in Electrical and Electronic Equipment (ROHS) European Community Directives.

Accordingly, it would be desirable to provide a thermosetting resin composition such as an epoxy resin composition which do not require conventional flame retardants such as those containing halogen and phosphorous or to provide alternative resin compositions to those known in the prior art.

SUMMARY OF THE INVENTION

Accordingly, in a first aspect, there is provided a thermosetting resin composition for sealing of semiconductor devices, comprising:

- (a) an epoxy resin;
- (b) a phenolic resin curing hardener;
- (c) an amine curing catalyst; and
- (d) a compound selected from the group consisting of a metal oxide, and a compound represented by the formula $M-Z-R^1$, where M is a metal, Z is an oxygen or sulfur radical and R^1 is selected from the group consisting of hydrogen and C_1 to C_5 alkyl, wherein the softening point of the final catalysed phenolic resin curing hardener is between 120°C and 180°C.

The thermosetting resin composition is preferably suitable for storage at a temperature from about 20°C to about 30 °C.

The radical Z in the formula $M-Z-R^1$ for compound (d) may be oxygen and R^1 may be selected from the group consisting of hydrogen and C_1 to C_3 alkyl.

The metal M in the formula $M-Z-R^1$ for compound (d) may be selected from the group consisting of an alkaline earth metal and other metals. The alkaline earth metal

may be selected from the group consisting of calcium, magnesium, strontium and barium. The other metals may include aluminum and iron.

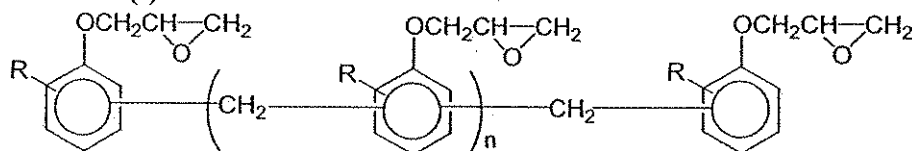
The formula $M-Z-R^1$ for compound (d) may include metal hydroxides and metal oxides including aluminum oxide, aluminum hydroxide, magnesium oxide and magnesium hydroxide.

Compound (d) of the thermosetting resin composition of the present invention may also be a flame retardant which does not contain halogen or phosphorous.

The epoxy resin (a) may be present in an amount of about 5% to about 50% by weight based on the total thermosetting resin composition, preferably about 5% to about 45wt %, more preferably about 5% to about 40%, still more preferably about 10% to about 45 %, still more preferably about 10% to about 40 %, still more preferably about 15% to about 40%, still more preferably about 20% to about 40%, still more preferably about 20% to about 35%, still more preferably about 20% to about 30%, still more preferably about 20% to about 25% by weight based on the total thermosetting resin composition.

The epoxy resin (a) may be a compound containing two or more epoxide groups in its molecular form. The epoxy resin (a) may include two or more epoxide groups, for example, a cresol novolac type epoxy resin (Formula I) as shown below:

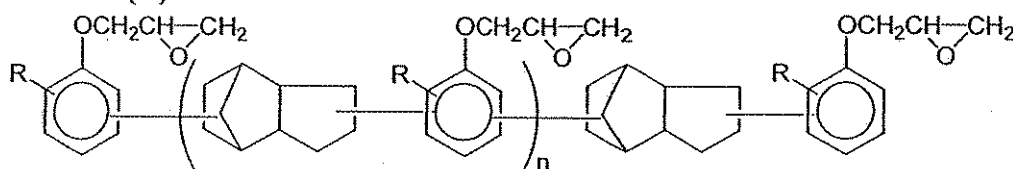
Formula (I)



wherein n is an integer of 0-10 and each R is independently an atom or group selected from hydrogen, a halogen and an alkyl group.

The epoxy resin (a) may be also be a dicyclopentadiene type epoxy resin (Formula II) as shown below:

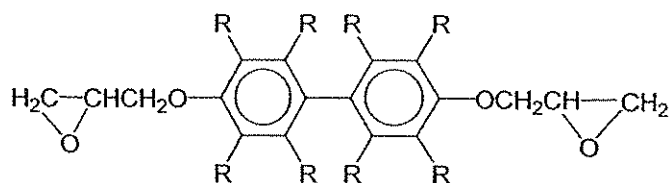
Formula (II)



wherein n is an integer of 0-10 and each R is independently an atom or group selected from hydrogen, a halogen and an alkyl group.

The epoxy resin (a) may be also be a biphenyl type epoxy resin (Formula III) as shown below:

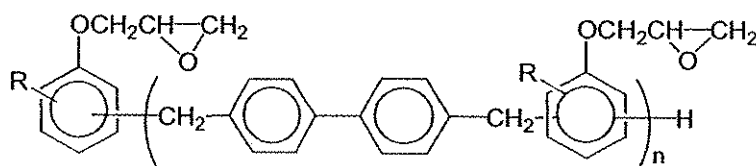
Formula (III)



wherein R is independently an atom or group selected from hydrogen, a halogen and an alkyl group.

5 The epoxy resin (a) may be also be a biphenyl aralkyl modified epoxy resin (Formula IV) as shown below:

Formula (IV)

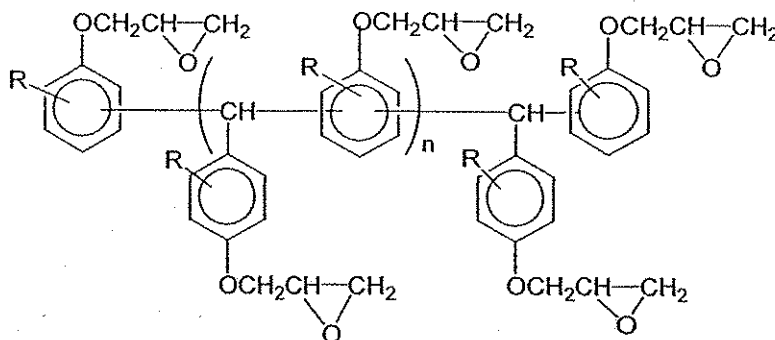


10 wherein n is an integer of 1-11 and each R is independently an atom or group selected from hydrogen, a halogen and an alkyl group.

The epoxy resin (a) may be also be a tri- or multi-functional type epoxy resin (Formula V) as shown below:

Formula (V)

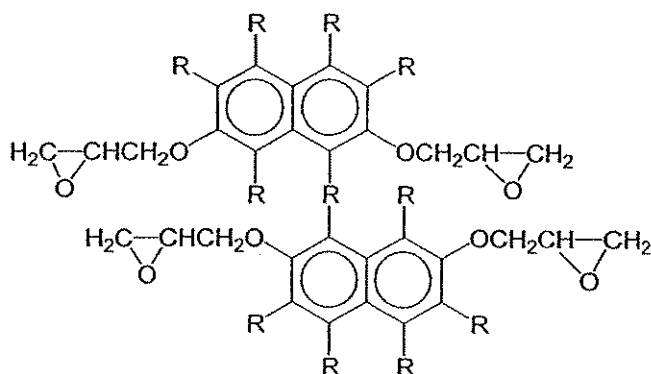
15



wherein n is an integer of 0-10 and each R is independently an atom or group selected from hydrogen, a halogen and an alkyl group.

20 The epoxy resin (a) may be also be a naphthalene type epoxy (Formula VI) as shown below:

Formula (VI)



wherein R is independently an atom or group selected from hydrogen, a halogen and an alkyl group.

The epoxy resin (a) may also include other compounds and/or polymeric structures which contain two or more epoxide functional groups.

The epoxy resin (a) present in the thermosetting resin composition may comprise a single epoxy resin or may also comprise two or more epoxy resins with the above-mentioned characteristics. When there are two or more epoxy resins, the total amount of epoxy resins present in the thermosetting resin composition may range from about 5% to about 50wt% based on the total thermosetting resin composition, preferably about 5% to about 45wt %, more preferably about 5% to about 40%, still more preferably about 10% to about 45 %, still more preferably about 10% to about 40 %, still more preferably about 15% to about 40%, still more preferably about 20% to about 40%, still more preferably about 20% to about 35%, still more preferably about 20% to about 30%, still more preferably about 20% to about 25% by weight based on the total thermosetting resin composition.

The epoxy resin (a) may be used in an amount of about 0.8 to about 1.3 times the epoxy equivalent per hydroxyl group equivalent of the total phenolic resin curing hardener present in component (b) of the thermosetting resin composition. The epoxy resin (a) may be used in an amount of 1.0 to 1.3 times the epoxy equivalents per hydroxyl group equivalent of the total phenolic resin present in component (b) of the thermosetting resin composition.

The phenolic resin curing hardener (b) in the epoxy resin composition may have a softening temperature ranging from about 50°C to about 170°C. The phenolic resin curing hardener (b) in the thermosetting resin composition may also have a softening temperature in the range of about 55°C to about 165°C. The phenolic resin curing hardener (b) in the thermosetting resin composition may also have a softening temperature in the range of about 60°C to about 160°C. The phenolic resin curing hardener (b) in the thermosetting resin composition may also have a softening temperature in the range of about 65°C to about 155°C. The phenolic resin curing hardener (b) in the thermosetting resin composition may also have a softening temperature ranging from about 70°C to about 150°C, preferably about 75°C to about 145°C, preferably 80°C to about 145°C, preferably 85°C to about 140°C, preferably 90°C to about 135°C, preferably about 95°C to about 130°C, preferably about 100°C to about 125°C, preferably about 105°C to about 120°C.

The phenolic resin curing hardener (b) may be in an amount of about 0.1 to about 50wt% based on the total phenolic resin composition. The phenolic resin curing hardener (b) may also be in an amount of about 0.1 to about 40wt%, preferably about 0.5 to about 30 wt%, more preferably about 1 to about 25 wt%, more preferably about 1 to about 20wt%, more preferably about 1 to about 15wt%, more preferably about 1 to about 10wt%, more preferably about 1 to about 5wt% based on the total phenolic resin curing agent composition in the thermosetting resin composition.

The phenolic resin curing hardener (b) in the thermosetting resin composition may comprise more than one phenolic resin curing hardeners. When more than one phenolic resin curing hardener (b) is employed in combination in the thermosetting resin composition, they can be, for example, selected from the group consisting of phenol novolac resins, cresol novolac resins, copolymers between dicyclopentadiene-modified phenolic resins and phenol novolac resins and/or cresol novolac resins, paraxylene-modified phenolic resins and biphenyl aralkyl modified phenolic resins.

The amine curing catalyst (c) may be present in an amount of about 0.05% to about 1.0% by weight based on the total resin composition to be reacted into a hardener resin in the thermosetting resin composition. A ratio of the amine curing catalyst (c) to the phenolic type hardener may be from about 3% to about 30%, more preferably about 3% to about 25%, still more preferably about 3% to about 15%, still more preferably about 3% to about 10% and yet still more preferably about 3% to about 7%.

The amine curing catalyst (c) may be an amine curing catalyst which is capable of reacting with the phenolic resin curing hardener (b) to form a catalysed phenolic resin

hardener. Suitable examples include primary amine catalysts, secondary amine catalysts and tertiary amine catalysts. Some examples include benzyldimethylamine (BDMA) and 1,8-Diazabicyclo [5,4,0] undecene-7 (DBU).

The compound (d) of the thermosetting resin composition is selected from the group consisting of a metal oxide, and a compound represented by the formula $M-Z-R^1$, where M is a metal, Z is an oxygen or sulfur radical and R^1 is selected from the group consisting of hydrogen and C_1 to C_5 alkyl.

The metal oxide which may form compound (d) present in the thermosetting resin composition of the present invention may include metal oxides where the metal is selected from an alkaline earth metal, a transition metal or other metals. The alkaline earth metal may include calcium, magnesium, strontium and barium. The transition metal may include iron and aluminum. Examples of alkaline earth metal oxides include aluminum oxide, calcium oxide and magnesium oxide.

The compound $M-Z-R^1$ which may form compound (d) present in the thermosetting resin composition of the present invention, where M is a metal, Z is an oxygen or sulfur radical and R^1 is selected from the group consisting of hydrogen and C_1 to C_5 alkyl, may include compounds where Z is oxygen and R is C_1 to C_4 alkyl or hydrogen. The alkaline earth metal may include calcium, magnesium, strontium and barium. The transition metal may include iron and aluminum.

The compound $M-Z-R^1$ preferably includes compounds selected from the group consisting of aluminum oxide, aluminum hydroxide, magnesium hydroxide and magnesium oxide.

When compound (d) is a metal oxide, the amount required may be generally higher than that used for the corresponding metal hydroxide. The amount of aluminum oxide may generally be in the range of about 1 to about 99wt%, about 5 to about 99wt%, about 10 to about 95wt%, about 15 to about 90wt%, about 20 to about 90wt%, about 25wt% to about 85wt%, about 30 to about 80 wt%, about 35 to about 90wt%, about 40 to about 90wt%, about 45 to about 90wt%, about 50 to about 90wt%, about 55 to about 90wt%, about 60 to about 90wt%, about 65 to about 90wt%, about 70 to about 90wt%, about 75 to about 90wt%, about 80wt% to about 90wt%. In another preferred embodiment, aluminum oxide or magnesium oxide may be used as flame retardants in the composition of the present invention.

When the compound (d) is a metal hydroxide, the compound (d) may be present in an amount of about 1% to about 20% by weight based on the total thermosetting resin composition. When the compound (d) is a metal hydroxide, the compound (d) may also

be in an amount of about 1% to about 15% by weight based on the total thermosetting resin composition. The compound (d) may still be in an amount of about 3% to about 15%, or about 5 to about 15%, or about 7% to about 15%, or about 10% to about 15%, or about 10% to about 12% by weight based on the total thermosetting resin composition.

An inorganic filler (e) may also be present in the thermosetting resin composition of the present invention. The amount of the inorganic filler (e), except the compound (d), may be present in an amount of about 40% to about 80 % by weight based on the total thermosetting resin composition. The inorganic filler (e) except the component (d) may be in an amount of about 50% to about 80% by weight based on the total thermosetting resin composition. The inorganic filler (e) except the component (d) may still be present in an amount of about 50% to about 70% by weight based on the total thermosetting resin composition. Still preferably, the inorganic filler (e) except the component (d) is present in an amount of about 60% to about 70% by weight based on the total thermosetting resin composition.

According to a second aspect, there is provided a semiconductor device encapsulated by the thermosetting resin composition as defined above.

According to a third aspect, there is provided a method for producing a thermosetting resin composition comprising the steps of:

- heating a phenolic resin curing hardener having a softening temperature ranging from about 50°C to about 170°C in a reactor to a temperature of about 190°C to about 200°C;
- adding an amine curing catalyst to the reactor to form a catalysed phenolic resin curing hardener; and
- blending the catalysed phenolic resin curing hardener with an epoxy resin and a compound selected from the group consisting of a metal oxide, and a compound represented by the formula $M-Z-R^1$, where M is a metal, Z is an oxygen or sulfur radical and R^1 is selected from the group consisting of hydrogen and C_1 to C_5 alkyl.

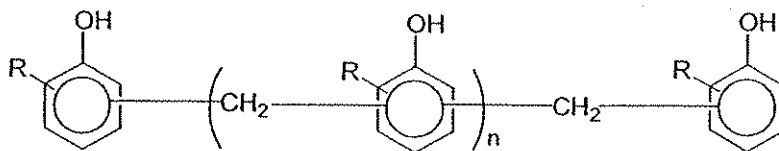
According to a fourth aspect, there is provided the thermosetting resin composition produced by the method as defined above.

DETAILED DESCRIPTION OF THE INVENTION

The phenolic resin used in the catalysed hardener for the thermosetting resin composition may be a phenol novolac (PN) type resin. The amine catalyst may be 1,8-Diazabicyclo [5,4,0] undecene-7 (or DBU) and is reacted with the PN hardener matrix and typically is only mobile when temperature rises above the hardener softening point through the application of heat.

The phenolic resin curing hardener (b) may be represented by the formula (VII), which is a phenol novolac type resin as set out below:

Formula (VII)



wherein n is an integer of 0-10 and each R is independently an atom or group selected from hydrogen atom, a halogen and an alkyl group.

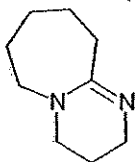
The curing hardener provides the resulting thermosetting resin composition with good modulus and processibility.

The original softening temperature of the phenolic resin curing hardener (b) may be from about 50°C to about 170°C. The phenolic resin curing hardener (b) may be present in an amount of about 0.1 to about 50% by weight based on the total phenolic resin curing hardener in the thermosetting resin composition. Also, one or more types of phenolic resin curing hardeners (b) may be present in combination in the thermosetting resin composition.

In regard to the blending ratio of the epoxy resin (a) to the total phenolic resin curing hardeners (b) and (c), the epoxy resin (a) may be used in an amount of about 0.8 to about 1.3 epoxy equivalents per hydroxyl group equivalent of the total amount of phenolic resin curing hardener (b) and (c).

An example of an amine curing catalyst used in the thermosetting resin composition of the present invention is 1,8-Diazabicyclo [5,4,0] undecene-7 (DBU), which is represented by formula (VIII) as shown below:

Formula (VIII)



DBU typically acts as a catalyst or an accelerator for the reaction between the epoxy group of the component (a) and the hydroxyl group of the phenolic resin components (b). The DBU may be reacted into a phenolic resin curing hardener (b) in a pre-determined ratio of about 3% to about 30%. The softening point of the resultant modified phenolic resin curing hardener is typically between about 120°C and about 180°C.

If the softening temperature of the resultant DBU modified phenolic resin is lower than 120°C then no room temperature storage capability is likely to be achieved due to the high reactivity. If the softening temperature of the resultant DBU modified phenolic resin is higher than 180°C then no filling property capability during transfer moulding is likely to be achieved due to the high viscosity of the moulding compound.

For the manufacturing procedure of the amine catalysed hardener, the following procedure is preferred. Firstly, the phenolic resin curing hardener (b), typically having a softening point ranging from about 50°C to about 170°C, was heated in an agitated reactor to about 190°C to about 200°C until all of the phenolic resin curing hardener had melted.

The amine curing catalyst, such as DBU, ranging from about 3% to about 30% of hardener weight content, was then slowly added to the melted phenolic resin curing hardener in a 20 to 30 minute time duration. After all the amine curing catalyst such as DBU was added to the reactor, the whole mixture was kept in the reactor for a suitable period of time (one example is for about 2 hours) at a temperature which may range from about 190°C to about 200°C.

Then, the reacted molten amine catalysed phenolic resin curing hardener was poured out and cooled typically in a water bath. The reacted amine catalysed phenolic resin curing hardener was then crushed before usage in the thermosetting resin composition of the present invention. The final amine catalysed hardener will typically have a softening point of about 120°C to about 180°C. The preferred amine catalyst is DBU.

Also, the present invention may include the use of more than one type of the amine catalysed hardener, which can be used in the same thermosetting resin composition. The different types of amine catalysed hardeners typically may include a different amine content or amount reacted with the same phenolic resin curing hardener, or the same amine content reacted with a different phenolic resin curing hardener and/or both together.

It is to be understood that by different phenolic resin curing hardeners, this also includes phenolic resin curing hardeners with different softening points or different types of phenolic resin curing hardeners. For example, the different types of phenolic resin curing hardeners may be selected from the group consisting of phenol novolac resins, cresol novolac resins, copolymers between dicyclopentadiene-modified phenolic resins and phenol novolac resins and/or cresol novolac resin, paraxylene-modified phenolic resins, biphenyl aralkyl modified phenolic resins and the like.

Further, the present invention also includes the use of other curing catalysts or accelerators such as triphenylphosphine (TPP), 2-methylimidazole (2-MZ) and other known curing accelerators to those skilled in the art which may be used in conjunction with the amine curing catalysts such as DBU in the thermosetting resin composition.

5 These curing accelerator compounds can either be used alone or in combination of two or more of such curing accelerator compounds.

The main amine curing catalyst or accelerators may be used in an amount of about 0.05 wt % to about 1.0 wt % in the total thermosetting resin composition. If an amount of less than about 0.05 wt % of the amine curing catalyst is used, then hardness of
10 the resulting moulded product is likely to decrease and the mould release property also may tend to deteriorate. If an amount of more than 1.0 wt % of DBU is used, the reaction may proceed in an undesirably fast manner and no room temperature storage capability may be achieved.

The thermosetting resin composition of the present invention demonstrates
15 improved physical properties after storage at room temperature for extended periods of time when compared to known epoxy resin compositions and these properties include flowability and moldability performance. In particular, the thermosetting resin according to the embodiments of the present invention may demonstrate a spiral flow percentage drop of no more than about 20% after storage at room temperature for an extended period
20 of time.

The thermosetting resin composition of the present invention may be used for sealing semiconductor packages.

The compound (d) in the thermosetting resin composition of the present invention typically acts as a flame retardant, which is an environmental friendly material.
25 The amount of compound (d) in the present thermosetting resin composition may be from about 1% to about 20% by weight in order to achieve V-0 in the UL-94 test with 3.2mm thickness. The amount of compound (d) in the present thermosetting resin composition may be about 5% to about 15% by weight, and may also be about 7% to about 12%.

The inorganic filler (e) used in the present thermosetting resin composition may
30 be selected from the group consisting of fused silica powder; spherical silica powder; crystalline silica powder; secondary agglomerated silica powder; porous silica powder; silica powder obtained by grinding secondary agglomerated silica powder; porous silica powder; alumina and mixtures thereof. The inorganic filler (e) may also be selected from the group consisting of fused silica powder, spherical silica powder and a mixture of the
35 two aforementioned silica powders.

The amount of the inorganic filler (e) except the component (d) in the present thermosetting resin composition is preferably about 40% to about 80% by weight in view of balance between the soldering stress resistance and moldability of the composition. Preferably, the amount of inorganic filler (e) in the present thermosetting resin composition is preferably about 50% to about 70% by weight, still preferably about 60% to about 70%.

The thermosetting resin composition may further comprise, if necessary, various other additives such as silane coupling agents, colouring agents (including for example, carbon black or red iron oxide), releasing agents (including for example, natural or synthetic wax), stress-reducing additives (including for example, silicone oil or rubber), ion trapper and other common additives for thermosetting resins known to the skilled person in the art.

Typically, in producing the thermosetting resin composition of the present invention for encapsulation of a semiconductor package and as a moulding material, typically an epoxy resin, a curing hardener, a curing accelerator, fillers and other additives are mixed sufficiently and uniformly using hot rolls or the like; and the kneaded product is preferably cooled and ground. The moulding material thus obtained may be used for sealing, coating, insulation, etc. of electronic or electrical part(s).

Typically, the encapsulated semiconductor packages utilising the thermosetting resin compositions of the present invention may be stored at room temperature and demonstrate excellent electrical reliability.

The applicant believes that compounds as described for compound (d) in this specification and claims, including metal oxides and metal hydroxides are an environmental friendly material as a flame retardant for thermosetting resin compositions. A preferred metal hydroxide is aluminum hydroxide or magnesium hydroxide.

In order to further illustrate and provide a particular example of the invention, the applicant believes that aluminum hydroxide retards fire mainly due to its endothermic decomposition to aluminum oxide and water.



The reaction takes place at the range from about 180 to about 200°C. Due to the endothermic breakdown of aluminum hydroxide, the applicant believes that the polymer is cooled and hence fewer pyrolysis products are formed. In addition to the charring production of aluminum oxide, it is believed that the aluminum oxide acts as an insulating protective layer. Thirdly, the applicant believes that the formation of water vapor has a diluting effect on the flammable gases.

Thus, this invention provides a thermosetting resin composition such as an epoxy resin composition which is able to stored at normal molding room temperatures of 20°C to 30°C with minimal effect on its physical properties and yet this invention also provide solutions for electronic parts to meet the requirement of Waste Electrical and Electronic Equipment (WEEE) and Restriction of Hazardous Substances in Electrical and Electronic Equipment (ROHS) European Community Directives.

DESCRIPTION OF PREFERRED EMBODIMENTS

The present invention is hereinafter described specifically by way of Examples. The examples serve merely to illustrate the invention and should not be construed as limiting the scope and generality of the claims. In the following Examples, the amount of each component used in the following compositions is parts by weight unless otherwise specified.

Preparation of DBU catalysed hardeners

For the manufacture of two DBU catalysed phenolic resin curing hardeners, the following procedure was conducted. First, the phenolic resin curing hardener was heated up in an agitated reactor to 190°C to 200°C until all the phenolic resin curing hardener had melted. Then, DBU with an amount of 3% to 30% of total phenolic resin curing hardener and DBU weight content and DBU are slowly added to the melted hardener in a 20 to 30 minute time duration. After all the DBU is added into the reactor, the whole mixture is kept in the reactor for another 2 hours at a temperature of 190°C to 200°C. Then, the reacted molten hardener is poured out, water-bath cooled and crushed for usage in the following examples.

EXAMPLES

Example 1

The following components and their respective proportions were mixed at room temperature using a mixer, then kneaded at 80°C to 130°C using a bi-axial roll, cooled and ground to obtain a moulding material.

The composition was as follows:

Cresol novolac type epoxy resin	15.5 parts by weight
(softening point: 65°C, epoxy equivalent: 200g/eq)	

Phenol novolac type resin 1.2 parts by weight
(softening point: 110°C, hydroxyl group equivalent: 104g/eq)

Phenol novolac type resin 1.3 parts by weight
5 (softening point: 81°C, hydroxyl group equivalent: 105g/eq)

Phenol novolac type resin, reacted with DBU 4.5 parts by weight
(softening point: 151°C, hydroxyl group equivalent: 104g/eq)

Fused silica powder 65.1 parts by weight
10 Aluminium hydroxide 11.0 parts by weight
Carbon black 0.3 parts by weight
Synthetic Wax 0.4 parts by weight
Epoxy Silane Coupling Agent 0.3 parts by weight
Mercaptane Silane Coupling Agent 0.2 parts by weight
15 Ion trapper 0.2 parts by weight

The mixed powder was kneaded at 70 to 100°C using a bi-axial roll, cooled and ground to obtain a moulding material.

Room Temperature Storage Test

20 After the moulding material had been formed, a small portion of the powder was separated from the bulk material and stored in a temperature-controlled chamber with the temperature setting of 25°C ± 5°C. The initial spiral flow of the material was measured and also at an interval of once per week. This constitutes the Room Temperature Storage Test.

25

Spiral Flow Measurement Test

A certain amount of moulding material which shall give a cull thickness of 3 ± 0.3mm was weighed. A spiral flow mould die as shown in Diagram 1 below was placed in the moulding machine and was heated up to 175°C ± 3°C. When the temperature reaches 175
30 ± 3°C, the certain amount of moulding material was poured into the transfer pot and a plunger was lowered. The material was moulded for 120sec after which the mould press was opened. The spiral flow length (up to the lustrous tip) was measured after the mould die was taken out from the moulding machine.

The measured spiral flow length provides an indication of the flowability of a particular
35 moulding material and thus also provides a measure of moulding performance. Any

significant changes or deterioration in spiral flow length of a moulding material can signify a compromise in moulding performance.

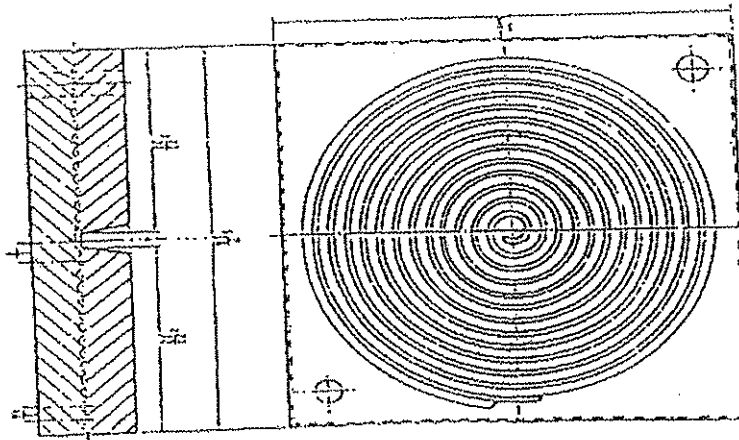


Figure 1

In Figure 1, there is shown a side view and top view of the spiral flow mould die used in the examples.

The Spiral Flow Measurement Test procedure described and performed above is known to persons skilled in the art and is described as an ASTM standard (ASTM designation D 3123-98 (Reapproved 1999)). In ASTM designation D 3123-98 (Reapproved 1999) standard there is additional description of test procedures and also includes additional diagrams.

Flammability test (Underwriters Laboratory flammability rating; UL-94 V-0, UL-94 V-1)

For epoxy resin composition flame retardant performance testing, UL-94, developed by Underwriters Laboratories, is one of the most widely used and commonly accepted tests used in the field of epoxy resins.

There is provided for this Flammability test, five samples of Test Pieces molded from a molding material having dimensions of 127mm by 12.7mm by 3.2mm and which were molded using a 37 ton molding machine. Before the test was conducted, each of the five samples was treated at the following conditions:

Temperature at $23 \pm 2^{\circ}\text{C}$; and
 $50 \pm 5\%$ relative humidity for at least 48 hours.

The five samples were each clamped vertically and burned for a period of 10 ± 0.5 seconds. The burning time of each sample and any burner residue dropping was recorded. After the burning of each sample ceases, the burner is immediately placed again under the
 5 respective sample. The burner is removed after 10 seconds of burning and the burning time, glowing time and any burned residue dropping after the burner is removed is recorded.

The burning time and glowing time for each sample was recorded together with the total burning time for all 5 samples. In order to pass the UL-94 V-0, the results must be within
 10 the criteria set out below in **Table 1** i.e the total burning time is less than or equal to 50 seconds.

Table 1

Criteria conditions	V-0
Afterflame time for each individual specimen ^t 1 or ^t 2	≤10s
Total afterflame time for any condition set (^t 1 plus ^t 2 for the 5 specimens)	≤50s
Afterflame plus afterglow time for each individual specimen after the second flame application (^t 2 + ^t 3)	≤30s
Afterflame or afterglow of any specimen up to the holding clamp	No

15 If the total burning time is more than 50 seconds then the sample is considered to have failed the UL-94 test and is classified as V-1 or V-2.

Pressure Cooker Test (PCT)

20 The moulding material was formed into tablets with a diameter of 48 mm and weighing 75 grams each. These tablets were then used to seal Test Electrical Grid (TEG) die for 16-pin Plastic Dual Inline Package (16p PDIP).

25 These TEG die have no surface protection and are “bare” IC chips which are used for electrical testing and which represent the most severe testing conditions which are likely to be encountered. The sealed 16p PDIP package devices were stored in saturated steam, at a pressure of 103 ± 7 kPa and a temperature of 125°C in a sealed autoclave containing deionised water. The package devices were suspended at a minimum height of 1cm above the initial water level in a chamber of the sealed autoclave. Electrical

measurements were made at intervals and the package devices were stored up to 1000 hours.

A failure of the package device was considered when an open circuit was detected and also by observation of the external damage or degradation of the package devices. For example, such observations were of such properties including corroded device leads or the formation of conducting matter between the leads. The results were reported in terms of percentage of failed units.

Examples 2 to 5

The thermosetting resin compositions were compounded in the respective formulations as shown in Table 2, and were subjected to the same procedure as in Example 1 to obtain the moulding materials.

Comparative Examples 1-3

The thermosetting resin compositions were compounded in the respective formulations shown in Table 2, and subjected to the same procedures as in Example 1 to obtain moulding materials. The package devices for test purposes were prepared using these moulding materials and were then subjected to the PCT test as described above. The results are shown below in Table 2.

Table 2

	Example					Comparative Example		
	1	2	3	4	5	1	2	3
Cresol novolak type epoxy resin (softening point = 65°C, epoxy equivalent: 200g/eq)	15.5	15.5	15.5	14.1	14.1	15.5	14.1	15.5
Phenolic resin hardener (softening point = 110°C, epoxy equivalent: 104g/eq)	1.2		1.2					1.2
Phenolic resin hardener (softening point = 81°C, epoxy equivalent: 105g/eq)	1.3	2.5	1.3	2.3	2.3	2.4	2.3	1.3
Phenolic resin curing hardener, reacted with DBU (softening point: 151°C., hydroxyl group equivalent: 104g/eq)	4.5	4.5	4.5	4.0	4.0			4.5

Phenolic resin curing hardener, reacted with DBU (softening point: 115°C., hydroxyl group equivalent: 106g/eq)							4.0	
Phenolic resin curing hardener, reacted with DBU (softening point: 185°C., hydroxyl group equivalent: 102g/eq)						4.5		
Aluminum hydroxide	11.0	11.0	11.0	10.0		10.0	8.0	4.0
Magnesium hydroxide					8.0			
2-methylimidazole		0.02			0.02	0.02		0.02
Flake fused silica powder			20.0		20.0		34.0	
Spherical fused silica powder	65.1	64.9	45.1	68.2	68.2	66.0	36.0	71.9

Carbon black	0.3							
Synthetic wax	0.4							
Silane Coupling Agent	0.5							
Others (Ion trapper, low stress additive)	0.2	0.4		0.2	0.2	0.4	0.4	0.4
Spiral flow (cm)	60	52		45	47	17	34	65
UL-94 (V0/V1) for 3.2mmt	V0	V0		V0	V0	V0	V0	V1
PCT (% of failed units)								
After 500hr	0	0		0	0	10	0	-
After 1000hr	0	0		0	0	20	0	-
After 500hr (after 60days)	0	0		0	0	10	-	-
After 1000hr (after 60days)	0	0		0	0	30	-	-
Storage Test (after 60 days)								
% of spiral flow drop	20%	17%		18%	20%	15%	33%	22%

It is to be understood that the silane coupling agent used in the examples and in the present invention is one that is selected from a wide range of such compounds and which is apparent to those skilled in the art.

The aforementioned thermosetting resin compositions shown in the examples and summarised in Table 2 demonstrate thermosetting resin compositions with the ability to be stored at room temperature for a long period of time, and which are able to pass UL-

94 flammability test and to offer latent curing effect during transfer moulding for the encapsulation of IC devices.

In particular, when the thermosetting resin compositions of the examples 1 to 4 are subjected to the performance tests as shown in Table 1; there is no significant change
5 in the key physical properties that affect the functional performance of the encapsulated integrated circuit device.

In particular, the results of the storage tests show that the spiral flow percentage drop for examples 1 to 4 were no more than 20% after 60 days. This demonstrates that the moldability performance of the compositions of the present invention is suitable for use at
10 normal room temperatures of 20°C to 30°C.

Also, the test results for PCT test in terms percentage of failed units demonstrates that after 500 hours (20 days) there were no failed units for examples 1 to 4 whilst for comparative examples 1 there was significant percentages of failed units which was due to spiral flow too short and caused poor wetting.

Thus, if the softening point of the DBU catalysed phenolic resin curing hardener
15 is too high, it will affect the flowability of the thermosetting resin. However, if the softening point of the DBU catalysed phenolic resin curing hardener is too low, e.g. comparative example 2, it will lose the room storage capability.

One of the typical advantages of the present invention as demonstrated above is
20 to provide a thermosetting resin composition such as an epoxy resin composition, which is capable of being stored at a normal moulding room temperatures of about 20°C to about 30 °C, and which has minimal effect on its critical physical properties.

A further typical advantage of the thermosetting resin composition is the subsequent elimination or substantial reduction of the requirement of cold room storage
25 for the thermosetting resin composition.

A further advantage of the thermosetting resin composition of the present invention is that the thermosetting resin composition provides environmental friendly flame retardant(s) which provide encapsulated electronic parts to meet the requirements of *Waste Electrical and Electronic Equipment (WEEE) and Restriction of Hazardous*
30 *Substances in Electrical and Electronic Equipment (ROHS) European Community Directives*.

Modifications and variations such as would be apparent to those skilled in the art are deemed to be within the scope of the present invention. It is also understood that the present invention should not be restricted to the particular embodiment(s) and example(s)
35 described above.

CLAIMS

What is claimed is:

1. A thermosetting resin composition for sealing of semiconductor devices, comprising:
 - (a) an epoxy resin;
 - (b) a phenolic resin curing hardener;
 - (c) an amine curing catalyst; and
 - (d) a compound selected from the group consisting of a metal oxide, and a compound represented by the formula $M-Z-R^1$, where M is a metal, Z is an oxygen or sulfur radical and R^1 is selected from the group consisting of hydrogen and C_1 to C_5 alkyl, wherein the softening point of the final catalysed phenolic resin curing hardener is between 120°C and 180°C.
2. The thermosetting resin composition of claim 1, wherein the resin composition is suitable for storage at a temperature from about 20°C to about 30 °C.
3. The thermosetting resin composition of claim 1 or 2, wherein the compound (d) is a flame retardant which does not contain halogen or phosphorous.
4. The thermosetting resin composition of claim 1, 2 or 3, wherein Z is oxygen.
5. The thermosetting resin composition of claim 1, 2, 3 or 4, wherein R^1 is selected from the group consisting of hydrogen and C_1 to C_3 alkyl.
6. The thermosetting resin composition of any one of claims 1 to 5, wherein M is an alkaline earth metal.
7. The thermosetting resin composition of claim 6, wherein the alkaline earth metal is selected from the group consisting of calcium, magnesium, strontium, and barium.
8. The thermosetting resin composition of any one of claims 1 to 5, wherein the metal is aluminum or iron.
9. The thermosetting resin composition of any one of the preceding claims, wherein the compound (d) is selected from the group consisting of aluminum oxide, aluminum hydroxide, magnesium oxide, and magnesium hydroxide.
10. The thermosetting resin composition of any one of claims 1 to 9, wherein the epoxy resin (a) is selected from the group consisting of phenol novolac type epoxy resins, cresol novolac type epoxy resins, dicyclopentadiene type epoxy resin, biphenyl type

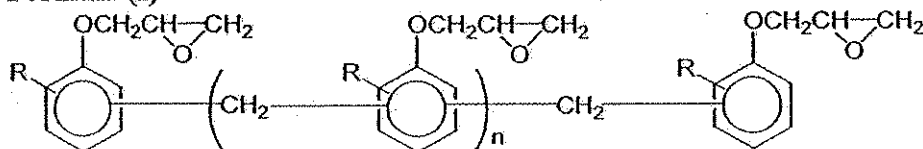
epoxy resins, biphenyl aralkyl modified epoxy resins, tri- or multi-functional type epoxy resins and naphthalene type epoxy resins.

11. The thermosetting resin composition of claim 10, wherein the epoxy resin (a) comprises a plurality of epoxy resins.

12. The thermosetting resin composition of claim 11, wherein there is provided more than one phenol novolac type epoxy resin.

13. The thermosetting resin composition of claim 10, 11, or 12 wherein the epoxy resin (a) is represented by Formula (I) shown below:

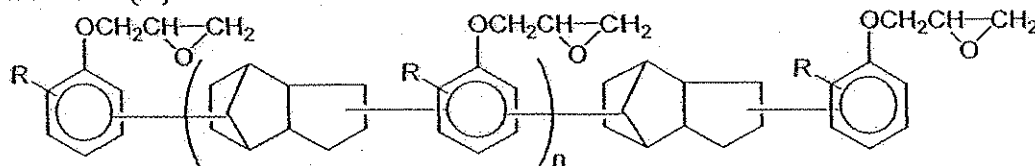
Formula (I)



wherein n is an integer of 0-10 and each R is independently an atom or group selected from a hydrogen atom, a halogen and an alkyl group.

14. The thermosetting resin composition of claim 10, 11 or 12 wherein the epoxy resin (a) is represented by Formula (II) shown below:

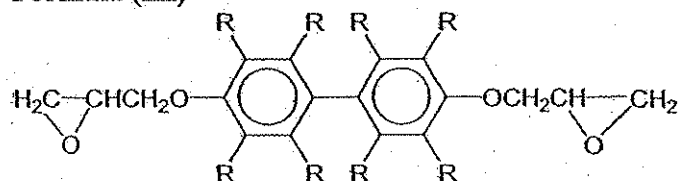
Formula (II)



wherein n is an integer of 0-10 and each R is independently an atom or group selected from hydrogen atom, a halogen and an alkyl group.

15. The thermosetting resin composition of claim 10, 11 or 12, wherein the epoxy resin (a) is represented by Formula (III) shown below:

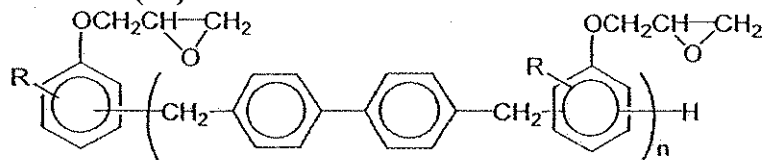
Formula (III)



wherein n is an integer of 0-10 and each R is independently an atom or group selected from a hydrogen atom, a halogen and an alkyl group.

16. The thermosetting resin composition of claim 10, 11 or 12, wherein the epoxy resin (a) is represented by Formula (IV) shown below:

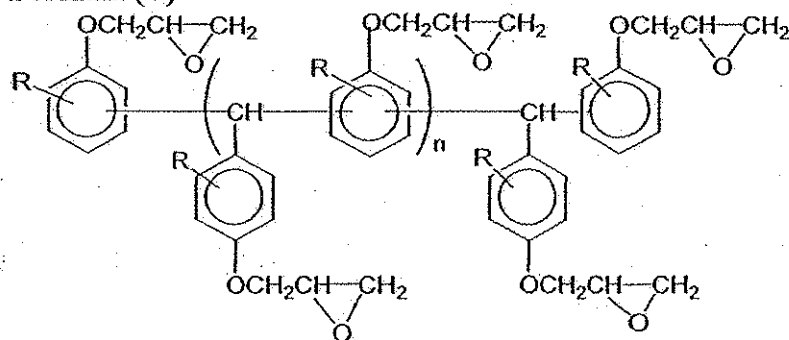
Formula (IV)



wherein n is an integer of 1-11 and each R is independently an atom or group selected from a hydrogen atom, a halogen and an alkyl group.

17. The thermosetting resin composition of claim 10, 11 or 12 wherein the epoxy resin (a) is represented by Formula (V) shown below:

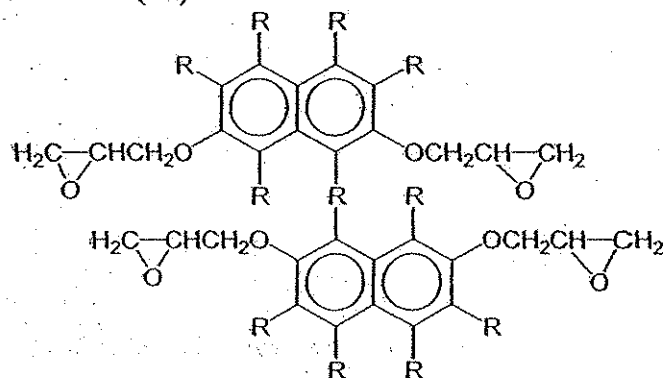
Formula (V)



wherein n is an integer of 0-10 and each R is independently an atom or group selected from a hydrogen atom, a halogen and an alkyl group.

18. The thermosetting resin composition of claim 10, 11 or 12, wherein the epoxy resin (a) is represented by Formula (VI) shown below:

Formula (VI)



wherein R is independently an atom or group selected from a hydrogen atom, a halogen and an alkyl group.

19. The thermosetting resin composition to any one of claims 1 to 18, wherein the epoxy resin (a) is used in an amount of 0.8 to 1.3 times the epoxy equivalent per hydroxyl group equivalent of the total amount of phenolic resin curing hardener.

20. The thermosetting resin composition according to any one of claims 1 to 19, wherein the epoxy resin (a) is present in an amount of about 5 to about 50 % by weight based on the total thermosetting resin composition.

21. The thermosetting resin composition according to claim 20, wherein the epoxy resin (a) is present in an amount of about 20 to about 25 % by weight based on the total thermosetting resin composition.

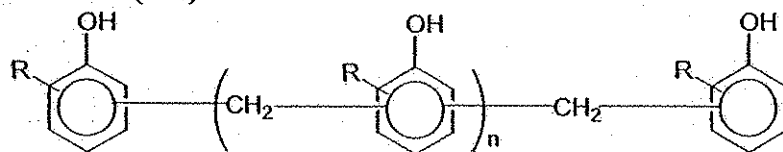
22. The thermosetting resin composition according to any one of claims 1 to 21, wherein the phenolic resin curing hardener (b) is present in an amount of about 0.1 to 50% by weight based on the total thermosetting resin composition.

23. The thermosetting resin composition according to claim 22, wherein the phenolic resin curing hardener (b) is present in an amount of about 0.1 to 10% by weight based on the total thermosetting resin composition.

24. The thermosetting resin composition according to any one of claims 22 or 23, wherein there is more than one phenolic resin curing hardener present as component (b) of the composition.

25. The thermosetting resin composition according to any one of claims 22 to 24, wherein the phenolic resin curing hardener (b) is represented by the following formula:

Formula (VII)



wherein n is an integer of 0-10 and each R is independently an atom or group selected from a hydrogen atom, a halogen and an alkyl group.

26. The thermosetting resin composition according to any one of claims 22 to 25, wherein the phenolic resin curing hardener (b) has a softening temperature ranging from 50°C to 170°C.

27. The thermosetting resin composition according to any one of claims 1 to 26, wherein an inorganic filler (e) is present in the composition and is selected from the group consisting of fused silica powder, spherical silica powder, crystalline silica powder,

secondary agglomerated silica powder, porous silica powder, silica powder obtained by grinding, secondary agglomerated silica powder or porous silica powder and alumina.

28. The thermosetting resin composition according to claim 27, wherein the inorganic filler (e) is used in an amount of about 40% to about 80% by weight based on the total thermosetting resin composition.
29. The thermosetting resin composition according to any one of claims 1 to 28, wherein the compound (d) is aluminum hydroxide.
30. The thermosetting resin composition according to claim 29, wherein the aluminium hydroxide is used in an amount of about 5% to about 20% by weight based on the total thermosetting resin composition.
31. The thermosetting resin composition according to any one of claims 1 to 30, wherein the amine curing agent is present in an amount of about 10% to 100% by weight based on total hardener content in the thermosetting resin composition.
32. The thermosetting resin composition according to claim 31, wherein the amine curing agent is DBU.
33. The thermosetting resin composition according to any one of claims 1 to 32, wherein a modified catalysed phenolic resin curing hardener is formed from a reaction of the amine curing agent to the phenolic type hardener.
34. The thermosetting resin composition according to claim 33, wherein the modified catalysed phenolic resin curing hardener is formed from a reaction ratio of the amine curing agent to the phenolic type hardener from about 3% to about 30%.
35. The thermosetting resin composition according to any one of claims 1 to 34, wherein the phenolic resin curing hardener is selected from the group consisting of phenol novolac resins, cresol novolac resins, copolymers between dicyclopentadiene-modified phenolic resins and phenol novolac resins and/or cresol novolac resin, biphenyl aralkyl modified phenolic resins and paraxylene-modified phenolic resins.
36. The thermosetting resin according to any one of claims 1 to 35, wherein the spiral flow percentage drop is less than 20% after storage at room temperature for 60 days.
37. A semiconductor device encapsulated by a thermosetting resin composition according to any one of claims 1 to 36.
38. A method for producing a thermosetting resin composition comprising the steps of:

- heating at least one phenolic resin curing hardener having a softening temperature ranging from about 50°C to about 170°C in a reactor to a temperature of about 190°C to about 200°C;
- adding an amine curing catalyst to the reactor to form a catalysed phenolic resin curing hardener; and
- blending the catalysed phenolic resin curing hardener with an epoxy resin and a compound selected from the group consisting of a metal oxide, and a compound selected from the group consisting of a metal oxide and a compound represented by the formula $M-Z-R^1$, where M is a metal, Z is an oxygen or sulfur radical and R^1 is selected from the group consisting of hydrogen and C_1 to C_5 alkyl.

39 • The method of claim 38, wherein the compound is a flame retardant which does not contain halogen or phosphorous.

40. The method of claim 38 or 39, wherein Z the formula $M-Z-R^1$ is oxygen.

41. The method of any one of claims 38, 39 or 40, wherein R^1 is selected from the group consisting of hydrogen and C_1 to C_3 alkyl.

42. The method of any one of claims 38 to 41, wherein M is selected from the group consisting of barium, strontium, magnesium, aluminum and iron.

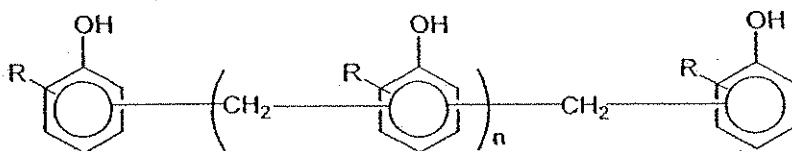
43. The method of any one of claims 38 to 42 wherein the compound is magnesium oxide, magnesium hydroxide, aluminum oxide and aluminum hydroxide.

44. The method of any one of claims 38 to 43, wherein the amine curing catalyst is DBU.

45. The method of any one of claims 38 to 44, wherein there is more than one phenolic resin curing hardener is present in the heating step.

46. The method of any one of claims 38 to 45, wherein the phenolic resin curing hardener is represented by the following formula:

Formula (VII)



wherein n is an integer of 0-10 and each R is independently an atom or group selected from a hydrogen atom, a halogen and an alkyl group.

47. The method of any one of claims 38 to 46, wherein the epoxy resin is selected from one or more from the group of epoxy resins represented by Formula (I), (II), (III), (IV), (V) or (VI) as described herein.

48. The thermosetting resin composition produced by the method of claims 38 to 47.

ABSTRACT

THERMOSETTING RESIN COMPOSITION FOR SEMICONDUCTOR DEVICES ENCAPSULATION AND SEMICONDUCTOR DEVICES

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The present invention provides a thermosetting resin composition for sealing of electronic parts, which has excellent storage stability at room temperature.

In an aspect of the present invention, there is provided a thermosetting resin composition used for sealing of semiconductor devices, comprising:

- 10 (e) an epoxy resin;
(f) a phenolic resin curing agent;
(g) an amine curing catalyst; and
(h) a compound having the formula $M-Z-R^1$, where M is a metal, Z is an oxygen or sulfur radical and R^1 is selected from the group consisting of hydrogen and C_1 to C_5 alkyl.

15 In another aspect of the present invention, there is provided a thermosetting resin composition.

In another aspect of the present invention, there is provided a semiconductor device encapsulated by the thermosetting resin composition of the present invention.