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(54) Title: EPOXY RESIN COMPOSITION FOR COPPER CLAD LAMINATE

(57) Abstract: The present invention relates to an epoxy resin composition for a printed circuit board (PCB). The composition of the invention comprises a) a bisphenol A type of novolak resin having an average epoxy equivalent of 100 to 500 and a multi-functional epoxy resin having at least 3 functional groups and having an average epoxy equivalent of 100 to 500, b) a curing accelerator comprising an imidazole compound, c) nanoclay as a filler, d) a brominated phenolic curing agent including 40 to 70% of bromine based on weight, and e) a bisphenol A type of novolak phenolic curing agent. Also provided are a prepreg and a copper clad laminate (CCL) using the composition. The epoxy resin composition of the present invention comprises nanoclay, which has an organic and inorganic structure, in which organic materials are intercalated into the interlayer of the layered silicate. Because it has superior heat resistance, a high glass transition temperature (T_g), and superior flame retardance and mechanical properties, it is useful in manufacturing copper clad laminates for printed circuit boards.



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Description

EPOXY RESIN COMPOSITION FOR COPPER CLAD LAMINATE

Technical Field

- [1] The present invention relates to an epoxy resin composition for a copper clad laminate, and more particularly to an epoxy resin composition for a printed circuit board(PCB) using nanoclay as a filler and having superior fireproofing properties, high heat resistance, and superior mechanical properties, and a prepreg and a copper clad laminate using the same.

Background Art

- [2] Currently, with the development of information communication technology, advancement in communication informationalization is progressing, in which computers and communication devices are united into one body. In addition, rapidly spreading mobile phones and notebook computers etc., are becoming smaller, lighter, and more capable. Therefore, as printed circuit boards used in these devices are becoming more highly integrated due to multi-layering, reduction of substrate thickness, and through-hole diameters, etc., better thermal reliability is required.
- [3] Also, with the transition from pin-grid arrays to ball-grid arrays, a rise of processing temperature is unavoidable because of the tendency to be lead free. Thus, development of a substrate material having superior thermal reliability to those of the conventional high glass transition temperature (T_g) level is required.
- [4] To satisfy these needs, many semiconductor packages having a pin-grid arrangement or plastic ball-grid arrangement have been developed, in which the semiconductor tip is directly mounted on the printed circuit board and the entire assembly is sealed with resin. When applied to a semiconductor package, the printed circuit board experiences a temperature of at least 170 °C during the line joining or resin sealing process. Therefore, if the printed circuit board has poor strength or elasticity, such problems as imperfect contact of joining lines and bending or twisting after resin sealing tend to occur. In order to improve high-temperature characteristics, including strength and elasticity, at 170 °C or above, the printed circuit board for a semiconductor package should have high T_g and superior heat resistance, mechanical properties, flame retardance, etc.
- [5] The conventional epoxy resin compositions for a printed circuit board typically comprise an epoxy resin, an amine-based curing agent, and a curing accelerator. Japan Patent Laid-Open No. Hei 10-240592 discloses a prepreg and a copper clad laminate manufactured by using an amine-based curing agent and a curing accelerator, as well

as a brominated di-functional epoxy resin and a multi-functional epoxy resin. Here, the brominated epoxy resin is used to offer flame retardance and the multi-functional epoxy resin with at least three functional groups is used to improve heat resistance and mechanical strength. Because it is difficult to initiate a thermosetting polymer reaction with the epoxy resins only, an amine-based curing agent is usually used. To accelerate curing of the functional groups of the epoxy resins, a curing accelerator such as imidazole is added. U.S. Patent Nos. 5,308,895 and 5,508,328 disclose a method of increasing the glass transition temperature (T_g) by adding boric acid to the resin composition, thereby controlling the curing rate and increasing curing density.

Disclosure of Invention

Technical Problem

- [6] However, if dicyanamide is used as the amine curing agent as in the mentioned patents, such toxic solvent as DMF (dimethylformamide) or NMP (N-methyl-2-pyrrolidone) has to be used to dissolve it. Also, dicyanamide may be deposited when the resin is stored at a low temperature. While the epoxy resins obtained by the mentioned patents have improved adhesiveness, they have poor heat resistance because of high hygroscopy and do not satisfy the heat resistance requirement for a semiconductor package.
- [7] If a multi-functional phenol resin is used instead of dicyanamide as the curing agent, a prepreg and a copper clad laminate for a printed circuit board having low hygroscopy, superior resistance to electrolytic corrosion, and high glass transition temperature (T_g) can be obtained. However, the resultant prepreg and copper clad laminate tend to be brittle and may break easily by external physical impact. Also, such properties as adhesion to copper film and interlayer adhesion tend to worsen.
- [8] The biggest problem of using dicyanamide or a multi-functional phenol resin as the curing agent is that they do not offer sufficient heat resistance required for a semiconductor package.

Technical Solution

- [9] It is an aspect of the present invention to provide an epoxy resin composition for a copper clad laminate having low moisture absorption, and superior heat resistance, high-temperature properties, and resistance to electrolytic corrosion as well as a high glass transition temperature (T_g) by using nanoclay as a filler, and thus being useful in manufacturing printed circuit boards.
- [10] It is another aspect of the invention to provide a prepreg which is prepared by using the epoxy composition, and a copper clad laminate for a printed circuit board with superior thermal and mechanical properties, which is prepared by the prepreg.
- [11] To attain the aspects, the present invention provides an epoxy resin composition for

a copper clad laminate comprising:

- [12] a) a bisphenol A type of novolak resin having an average epoxy equivalent of 100 to 500, and a multi-functional epoxy resin having at least 3 functional groups and an average epoxy equivalent of 100 to 500;
 - [13] b) a curing accelerator comprising an imidazole compound;
 - [14] c) nanoclay as a filler;
 - [15] d) a brominated phenolic curing agent including 40 to 70% of bromine by weight; and
 - [16] e) a bisphenol A type of novolak phenolic curing agent.
- [17] The invention also provides a prepreg obtained by impregnating the epoxy resin composition into a glass fabric.
- [18] The invention also provides a copper clad laminate for a printed circuit board in which the prepreg is laminated into at least one layer, and a copper film is laminated on one or both sides of the prepreg.

Advantageous Effects

- [19] The epoxy resin composition for a copper clad laminate of the present invention, which comprises nanoclay as a filler, has superior heat resistance, solder resistance, T_g , and mechanical properties compared with the conventional epoxy resin compositions. Thus, it can be utilized in manufacturing prepregs and copper clad laminates for printed circuit boards. The epoxy resin composition of the present invention may be pressed along with copper film into a C stage. It can be used along with B-stage prepregs.

Brief Description of the Drawings

- [20] Fig. 1 is a cross-sectional view showing the structure of the copper clad laminate for a printed circuit board according to one embodiment of the present invention.

Best Mode for Carrying Out the Invention

- [21] Hereinafter, the present invention is described in more detail.
- [22] The epoxy resin composition of the present invention is characterized in that it has a high glass transition temperature (T_g) while having low hygroscopy and superior heat resistance, and good high-temperature properties and resistance to electrolytic corrosion by comprising nanoclay as filler.
- [23] The epoxy resin adhesive composition for a copper clad laminate according to the invention comprises a) a bisphenol A type of novolak resin having an average epoxy equivalent of 100 to 500 and a multi-functional epoxy resin having at least 3 functional groups and an average epoxy equivalent of 100 to 500, b) a curing accelerator comprising an imidazole compound, c) nanoclay as a filler, d) a brominated phenolic curing agent including 40 to 70% of bromine by weight and e) a bisphenol A type of

novolak phenolic curing agent. Each constituent of the epoxy resin composition of the invention is described in further detail below.

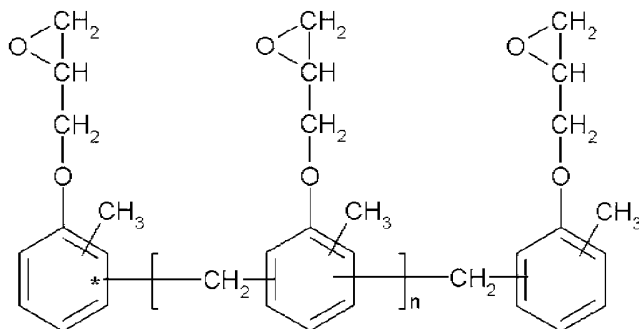
[24] In general, it is quite difficult to improve different physical properties of the epoxy composition for a printed circuit board with good balance. If the epoxy equivalent is below 100, the crosslinking density increases making the composition hard, and adhesiveness worsens. On the other hand, if the epoxy equivalent exceeds 1,000, adhesiveness improves but the glass transition temperature decreases.

[25] In the present invention, a bisphenol A type of novolak epoxy resin having an average epoxy equivalent in the range of 100 to 500 is used in order to satisfy various properties. It is used when dissolved in such solvent as methyl cellosolve (MCS), methyl ethyl ketone (MEK), etc. Preferably, the bisphenol A type of novolak resin is comprised at 20 to 120 parts by weight per 100 parts by weight of the entire epoxy resin. If the content of the bisphenol A type of novolak epoxy resin is below 20 parts by weight, the glass transition temperature decreases. Otherwise, if it exceeds 120 parts by weight, heat resistance worsens because of unreacted epoxy resin.

[26] For the multi-functional epoxy resin having at least 3 functional groups, a cresol resin having an average epoxy equivalent in the range of 100 to 500 is used. It is also preferably used when dissolved in such solvent as methyl ethyl ketone. The multi-functional epoxy resin having at least 3 functional groups is comprised at 10 to 80 parts by weight per 100 parts by weight of the epoxy resin. If the content of the multi-functional epoxy resin is below 10 parts by weight, adhesiveness worsens. Otherwise, if it exceeds 80 parts by weight, the crosslinking density of the resin increases, so that it becomes brittle after curing, despite the improvement in heat resistance.

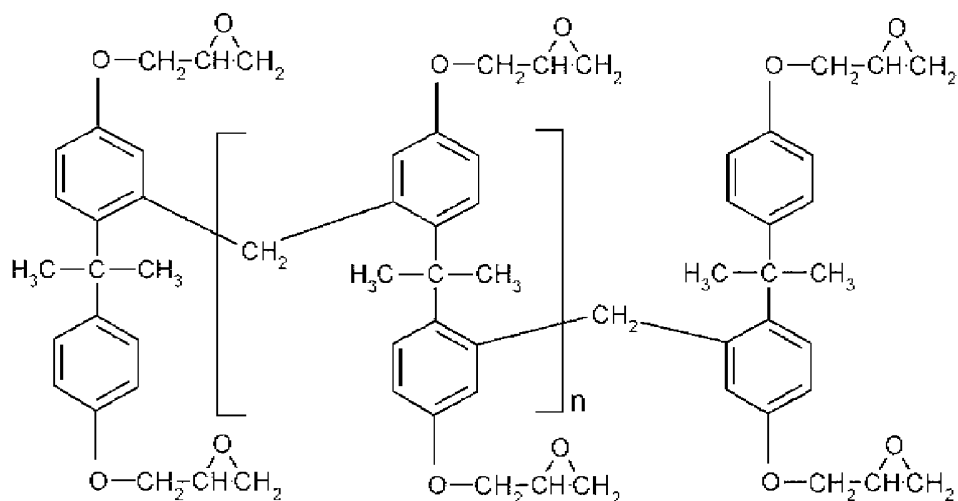
[27] For the bisphenol A type of novolak resin used in the invention, as an example, the compound represented by Formula 1 below may be used, but is not limited to them. In addition, for the multi-functional epoxy resin having at least 3 functional groups used in the invention, as an example, the compound represented by Formula 2 below may be used, but is not limited to them.

[28]



(1)

[29]



(2)

[30] For the curing agent, a phenolic curing agent, including a brominated phenolic curing agent and a bisphenol A type of novolak phenolic curing agent, is used. Preferably, the phenolic curing agent is used in the range of 0.5-1.5 equivalent for the epoxy equivalent. If its equivalent is below 0.5, many epoxy groups remain unreacted, so a high temperature or heating for a long time is necessary to attain the desired glass transition temperature and treat unreacted epoxy groups. Otherwise, if it exceeds 1.5, almost all epoxy groups participate in the reaction, but hygroscopy, storage stability, etc. worsen because of hydroxy (OH) groups which are sensitive to moisture. The content of the phenol curing agent is suggested in epoxy equivalent units, or as the equivalent number of functional groups of the epoxy resin. The amount of the epoxy resin is that including the novolak epoxy resin and the cresol epoxy resin.

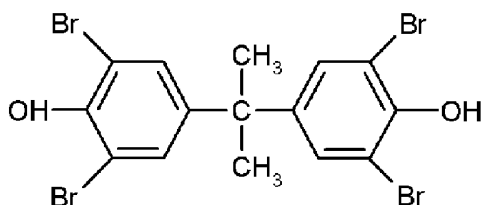
[31] For the brominated phenolic curing agent, a phenolic curing agent containing 40-70% of bromine by weight is used. The brominated phenolic curing agent is used to offer flame retardance to the resultant copper clad laminate, as well as acting as a curing agent. Preferably, the brominated phenolic curing agent is used at 0.1 to 0.7 epoxy equivalent. If the content is below 0.1 epoxy equivalent, flame retardance worsens. Otherwise, if it exceeds 0.7 epoxy equivalent, T_g and heat resistance worsen.

[32] The bisphenol A type of novolak phenolic curing agent reacts with the epoxy group of the epoxy resin for curing. Preferably, it is used at 0.3 to 1.0 epoxy equivalent. If the content is below 0.3 epoxy equivalent, T_g and heat resistance worsen. Otherwise, if it exceeds 1.0, heat resistance worsens because of unreacted curing agent.

[33] An example of the brominated phenolic curing agent used in the present invention is tetrabromobisphenol A (TBBPA) represented by Formula 3 below. And one example of the bisphenol A type of novolak resin used in the present invention is the

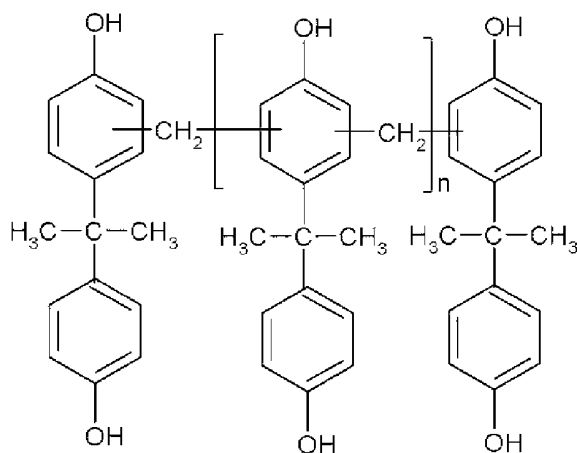
compound (VH-4290) represented by Formula 4 below.

[34]



(3)

[35]



(4)

[36]

For the curing accelerator comprising an imidazole compound, 2-ethyl-4-methylimidazole, 1-(2-cyanoethyl)-2-alkylimidazole, 2-phenylimidazole, isocyanate-masked imidazole, etc., may be used alone or in admixture. Preferably, the curing accelerator comprising an imidazole compound is comprised at 0.001 to 4 parts by weight per 100 parts by weight of the epoxy resin. If the content is below 0.001 parts by weight, acceleration of curing is insufficient. Otherwise, if it exceeds 4 parts by weight, storage stability of the epoxy resin composition worsens. More preferably, it is used at 0.01 to 1 part by weight.

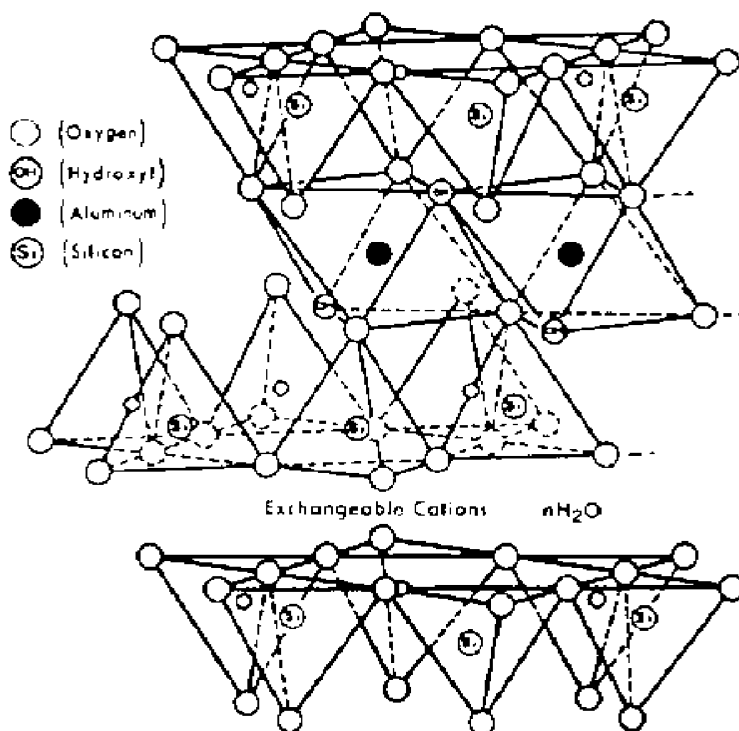
[37]

The epoxy resin composition of the present invention also comprises nanoclay as a filler. Preferably, the nanoclay is comprised at 0.1 to 20 parts by weight, more preferably at 1 to 10 parts by weight, per 100 parts by weight of the epoxy resin. If the content of the nanoclay is below 1 part by weight, the improvement of heat resistance and mechanical properties is only slight. Otherwise, if it exceeds 20 parts by weight, the viscosity of varnish increases, so that impregnation becomes impossible.

[38]

Hereunder, a supplementary description on the filler used in the present invention is given.

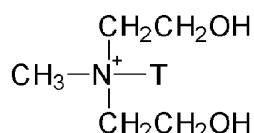
- [39] The filler is added to plastics in order to improve product quality or processing properties. The effect of adding the filler to plastics on processing, mechanical, electrical, and thermal properties of the plastics greatly varies depending on particle shape, for example, fibrous, planar, or spherical. The main purpose for using the filler is to improve mechanical properties, including reduction of thermal expansion, reduction of contraction after curing, improvement of wear resistance, and improvement of flame retardance. For an inorganic filler, silica, talc, calcium carbonate, etc., are mainly used. For a metallic filler, aluminum, aluminum oxide, etc. are widely used. For organic/inorganic fillers, there is nanoclay.
- [40] In the present invention, nanoclay, which has both organic and inorganic structures, is used as a filler. More specifically, the nanoclay has a structure in which organic materials are intercalated (bonded) into the interlayer of the layered silicate.
- [41] The basic form of nanoclay is montmorillonite (MMT), which is represented by Formula 5 below. The montmorillonite has a structure in which an octahedral sheet including at least one alumina or magnesia lies between two tetrahedral silica sheets, which is about 1 nm thick. When these layers are stacked, interlayers having a thickness of about 1 nm are formed between the layers. Strongly hydrophilic cations such as Na^+ and Ca^{2+} present in these interlayers offset the negative charge of oxide layers. Resulting from exchange reactions of cations and organic materials in the layers, nanoclays having a variety of forms are obtained.
- [42]



(5)

[43] In the present invention, commercially available nanoclay can be used. Its kind is classified depending on the organic substituents. Preferably, the nanoclay of the present invention contains an organic substituent selected from the group consisting of the compounds represented by Formula 6 (Cloisite 30B), Formula 7 (Cloisite 93A), and Formula 8 (Cloisite 20A) below.

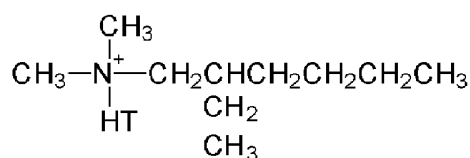
[44]



(6)

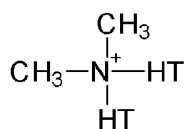
[45] In Formula 6, T is tallow (~65% C₁₈, ~30% C₁₆, ~5% C₁₄).

[46]



(7)

[47]



(8)

[48] In Formulas 7 and 8, HT is hydrogenated tallow (~65% C₁₈, ~30% C₁₆, ~5% C₁₄).

[49] In developing organic-inorganic hybrid nanocomposites, the process of intercalating polymers between layers of nano sized inorganic materials or dispersing inorganic materials in polymers to a nano size is indispensable. Even if inorganic materials the surface of which has been adequately modified by the molecular control technique are used, the high viscosity and low diffusion rate of the polymer resin makes uniform dispersion of particles impossible, let alone intercalation or dispersion into nano sized layers, thereby causing coagulation, with the conventional mixing method. This is the bottleneck in nanocomposite development. Many strategies are being tried to improve dispersibility. Such strategies can be largely classified into intercalation of the space between the layers, in-situ methods, molecular composite formation, and direct dispersion of ultrafine particles. In the intercalation method, a layered inorganic material is exfoliated and stably dispersed in a polymer one layer after another. This

method basically consists of an intercalation process and exfoliation process. In the intercalation process, the space between the layers of the layered inorganic material is modified with an organic material to improve affinity to monomers or polymers. The exfoliation process can be either a polymerization process or a blending process. In the polymerization process, monomers are polymerized and mixed with modified clay. Resultantly, polymer production and exfoliation of clay are performed simultaneously. In the blending process, exfoliation is performed while blending a polymer with modified clay, mainly by melt mixing using a twin screw extruder. In general, composites obtained by the polymerization process have better properties. This is because exfoliation of clay is greatly affected by the structure of the extruder and mixing conditions in the melt mixing process, and thus complete exfoliation is difficult. The representative in-situ method is the sol-gel method. In this method, such inorganic alkoxy compounds as alumina, titania, zirconia, and TEOS (tetraethoxysilane) are used. The sol-gel method is disadvantageous in mass production because, in general, water is used as a catalyst. But currently, a continuous process is being developed. In the future, it will be a promising nano-composite manufacturing method. In the sol-gel method, formation of nano particles and polymerization take place simultaneously. The particle size varies depending on the kind of nano particle, but is mostly within the range of 1 to 10 nm. The presence of nano particles significantly improves elasticity and heat resistance. Alternatively, monomers polymerized in the mixture solution of monomers and polymers may be dispersed with nano particles. In the molecular composite formation method, a rigid polymer, such as LCP, is dispersed in a soft polymer, such as PA and PET, in the molecular or microfibril level to prepare a composite. In the ultrafine particle direct dispersion method, the surface of ultrafine particles is modified to increase affinity to the polymer, so that uniform dispersion without coagulation is attained.

[50] If the planar nanoclay is peeled off, it remains in the polymer matrix, so that the surface area of the nanoclay increases by tens to thousands of times depending on the dispersion method, and a specific barrier structure is obtained. Therefore, nanoclay can significantly improve thermal and mechanical properties, including strength, hardness, wear resistance, heat resistance, flame retardance, etc., as well as gas barrier properties and electrical properties, compared with the conventional polymer materials.

[51] The epoxy resin composition of the present invention may further comprise common additives, as required, in order to improve such properties as storage stability, UV shielding ability, etc. The kinds of the additives are not particularly limited. Preferably, the additives are comprised at 0.01 to 7 parts by weight per 100 parts by weight of the epoxy resin. If the content is below 0.01 part by weight, improvement of storage stability, UV shielding ability, etc., is slight. Otherwise, if it exceeds 7 parts by

weight, other properties such as T_g and heat resistance worsen.

[52] The present invention also provides a method of preparing a prepreg and a copper clad laminate using the epoxy resin composition in which nanoclay is used as a filler.

[53] The present invention provides a composition in the varnish state by mixing the constituents of the epoxy resin composition. After impregnating glass fiber into the composition, it is dried at 100-200 °C to obtain a B-stage prepreg. Here, drying means removal of solvent.

[54] At least one prepreg is stacked to form a composite having a desired number of prepregs. Then, at least one metal film is formed on one or both sides of the composite. It is heated to 150-250 °C and a pressure of 1 to 80 kgf/cm² is applied to prepare a copper clad laminate for a printed circuit board. Preferably, the metal film is a copper film. Fig. 1 is a cross-sectional view showing the structure of the copper clad laminate for a printed circuit board according to one embodiment of the present invention. In FIG. 1, numeral 10 is copper film, numeral 20 is glass, numeral 30 is nanoclay, and numeral 40 is epoxy resin.

Mode for the Invention

[55] Hereinafter, the present invention is described in more detail through examples. However, the following examples are only for the understanding of the present invention and they do not limit the present invention.

[56] [Examples]

[57] Epoxy resins presented in Table 1 below were used. For the phenolic curing agents, the compounds presented in Table 2 below were used.

[58] Table 1

| | Number of functional groups | EEW | Solvent | Manufactured by |
|-----------------------|-----------------------------|-----|---------|-----------------|
| N-673 B80 (Formula 1) | Multi | 215 | MEK | Bakelite |
| N-865 (Formula 2) | Multi | 205 | MEK | DIC |

[59] Table 2

| | OH value | Br content | Solvent | Manufactured by |
|---------------------|----------|------------|---------|------------------|
| VH-4290 (Formula 3) | 118 | 58% | MCS | Kangnam Chemical |
| TBBPA (Formula 4) | 272 | - | - | Tosoh |

[60] Example 1

[61] 70 g of a bisphenol A type of epoxy resin having an average epoxy equivalent of

100 to 500 (DIC, N-865), 30 g of a multi-functional epoxy resin having at least three functional groups (Bakelite, LER-673), 35 g of a bisphenol A type of novolak phenolic curing agent (Kangnam Chemical, VH-4290), 40 g of a brominated phenolic curing agent (Tosho, TBBPA), 0.5 g of a curing accelerator comprising an imidazole compound, 1 g of an antioxidant and 1 g of a UV stabilizer as additives, and 4 g of Cloisite 20A (Southern Clay Products) as the nanoclay, were dissolved in methyl cellosolve (MCS), so that the content of non-volatile materials was 64%, to prepare a varnish.

[62] Example 2

[63] A varnish having a non-volatile material content of 64% was prepared in the same manner of Example 1, except for using 4 g of Cloisite 30B (Southern Clay Products) instead of Cloisite 20A (Southern Clay Products).

[64] Comparative Example 1

[65] A varnish having a non-volatile material content of 64% was prepared in the same manner of Example 1, except for using 4 g of Na-MMT (Southern Clay Products) instead of Cloisite 20A (Southern Clay Products).

[66] Comparative Example 2

[67] A varnish having a non-volatile material content of 64% was prepared in the same manner of Example 1, except for using 4 g of Cloisite 93A (Southern Clay Products) instead of Cloisite 20A (Southern Clay Products).

[68] Comparative Example 3

[69] A varnish was prepared in the same manner of Example 1, except for not using nanoclay.

[70] Example 3

[71] (Preparation of prepreg)

[72] Main components and their contents of the varnishes prepared in Examples 1 and 2 and Comparative Examples 1 to 3 are presented in Table 3 below. The values given in Table 3 are in grams.

[73] Gelation time was measured for the varnishes prepared in Examples 1 and 2 and Comparative Examples 1 to 3. After impregnating glass fiber to each varnish, it was heated to 150 °C for 3 to 8 minutes to obtain a prepreg.

[74] Example 4

[75] (Preparation of copper clad laminate)

[76] 6 sheets of the prepreps obtained in Example 3 were put one upon another. Two sheets of 36 μ -thick copper film were respectively put on both sides of the composite and a pressure of 20 kgf/cm² was applied at 190 °C for 150 minutes to obtain a copper clad laminate. After etching and other processes, T_g, solder resistance, 5% weight loss, and heat resistance were tested. The results are given in Table 4 below. Measurement

was taken as follows.

- [77] 1) Glass transition temperature (T_g): Measured using DSC (Q100) of TA while heating the sample at a rate of 10 °C/min.
- [78] 2) 5% weight loss: Measured using TGA (Q500) of TA while heating the sample at a rate of 10 °C/min.
- [79] 3) Solder resistance: The copper clad laminate was cut to a size of 5 cm X 5 cm. The sample was floated at 288 °C and the time for delamination at the copper film or in between layers was measured.
- [80] 4) Heat resistance: Etched copper clad laminate was cut to a size of 5 cm X 5 cm. The sample was kept under the condition of 121 °C and 2 atm for 2 hours. The sample was immersed in a soldering bath of 288 °C for 10 seconds. Appearance of the laminated sample was observed by eye. Presence of measling, exfoliation (delamination), etc. was examined.

[81] (×= very poor, △ = poor, ○ = moderate, ⊙ = good, ⊙⊙ = very good)

[82] Table 3

| | Examples | | Comparative Examples | | |
|--------------|----------|-----|----------------------|-----|-----|
| | 1 | 2 | 1 | 2 | 3 |
| N-865 | 70 | 70 | 70 | 70 | 70 |
| LER-673 | 30 | 30 | 30 | 30 | 30 |
| VH-4290 | 35 | 35 | 35 | 35 | 35 |
| TBBPA | 40 | 40 | 40 | 40 | 40 |
| Imidazole | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| Additives | 2 | 2 | 2 | 2 | 2 |
| Cloisite 20A | 4 | - | - | - | - |
| Cloisite 30B | - | 4 | - | - | - |
| Na-MMT | - | - | 4 | - | - |
| Cloisite 93A | - | - | - | 4 | - |
| MCS | 100 | 100 | 100 | 100 | 100 |

[83] Table 4

| | Examples | | Comparative Examples | | |
|----------------------------|----------|-----|----------------------|-----|-----|
| | 1 | 2 | 1 | 2 | 3 |
| Vanish gelation time (sec) | 320 | 345 | 220 | 370 | 340 |
| DSC T_g (°C) | 183 | 182 | 185 | 170 | 187 |

| | | | | | |
|-------------------------|-----|-----|-----|-----|-----|
| TGA (5wt% loss, °C) | 340 | 346 | 336 | 342 | 338 |
| Solder resistance (sec) | 712 | 755 | 120 | 534 | 620 |
| Heat resistance | ○ | ⊙ | × | △ | △ |

[84] Table 5

| | Na-MMT | Cloisite 93A | Cloisite 20A | Cloisite 30B |
|----------------------|--------|--------------|--------------|--------------|
| Vanish gelation time | ↓↓ | ↑ | = | ↓ |
| Vanish viscosity | ↑↑ | = | ↑ | ↑ |
| Adhesiveness | ↓↓ | = | ↓ | = |
| Hygroscopy | ↑↑ | = | ↑ | ↓ |
| Heat resistance | ↓ | = | ↑ | ↑↑ |

[85] As is apparent from the above results, physical properties were different depending on the kind of nanoclay. When Na-MMT was used (Comparative Example 1), T_g was almost the same, but varnish gelation time decreased and solder resistance and heat resistance worsened significantly. When Cloisite 93A was used (Comparative Example 2), solder resistance and heat resistance were comparable, but T_g dropped significantly. On the other hand, when Cloisite 20A was used (Example 1), T_g was comparable and solder resistance and heat resistance improved. Also, when Cloisite 30B was used (Example 2), solder resistance and heat resistance improved significantly.

[86] Testing Example 1

[87] Cloisite 30B, which had been confirmed as a nanoclay offering superior solder resistance and heat resistance, was used to prepare a varnish.

[88] Example 5

[89] A varnish having a non-volatile material content of 64% was prepared in the same manner of Example 2, except for reducing the amount of Cloisite 30B to 2 g.

[90] Example 6

[91] A varnish having a non-volatile material content of 64% was prepared in the same manner of Example 2, except for reducing the amount of Cloisite 30B to 3 g.

[92] Example 7

[93] A varnish having a non-volatile material content of 64% was prepared in the same manner of Example 2, except for increasing the amount of Cloisite 30B to 5 g.

[94] Physical properties were measured for Examples 2, 5, 6, and 7 in the same manner as described above. Compositions and measurement results are given in Tables 6 and 7 below.

[95] Table 6

| | Examples | | | | Comparative Example 1 |
|--------------|----------|-----|-----|-----|--------------------------|
| | 5 | 6 | 2 | 7 | |
| N-865 | 70 | 70 | 70 | 70 | 70 |
| LER-673 | 30 | 30 | 30 | 30 | 30 |
| VH-4290 | 35 | 35 | 35 | 35 | 35 |
| TBBPA | 40 | 40 | 40 | 40 | 40 |
| Imidazole | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| Additives | 2 | 2 | 2 | 2 | 2 |
| Cloisite 30B | 2 | 3 | 4 | 5 | - |
| MCS | 100 | 100 | 100 | 100 | 100 |

[96] Table 7

| | Examples | | | | Comparative Example 1 |
|-------------------------------|----------|-----|-----|-----|--------------------------|
| | 5 | 6 | 2 | 7 | |
| Vanish gelation time (sec) | 380 | 370 | 345 | 330 | 340 |
| DSC T _g (°C) | 185 | 183 | 182 | 176 | 187 |
| TGA (5wt% loss, °C) | 345 | 345 | 346 | 349 | 338 |
| Solder resistance (sec) | 710 | 724 | 755 | 800 | 620 |
| Heat resistance | ○ | ○ | ⊙ | ⊙ | △ |

[97] As is apparent from the above results, varnish gelation time reduces as the amount of Cloisite 30B increases, decreases compared with Comparative Example 1, and solder resistance and heat resistance are improved.

[98] Testing Example 2

[99] A test was performed by reducing bromine content (reducing TBBPA and increasing VH-4290) in order to improve T_g. Cloisite 30B, which had been confirmed as a nanoclay offering superior solder resistance and heat resistance, was used to prepare a varnish.

[100] Example 8

[101] 70 g of a bisphenol A type of epoxy resin having an average epoxy equivalent of 100 to 500 (DIC, N-865), 30 g of a multi-functional epoxy resin having at least three functional groups (Bakelite, LER-673), 40 g of a bisphenol A type of novolak phenolic curing agent (Kangnam Chemical, VH-4290), 35 g of a brominated phenolic curing

agent (Tosho, TBBPA), 0.5 g of a curing accelerator comprising an imidazole compound, 1 g of an antioxidant, 1 g of a UV stabilizer, and 4 g of Cloisite 30B (Southern Clay Products) were dissolved in MCS, so that the content of non-volatile materials was 64%, to prepare a varnish.

[102] Example 9

[103] 70 g of a bisphenol A type of epoxy resin having an average epoxy equivalent of 100 to 400 (DIC, N-865), 30 g of a multi-functional epoxy resin having at least three functional groups (Bakelite, LER-673), 45 g of a bisphenol A type of novolak phenolic curing agent (Kangnam Chemical, VH-4290), 30 g of a brominated phenolic curing agent (Tosho, TBBPA), 0.5 g of a curing accelerator comprising an imidazole compound, 1 g of an antioxidant, 1 g of a UV stabilizer, and 4 g of Cloisite 30B (Southern Clay Products) were dissolved in MCS, so that the content of non-volatile materials was 64%, to prepare a varnish.

[104] Physical properties were measured for Examples 4, 8, and 9 in the same manner as described above. Compositions and measurement results are given in Tables 8 and 9 below.

[105] Table 8

| | Example | | | Comparative Example 1 |
|--------------|---------|-----|-----|--------------------------|
| | 4 | 8 | 9 | |
| N-865 | 70 | 70 | 70 | 70 |
| LER-673 | 30 | 30 | 30 | 30 |
| VH-4290 | 35 | 40 | 45 | 35 |
| TBBPA | 40 | 35 | 30 | 40 |
| Imidazole | 0.5 | 0.5 | 0.5 | 0.5 |
| Additives | 2 | 2 | 2 | 2 |
| Cloisite 30B | 4 | 3 | 4 | - |
| MCS | 100 | 100 | 100 | 100 |

[106] Table 9

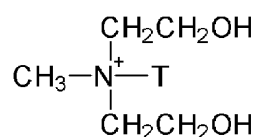
| | Example | | | Comparative Example 1 |
|----------------------------|---------|-----|-----|--------------------------|
| | 4 | 8 | 9 | |
| Vanish gelation time (sec) | 345 | 350 | 360 | 340 |
| DSC T _g (°C) | 182 | 183 | 181 | 187 |
| TGA (5wt% loss, °C) | 346 | 349 | 355 | 338 |

| | | | | |
|-------------------------|-----|-----|-----|-----|
| Solder resistance (sec) | 755 | 746 | 750 | 620 |
| Heat resistance | ⊙ | ⊙ | ⊙ | △ |

- [107] As is apparent from the above results, there was no change in physical properties including T_g , heat resistance, etc. with the change in Br content. However, the properties were significantly superior to those of Comparative Example 1.
- [108] As described above, the epoxy resin composition for a copper clad laminate of the present invention, which comprises nanoclay as a filler, has superior heat resistance, solder resistance, T_g , and mechanical properties compared with the conventional epoxy resin compositions. Thus, it can be utilized in manufacturing prepregs and copper clad laminates for printed circuit boards. The epoxy resin composition of the present invention may be pressed along with copper film into a C stage. It can be used along with B-stage prepregs.
- [109] While the present invention has been described in detail with reference to the preferred embodiments, those skilled in the art will appreciate that various modifications and substitutions can be made thereto without departing from the spirit and scope of the present invention as set forth in the appended claims.

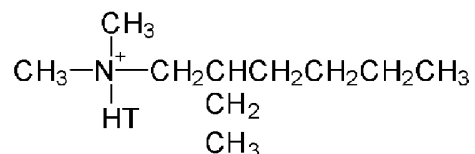
Claims

- [1] An epoxy resin composition for a copper clad laminate, comprising:
- a) a bisphenol A type of novolak resin having an average epoxy equivalent of 100-500, and a multi-functional epoxy resin having at least 3 functional groups and having an average epoxy equivalent of 100 to 500;
 - b) a curing accelerator comprising an imidazole compound;
 - c) nanoclay as a filler;
 - d) a brominated phenolic curing agent including 40 to 70% of bromine by weight; and
 - e) a bisphenol A type of novolak phenolic curing agent.
- [2] The epoxy resin composition of claim 1, which comprises:
- 100 parts by weight of an epoxy resin comprising 20 to 120 parts by weight of a bisphenol A type of novolak resin and 10 to 80 parts by weight of a multi-functional epoxy resin having at least 3 functional groups;
- 0.001 to 4 parts by weight of a curing accelerator and 0.1 to 20 parts by weight of a filler per 100 parts by weight of the epoxy resin; and
- 0.1 to 0.7 epoxy equivalent of a phenolic curing agent and 0.3 to 1.0 epoxy equivalent of a bisphenol A type of novolak phenolic curing agent.
- [3] The epoxy resin composition of claim 1, wherein the nanoclay has an organic and inorganic structure in which organic materials are intercalated into the interlayer of the layered silicate.
- [4] The epoxy resin composition of claim 3, wherein the nanoclay comprises an organic substituent selected from the group consisting of the compounds represented by Formula 6, Formula 7, and Formula 8 below:

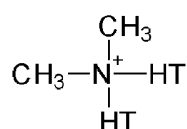


(6)

where T is tallow (~65% C₁₈, ~30% C₁₆, ~5% C₁₄)



(7)

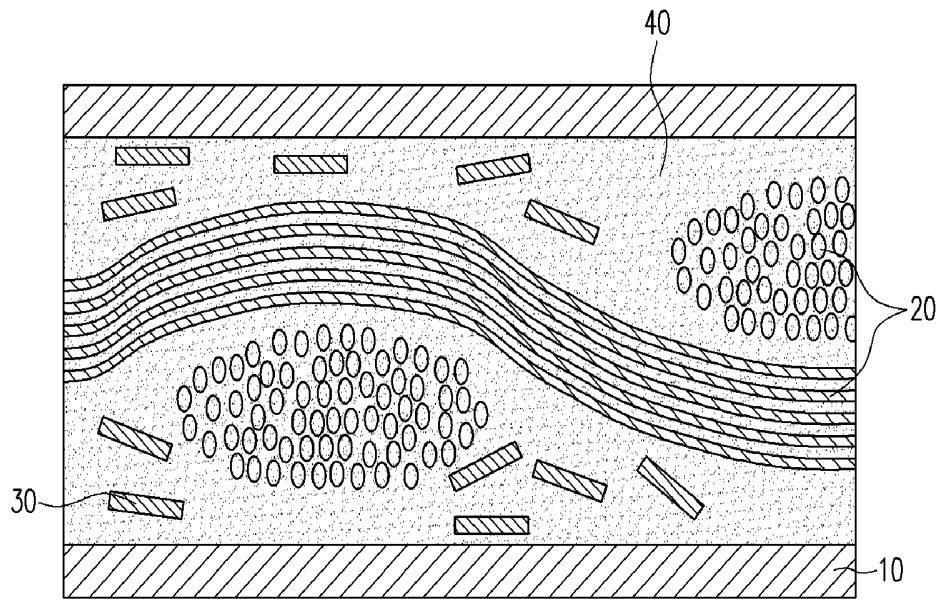


(8)

where HT is hydrogenated tallow.

- [5] The epoxy resin composition of claim 1, wherein the curing accelerator is at least one selected from the group consisting of 2-ethyl-4-methylimidazole, 1-(2-cyanomethyl)-2-alkylimidazole, 2-phenylimidazole, and an isocyanate-masked imidazole-based compound.
- [6] The epoxy resin composition of claim 1, which further comprises 0.01 to 7 parts by weight of additives per 100 parts by weight of the epoxy resin.
- [7] A prepreg obtained by impregnating glass fabric into the epoxy resin composition of any one of claims 1 to 6.
- [8] A copper clad laminate for a printed circuit board, in which the prepreg of claim 7 is laminated into at least one layer and copper film is formed on one or both sides of the prepreg.
- [9] The copper clad laminate of claim 8, wherein the prepreg and the copper film are united by heating and pressing.

[Fig. 1]



INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR 2005/001358

A. CLASSIFICATION OF SUBJECT MATTER

IPC⁷: C08L 63/02, C08K 3/34

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC⁷: C08L 63/02, C08K 3/34

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

Questel WPIL

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|-----------|--|-----------------------|
| A | US 5061744 A (OGITANI et al.) 29 October 1991 (29.10.1991) <i>claims.</i> | 1 |
| | -- | |
| A | JP 63 162775 A (SOMAR MFG CO LTD), 6 July 1988 (06.07.1988) , (abstract) World Patent Index (online), London, UK.: Retrieved from: Questel/Orbit, Paris, France, DW199704 Accession No. 1988-230 545 <i>abstract.</i> | 1 |
| | ---- | |

☐ Further documents are listed in the continuation of Box C.☒ See patent family annex.

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Date of the actual completion of the international search
13 June 2005 (13.06.2005)Date of mailing of the international search report
1 July 2005 (01.07.2005)Name and mailing address of the ISA/ AT
Austrian Patent Office
Dresdner Straße 87, A-1200 ViennaAuthorized officer
PAMMINGER W.

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/KR 2005/001358

| Patent document cited in search report | | | Publication date | Patent family member(s) | Publication date |
|---|---|----------|---------------------|----------------------------|---------------------|
| JP | A | 63162775 | | none | |
| | | A2 | | | |