

Description

Title of Invention: **GLASS CLOTH, PREPREG, AND PRINTED CIRCUIT BOARD**

Technical Field

[0001] The present invention relates to a glass cloth, a prepreg, and a printed wiring board (also referred to as a printed circuit board).

Background Art

[0002] A propagation speed of a transmission line formed on a printed wiring board is typically affected by a dielectric constant of a substrate therearound. For example, the propagation speed is represented by the following expression in a case of a microstrip line.

$$V = C/\epsilon_{\text{eff}}^{1/2}$$

In the formula, C represents the velocity of light, and ϵ_{eff} represents an effective dielectric constant of a substrate.

[0003] Data communication technology with large capacity and high speed has been demanded in recent years due to development of electronic devices, and reduction in a delay time difference (skew) between differential wiring also becomes important for increasing the communication speed.

[0004] Since a prepreg containing glass cloth used for the printed wiring board has a different dielectric property between glass and a resin, sparseness and denseness of the resin and the glass cloth affect transmission of communication signals. For example, when differential traces are arranged, respectively, in a sparse portion of the glass and in a dense portion of the glass, signal skew occurs in the transmission signals between the traces due to the different effective dielectric constants to cause a problem of deterioration in the transmission property.

[0005] As a method for improving the sparseness and denseness of the glass cloth to reduce the skew, conventionally known is a technique of opening the glass cloth and reducing gap in the glass cloth to uniformize the density of glass (see Patent Literature 1, for example).

Citation List

Patent Literature

[0006] Patent Literature 1: Japanese Patent Laid-Open No. 2006-232952

Summary of Invention

Technical Problem

[0007] However, it needs to convey the glass cloth with applying tension to warp of the glass cloth in order to stably perform the opening treatment of the glass cloth, and thus, the warp is hard to be opened compared with weft. When the differential traces are arranged in the warp direction, the effect by sparseness and denseness of the glass fiber tends to occur, and when the glass cloth has thickness to some extent, the effect by sparseness and denseness of the glass fiber tends to be obvious. Therefore, there is inconvenience in which the printed wiring board using the prepreg containing the glass cloth has large skew.

[0008] An object of the present invention is to solve the above inconvenience and to provide glass cloth that can reduce skew when used for a printed wiring board.

Solution to Problem

[0009] The present inventors have intensively investigated a means for reducing the skew of the printed wiring board using the prepreg containing glass cloth, and consequently found that the skew of the printed wiring board can be reduced by setting variation of strand thicknesses of warp and weft to be within a certain range even when the warp cannot be sufficiently opened compared with the weft. It is presumed that reducing the variation in thicknesses of warp hard to be opened and allowing the thicknesses of weft to vary to a certain extent allow the glass fiber to be appropriately distributed to enable prevention of a locally dense state, but the present invention is not limited by this presumption.

[0010] To achieve the above object, the glass cloth of the present invention is a glass cloth comprising glass fibers as warp and weft, wherein a ratio $\sigma t / \sigma y$ of a standard deviation σt

of a glass strand thickness of the warp to a standard deviation σ_y of a glass strand thickness of the weft of the glass cloth is within a range of 0.3 to 0.9.

[0011] In the glass cloth of the present invention, the ratio σ_t/σ_y of the standard deviation σ_t of the glass strand thickness of the warp to the standard deviation σ_y of the glass strand thickness of the weft of the glass cloth is within the above range, and the skew of the printed wiring board can be consequently reduced.

[0012] In the glass cloth of the present invention, if the ratio σ_t/σ_y of the standard deviation σ_t of the glass strand thickness of the warp to the standard deviation σ_y of the glass strand thickness of the weft of the glass cloth is more than 0.9, the skew of the printed wiring board cannot be reduced. Meanwhile, in the glass cloth of the present invention, it is technically difficult to set the ratio σ_t/σ_y of the standard deviation σ_t of the glass strand thickness of the warp to the standard deviation σ_y of the glass strand thickness to be less than 0.3.

[0013] The glass cloth of the present invention preferably has an opening area rate S within a range of 90 to 100%, wherein the opening area rate S is determined by the following formula (1) from a weaving density W_t of the warp, an average yarn width B_t of the warp, a weaving density W_y of the weft, and an average yarn width B_y of the weft.

(Expression 1)

$$S = \frac{\left(\frac{25000}{W_t}\right) \times \left(\frac{25000}{W_y}\right) - \left(\left(\frac{25000}{W_t}\right) - B_t\right) \times \left(\left(\frac{25000}{W_y}\right) - B_y\right)}{\left(\frac{25000}{W_t}\right) \times \left(\frac{25000}{W_y}\right)} \times 100 \quad \cdot \cdot \cdot (1)$$

[0014] In the glass cloth of the present invention, the opening area rate S is within the above range, and the skew of the printed wiring board can be consequently more reduced.

[0015] The glass cloth of the present invention preferably has a ratio R_t/R_y within a range of 0.3 to 0.9, wherein R_t/R_y is a ratio of a maximum-minimum difference R_t being a difference between a maximum value and a minimum value of the glass strand thickness of the warp to a maximum-minimum difference R_y being a difference between a maximum value and a minimum value of the glass strand thickness of the weft.

[0016] In the glass cloth of the present invention, the ratio R_t/R_y is within the above range, and the skew of the printed wiring board can be further reduced.

[0017] The glass cloth of the present invention preferably has a yarn width opening rate L_t of the warp determined by the following formula (2) within a range of 60 to 83%, and preferably has a yarn width opening rate L_y of the weft determined by the following formula (3) within a range of, for example, 85% or more.

(Expression 2)

$$L_t = \frac{B_t}{\left(\frac{25000}{W_t}\right)} \times 100 \quad \cdot \cdot \cdot (2)$$

(Expression 3)

$$L_y = \frac{B_y}{\left(\frac{25000}{W_y}\right)} \times 100 \quad \cdot \cdot \cdot (3)$$

[0018] In the glass cloth of the present invention, even when the yarn width opening rate L_t of the warp and the yarn width opening rate L_y of the weft are respectively within the above ranges, the skew of the printed wiring board can be reduced.

[0019] Further, the glass cloth of the present invention preferably has a thickness within a range of 18 to 100 μm . In the glass cloth of the present invention, even when the thickness is within the above range, the skew of the printed wiring board can be reduced.

[0020] The prepreg of the present invention comprises the glass cloth of the present invention. The prepreg of the present invention can reduce the skew of the printed wiring board by containing the glass cloth of the present invention.

[0021] In this case, in the prepreg of the present invention, a difference between a relative dielectric constant of the glass cloth and a relative dielectric constant of a matrix resin of the prepreg is preferably within a range of 1.5 to 3.0. In the prepreg of the present invention, even when the difference between the relative dielectric constant of the glass cloth and the relative dielectric constant of the matrix resin of the prepreg is within the range of 1.5 to 3.0, the effect on transmission of communication signals caused by sparseness and denseness of the resin and the glass cloth in the printed wiring board can be reduced.

[0022] The printed wiring board of the present invention comprises the prepreg of the present invention. The printed wiring board of the present invention can reduce the skew by containing the prepreg of the present invention.

Description of Embodiments

[0023] Next, embodiments of the present invention will be described in further detail.

[0024] The glass cloth of the present embodiment is a glass cloth having glass fibers as warp and weft, and the glass fibers are glass strands composed of a plurality of glass filaments.

[0025] In the glass cloth of the present embodiment, a ratio σ_t/σ_y of a standard deviation σ_t of a glass strand thickness of the warp to a standard deviation σ_y of a glass strand thickness of the weft of the glass cloth is within a range of 0.3 to 0.9, preferably within a range of 0.35 to 0.85, more preferably within a range of 0.35 to 0.71, further preferably within a range of 0.5 to 0.71, and most preferably within a range of 0.6 to 0.71. The glass strand thickness of the weft and the glass strand thickness of the warp of the glass cloth can be measured by a method described later.

[0026] In the glass cloth of the present embodiment, an opening area rate S determined by the following formula (1) from a weaving density W_t of the warp, an average yarn width B_t of the warp, a weaving density W_y of the weft, and an average yarn width B_y of the weft is preferably within a range of 90 to 100%. The yarn widths of the warp and the weft of the glass cloth can be measured by a method described later, and the average yarn width B_t of the warp and the average yarn width B_y of the weft can be calculated from the yarn widths of the warp and the weft respectively measured.

(Expression 4)

$$S = \frac{\left(\frac{25000}{W_t}\right) \times \left(\frac{25000}{W_y}\right) - \left(\left(\frac{25000}{W_t}\right) - B_t\right) \times \left(\left(\frac{25000}{W_y}\right) - B_y\right)}{\left(\frac{25000}{W_t}\right) \times \left(\frac{25000}{W_y}\right)} \times 100 \quad \cdot \cdot \cdot (1)$$

[0027] The opening area rate S is more preferably within a range of 95 to 100%, further preferably within a range of 96 to 99.9%, and most preferably within a range of 98.5 to 99.9%.

[0028] The weaving density W_t of the warp and the weaving density W_y of the weft are not particularly limited, and may be each within a range of 20 to 120 yarn/25-mm. The weaving density W_t of the warp and the weaving density W_y of the weft may be densities

different from each other. The weaving density W_t of the warp is more preferably within a range of 30 to 110 yarn/25-mm, further preferably within a range of 40 to 100 yarn/25-mm, and most preferably within a range of 50 to 70 yarn/25-mm. The weaving density W_y of the weft is more preferably within a range of 30 to 110 yarn/25-mm, further preferably within a range of 40 to 100 yarn/25-mm, and most preferably within a range of 50 to 70 yarn/25-mm.

[0029] In the glass cloth of the present embodiment, a ratio R_t/R_y is preferably within a range of 0.3 to 0.9, wherein R_t/R_y is a ratio of a maximum-minimum difference R_t being a difference between a maximum value and a minimum value of the glass strand thickness of the warp to a maximum-minimum difference R_y being a difference between a maximum value and a minimum value of the glass strand thickness of the weft.

[0030] The ratio R_t/R_y is more preferably within a range of 0.4 to 0.9, further preferably within a range of 0.4 to 0.8, and most preferably within a range of 0.6 to 0.7.

[0031] In the glass cloth of the present embodiment, a yarn width opening rate L_t of the warp determined by the following formula (2) is preferably within a range of 60 to 83%, and a yarn width opening rate L_y of the weft determined by the following formula (3) is preferably within a range of 85% or more.

(Expression 5)

$$L_t = \frac{B_t}{\left(\frac{25000}{W_t}\right)} \times 100 \quad \cdot \cdot \cdot (2)$$

(Expression 6)

$$L_y = \frac{B_y}{\left(\frac{25000}{W_y}\right)} \times 100 \quad \cdot \cdot \cdot (3)$$

[0032] The yarn width opening rate L_t of the warp is more preferably within a range of 63 to 83%, further preferably within a range of 63 to 75%, and most preferably within a range of 63 to 68%. The yarn width opening rate L_y of the weft is more preferably within a range of 88% or more, further preferably within a range of 90% or more, and most preferably within a range of 95% or more.

[0033] The yarn width opening rate L_t of the warp and the yarn width opening rate L_y of the weft can be respectively calculated from the yarn widths of the warp and the weft measured by a method described later.

[0034] The glass cloth of the present embodiment preferably has a thickness within a range of 18 to 100 μm . The thickness of the glass cloth of the present embodiment is more preferably within a range of 25 to 90 μm , further preferably within a range of 30 to 80 μm , and most preferably within a range of 30 to 50 μm .

[0035] The thickness of the glass cloth is an average value of measurement values when the thickness is measured at 15 points in the glass cloth with a micrometer in accordance with JIS R 3420:2013.

[0036] The glass cloth of the present embodiment is woven with the glass fiber (the glass strand) as warp and weft, and can be manufactured as follows, for example.

[0037] First, a predetermined glass batch (a glass raw material) is melted and subjected to fibrillization to obtain a glass filament. A filament diameter of the glass filament is not particularly limited, but preferably within a range of 10 μm or less, more preferably within a range of 8 μm or less, and particularly preferably within a range of 3 to 7 μm for application of the printed wiring board.

[0038] Within a range of, for example, 25 to 500, preferably within a range of 40 to 300, of the glass filaments are bundled by a known method to form the glass fiber. Note that, a method of melting and subjecting the glass batch to fibrillization to obtain the glass filament, and then bundling a plurality of the glass filaments to obtain the glass fiber (the glass strand) is called spinning.

[0039] A mass per unit length of the glass fiber (the glass strand) is preferably within a range of 2 to 30 g/1000-m, more preferably within a range of 4 to 25 g/1000-m, and further preferably within a range of 4 to 15 g/1000-m.

[0040] Glass composition of the glass fiber is not particularly limited, and examples thereof include E-glass composition, high-strength and high-elasticity glass composition, high-elasticity and easily-manufacturing glass composition, or low-dielectric-constant and low-dielectric-loss-tangent glass composition. For the high-speed communication

application, the low-dielectric-constant and low-dielectric-loss-tangent glass composition is preferable, and examples thereof include NE glass, L glass, or D glass.

[0041] The E-glass composition is the most generic glass composition, and contains SiO_2 in a range of 52.0 to 56.0 mass%, Al_2O_3 in a range of 12.0 to 16.0 mass%, MgO and CaO in a range of 20.0 to 25.0 mass% in total, and B_2O_3 in a range of 5.0 to 10.0 mass% relative to the total amount of the glass fiber.

[0042] The high-strength and high-elasticity glass composition contains SiO_2 in a range of 60.0 to 70.0 mass%, Al_2O_3 in a range of 20.0 to 30.0 mass%, MgO in a range of 5.0 to 15.0 mass%, Fe_2O_3 in a range of 0 to 1.5 mass%, and Na_2O , K_2O , and Li_2O in a range of 0 to 0.2 mass% in total relative to the total amount of the glass fiber. The high-strength and high-elasticity glass composition preferably contains Fe_2O_3 in a range of 0.15 to 1.50 mass%, ZrO_2 in a range of 0.01 to 0.10 mass%, and Na_2O , K_2O , and Li_2O in a range of 0.02 to 0.20 mass% in total.

[0043] The high-elasticity and easily-manufacturing glass composition contains SiO_2 in a range of 57.0 to 60.0 mass%, Al_2O_3 in a range of 17.5 to 20.0 mass%, MgO in a range of 8.5 to 12.0 mass%, CaO in a range of 10.0 to 13.0 mass%, and B_2O_3 in a range of 0.5 to 1.5 mass% relative to the total amount of the glass fiber, and contains SiO_2 , Al_2O_3 , MgO , and CaO in a range of 98.0 mass% or more in total.

[0044] The low-dielectric-constant and low-dielectric-loss-tangent glass composition contains SiO_2 in a range of 48.0 to 62.0 mass%, B_2O_3 in a range of 17.0 to 26.0 mass%, Al_2O_3 in a range of 9.0 to 18.0 mass%, CaO in a range of 0.1 to 9.0 mass%, MgO in a range of 0 to 6.0 mass%, Na_2O , K_2O , and Li_2O in a range of 0 to 0.5 mass% in total, TiO_2 in a range of 0 to 5.0 mass%, SrO in a range of 0 to 6.0 mass%, F_2 and Cl_2 in a range of 0 to 3.0 mass% in total, and P_2O_5 in a range of 0 to 6.0 mass% relative to the total amount of the glass fiber.

[0045] A content of each component in the aforementioned glass composition can be measured by using an ICP emission spectrometer for Li, which is a light element, and can be measured by using a wavelength dispersive fluorescent X-ray analyzer for the other elements. The content of each component in the glass composition can be specifically measured as follows.

[0046] First, the glass cloth is cut into an appropriate size, then put into a platinum crucible, and the mixture is melted in an electric furnace while holding the temperature at 1400 to 1650°C for 6 hours and stirring to obtain homogeneous melted glass. Here, when an organic substance adheres to the glass cloth surface or when the glass fiber is contained in an organic substance (resin) as mainly a reinforcing material, the organic substance is removed for use by, for example, heating in a muffle furnace at 300 to 650°C for about 2 to 24 hours.

[0047] Then, the obtained melted glass is flowed on a carbon plate to produce a glass cullet, and the cullet is crushed and then powdered into glass powder. Li, which is a light element, is quantitatively analyzed by using the ICP emission spectrometer after the glass powder is thermally decomposed with an acid. The other elements are quantitatively analyzed by using the wavelength dispersive fluorescent X-ray analyzer after the glass powder is formed into a disk shape with a pressing machine.

[0048] The quantitative analysis using the wavelength dispersive fluorescent X-ray analyzer can be performed by the following method. First, the content of each component in a sample for measurement is measured by a fundamental parameter method. Then, based on this measurement result, at least three samples for a calibration curve are produced, and the analysis is performed by a calibration curve method. The content of each component in the samples for a calibration curve can be quantitatively analyzed with the ICP emission spectrometer. Then, these quantitative analysis results are converted as an oxide to calculate the content of each component and the total amount, and from these values, the aforementioned content rate (mass%) of each component can be determined.

[0049] Then, the glass fiber (the glass strand) is woven as warp or weft by using a known loom to obtain the glass cloth of the present embodiment. Examples of the loom include a jet-type loom such as air jet or water jet, a shuttle-type loom, and a rapier loom. Examples of a weaving method with the loom include plain weaving, satin weaving, basket weaving, and twill weaving, and plain weaving is preferable from the viewpoint of manufacturing efficiency.

[0050] In the weaving, a sizing agent can be used in order to bundle the glass filaments and to protect the glass fiber (the glass strand). Examples of the sizing agent include

sizing agents in which a coating-forming component is starch-based or polyvinyl alcohol (PVA)-based. The sizing agent may contain an oil agent, a softening agent, etc.

[0051] In the glass cloth of the present embodiment, an adhering amount of the sizing agent relative to 100 parts by mass of the glass fiber yarn is preferably within a range of 0.1 to 5 parts by mass, more preferably within a range of 0.3 to 3 parts by mass, and further preferably within a range of 0.5 to 2 parts by mass.

[0052] The glass cloth of the present embodiment may be subjected to an opening treatment and further subjected to a deoiling treatment and a surface treatment after the weaving. Any of the opening treatment, the deoiling treatment, and the surface treatment may be performed first, and the order is not limited.

[0053] Examples of the opening treatment include a treatment of increasing yarn widths of the warp and the weft by performing: a treatment (a highly pressurized water opening treatment) of opening with a pressure of fluid such as water jet having a surface pressure within a range of 1 to 8 MPa while applying tension to the warp of the glass cloth of the present embodiment within a range of 30 to 500 N; a treatment of opening with water flow pressure such as a generic spray; a treatment of opening with high-frequency vibration such as ultrasonic wave though liquid as a medium; a treatment of opening with pressurizing with a roll; etc.

[0054] Examples of the deoiling treatment include a treatment in which the glass cloth of the present embodiment is arranged in a heating furnace at an atmospheric temperature within a range of 300 to 500°C for a time within a range of 40 to 80 hours to thermally decompose the organic substance adhering to the glass fiber.

[0055] Examples of the surface treatment include a treatment in which the glass cloth is immersed in a solution containing a silane coupling agent or containing the silane coupling agent and a surfactant, excess water is squeezed, and then the glass cloth is heated and dried at a temperature within a range of 90 to 120°C for a time within a range of 1 to 10 minutes.

[0056] Examples of the silane coupling agent include an aminosilane, an ureidosilane, a chlorosilane, an epoxysilane, a mercaptosilane, a vinylsilane, a (meth)acrylsilane, a phenylsilane, a styrylsilane, and an isocyanatesilane. In the present embodiment, the

silane coupling agent may be used singly, or may be used in combination of two or more thereof.

[0057] Examples of the aminosilane include γ -aminopropyltriethoxysilane, N- β -(aminoethyl)- γ -aminopropyltrimethoxysilane, N- β -(aminoethyl)-N'- β -(aminoethyl)- γ -aminopropyltrimethoxysilane, and γ -anilinopropyltrimethoxysilane.

[0058] Examples of the ureidosilane include γ -ureidopropyltriethoxysilane.

[0059] Examples of the chlorosilane include γ -chloropropyltrimethoxysilane.

[0060] Examples of the epoxysilane include β -(3,4-epoxycyclohexyl)ethyltrimethoxysilane and γ -glycidoxypropyltrimethoxysilane.

[0061] Examples of the mercaptosilane include γ -mercaptotrimethoxysilane and γ -mercaptopropyltrimethoxysilane.

[0062] Examples of the vinylsilane include vinyltrimethoxysilane, N- β -(N-vinylbenzylaminoethyl)- γ -aminopropyltrimethoxysilane, and N-benzyl- β -aminoethyl- γ -aminopropyltrimethoxysilane.

[0063] Examples of the (meth)acrylsilane include γ -acryloxypropyltrimethoxysilane and γ -methacryloxypropyltrimethoxysilane.

[0064] Examples of the phenylsilane include phenyltrimethoxysilane.

[0065] Examples of the styrylsilane include p-styryltrimethoxysilane.

[0066] Examples of the isocyanatesilane include γ -isocyanatepropyltriethoxysilane.

[0067] Examples of the surfactant include a nonionic surfactant, a cationic surfactant, an anionic surfactant, and an amphoteric surfactant. In the present embodiment, the surfactant may be used singly, or may be used in combination of two or more thereof.

[0068] Examples of the nonionic surfactant include an ethylene-oxide propylene-oxide alkyl ether, a polyoxyethylene alkyl ether, a polyoxyethylene-polyoxypropylene block copolymer, an alkylpolyoxyethylene-polyoxypropylene block copolymer ether, a polyoxyethylene fatty acid ester, a polyoxyethylene fatty acid monoester, a polyoxyethylene fatty acid diester, a polyoxyethylene sorbitan fatty acid ester, a glycerol fatty acid ester ethylene oxide adduct, a polyoxyethylene castor oil ether, a hardened castor oil ethylene oxide adduct, an alkylamine ethylene oxide adduct, a fatty acid amide ethylene oxide adduct, a glycerol fatty acid ester, a polyglycerol fatty acid ester, a

pentaerythritol fatty acid ester, a sorbitol fatty acid ester, a sorbitan fatty acid ester, a sucrose fatty acid ester, a polyhydric alcohol alkyl ether, a fatty acid alkanolamide, acetylene glycol, acetylene alcohol, an ethylene oxide adduct of acetylene glycol, and an ethylene oxide adduct of acetylene alcohol.

[0069] Examples of the cationic surfactant include an alkyl dimethylbenzylammonium chloride, an alkyl trimethylammonium chloride, an alkyl dimethylethylammonium ethylsulfate, a higher alkylamine salt (such as an acetate salt and a hydrochloric acid salt), an ethylene oxide adduct to a higher alkylamine, a condensate between a higher fatty acid and a polyalkylene polyamine, a salt of an ester between a higher fatty acid and an alkanolamine, a salt of a higher fatty acid amide, an imidazoline-type cationic surfactant, and an alkylpyridinium salt.

[0070] Examples of the anionic surfactant include a higher alcohol sulfate ester salt, a higher alkyl ether sulfate ester salt, an α -olefin sulfate ester salt, an alkylbenzenesulfonate salt, an α -olefin sulfonate salt, a reaction product between a fatty acid halide and N-methyltaurine, a sulfosuccinic acid dialkyl ester salt, a higher alcohol phosphate ester salt, and a phosphate ester salt of a higher alcohol ethylene oxide adduct.

[0071] Examples of the amphoteric surfactant include an amino-acid-type amphoteric surfactant such as an alkylaminopropionate alkali metal salt, a betaine-type amphoteric surfactant such as an alkyl dimethylbetaine, and an imidazoline-type amphoteric surfactant.

[0072] Next, the prepreg of the present embodiment can be obtained by impregnating at least a part of the glass cloth of the present embodiment with a resin by a known method, and semi-curing the resin.

[0073] In the prepreg of the present embodiment, a difference between a relative dielectric constant of the glass cloth of the present embodiment and a relative dielectric constant of the matrix resin of the prepreg is preferably within a range of 1.5 to 3.0, more preferably within a range of 1.6 to 2.8, further preferably within a range of 1.7 to 2.6, and particularly preferably within a range of 1.9 to 2.5.

[0074] When the glass fiber (the glass strand) has glass composition such as the E-glass composition, the high-strength and high-elasticity glass composition, the high-elasticity and easily-manufacturing glass composition, or the low-dielectric-constant and low-

dielectric-loss-tangent glass composition, the relative dielectric constant of the glass cloth of the present embodiment is within a range of 3.0 to 7.0, preferably within a range of 3.5 to 6.0, and further preferably within a range of 4.0 to 5.0 at a measurement frequency of 10 GHz.

[0075] In this time, examples of the matrix resin that allows the difference with the relative dielectric constant of the glass cloth of the present embodiment to be within the above range include an epoxy resin, a polyphenylene ether resin, a maleimide resin, a cycloolefin polymer resin, and an ODV resin. The matrix resin is preferably a thermosetting resin with a low dielectric property for the high-speed communication application, and examples of such a thermosetting resin include modified polyphenylene ether or reactive low-molecular-weight polyphenylene ether.

[0076] Next, the printed wiring board of the present embodiment can be obtained by curing the prepreg of the present embodiment, stacking a plurality of the cured prepregs, overlapping copper foil such as, for example, low-roughness electrolytic copper foil above and under the cured prepregs and hot-pressing the stacked body to form a copper-clad laminate, and then patterning the copper foil to form a predetermined wiring pattern. The patterning can be performed by a known method such as photolithography.

[0077] Next, Examples and Comparative Examples of the present invention will be described.

Examples

[0078] (Example 1)

In this Example, by using a glass fiber (a glass strand) composed by bundling 200 glass filaments having low-dielectric-constant low-dielectric loss tangent glass composition and having a relative dielectric constant of 4.7 (measurement frequency: 10 GHz) as warp and weft, produced was a glass cloth corresponding to IPC4412 standard #1078 (used yarn: D500 (fiber diameter: 5.0 μm , yarn weight: 10.1 g/1000-m), warp weaving density: 53 yarn/25-mm, weft weaving density: 53 yarn/25-mm, weight per unit area: 43 g/m²).

[0079] Used for the warp of the glass cloth was yarn in which a glass-fiber protecting agent (a sizing agent) was applied in a warping step, and then the warp is pressed against a drum-type cylinder having a surface at a temperature held at 120°C to be dried.

[0080] Then, the produced glass cloth was subjected to a deoiling treatment by heating at a temperature of 450°C for 60 hours, then subjected to a water-pressure opening treatment with a jet spray at a water pressure of 6.0 MPa, the opened glass cloth was subjected to a surface treatment by immersion in a glass treating agent aqueous solution in which 3-methacryloxypropyltrimethoxysilane (manufactured by Dow Corning Toray Co., Ltd., trade name: OFS6030) and acetic acid were dispersed in water, and heating and drying to obtain a surface-treated opened glass cloth having a thickness of 43.2 μm .

[0081] Next, as for the surface-treated opened glass cloth obtained in this Example, yarn widths of the warp and the weft that constituted the surface-treated opened glass cloth were measured by a method described later to calculate an average warp width, an average weft width, an opening area rate S, a warp yarn width opening rate Lt, and a weft yarn width opening rate Ly. Table 1 shows the results.

[0082] (Method for measuring yarn width)

As for the surface-treated opened glass cloth obtained in this Example, glass cloth specimens having a size of 110 mm in length $\times$ 60 mm in width were cut from three points in the width direction of the glass cloth (portions with 100 mm from both the ends and the center portion) by using a digital microscope (manufactured by KEYENCE CORPORATION) with a magnification of 100, and warp widths and weft widths were continuously measured at 100 points in each of the yarn direction, and from an average value of the 300 measurement points in total, the average warp width and the average weft width were determined.

[0083] Then, a surface-treated opened glass cloth specimen obtained by cutting the surface-treated opened glass cloth into a size of 450 mm in length $\times$ 400 mm in width was immersed in a modified polyphenylene ether resin vanish, and preliminarily dried at a temperature of 150°C for 10 minutes to obtain a prepreg having a resin content of 60 mass%. The modified polyphenylene ether resin vanish was prepared by adding toluene (manufactured by FUJIFILM Wako Pure Chemical Corporation) as a solvent into 70 parts

by mass of reactive low-molecular-weight polyphenylene ether (manufactured by SABIC Corporation, trade name: SA9000, dielectric constant: 2.5 (measurement frequency: 1 MHz)), 30 parts by mass of triallyl isocyanurate (manufactured by Evonik Japan Co., Ltd., trade name: TAICROS), and 1 part by mass of α,α' -di(tertiarybutylperoxy)diisopropylbenzene (manufactured by NOF CORPORATION, trade name PERBUTYL P).

[0084] Then, two of the prepregs were stacked, low-roughness electrolytic copper foil (manufactured by FUKUDA METAL FOIL & POWDER CO., LTD., trade name: CF-T4X-SV18, thickness: 18 μm) was overlapped above and under the prepregs, and the stacked body was heated and pressurized by using a vacuum hot-press (manufactured by Kitagawa Seiki Co., Ltd.) at 205°C under a surface pressure condition of 4 MPa in vacuo for 1 hour to obtain a copper-clad laminate having a plate thickness of 0.21 mm.

[0085] Then, as for the copper-clad laminate obtained in this Example, strand thicknesses of the warp and the weft of the glass cloth contained in the copper-clad laminate were measured by a method described later to calculate: a ratio σ_t/σ_y of a standard deviation σ_t of the glass strand thickness of the warp to a standard deviation σ_y of the glass strand thickness of the weft; and a ratio R_t/R_y of a maximum-minimum difference R_t in the glass strand thickness of the warp to a maximum-minimum difference R_y in the glass strand thickness of the weft. Table 1 shows the results.

[0086] (Method for measuring strand thickness)

The copper-clad laminate obtained in this Example was cut to a size of 14 mm $\times$ 10 mm, embedded by using an epoxy resin (manufactured by CEMEDINE CO., LTD., trade name: 1500), and the cross section was grinded parallel to the warp or weft direction so that an intersection point of the warp and the weft of the glass cloth was exposed to the surface. By using a scanning electron microscope (manufactured by JEOL Ltd., trade name: IT700HR), thicknesses of the continued strands adjacent to each other of the glass cloth contained in the copper-clad laminate were measured at 30 points with a magnification of 300. Here, the thickness of the strand of the warp refers to a distance between lines drawn parallelly to the weft direction from each of the glass filament upper portion positioned at the uppermost portion of the yarn (glass filament) bundle of the warp

and the glass filament lower portion positioned at the lowermost portion of the yarn bundle of the warp. Similarly, the thickness of the strand of the weft refers to a distance between lines drawn parallelly to the warp direction from each of the glass filament upper portion positioned at the uppermost portion of the yarn bundle of the weft and the glass filament lower portion positioned at the lowermost portion of the yarn bundle of the weft. The strand thickness was measured at the intersection point of the warp and the weft. That is, when the strand thickness of the warp of the glass cloth was measured, measured was a thickness of a strand in a position where one or more wefts were present above or under the yarn bundle of the warp, and when the strand thickness of the weft of the glass cloth was measured, measured was a thickness of a strand in a position where one or more warps were present above or under the yarn bundle of the weft.

[0087] Then, as for a printed wiring board obtained by patterning the copper foil on one surface of the copper-clad laminate obtained in this Example, skew was measured by a method described later, and evaluated. Table 1 shows the results.

[0088] (Method for measuring and evaluating skew)

The copper foil on one surface of the copper-clad laminate obtained in this Example was subjected to patterning to form eight pairs of differential microstrip lines parallel to the warp direction of the glass cloth. The wiring width was set to 130 μm in width. A gap between two lines constituting the differential was set to a distance of $1/2$ of a pitch ($25000 / Wt$) of the warp of the used glass cloth, and each pair of the differential traces was arranged to be shifted in the weft direction with $9/8$ of the pitch of the warp. The line arrangement as above can obtain data of skew including a combination of a line with the maximum effective dielectric constant having the maximum glass component directly under the line and a line with the minimum effective dielectric constant having the maximum resin component directly under the line. By using a network analyzer (manufactured by Keysight Technologies, trade name: N5227B), skew corresponding to 100-mm line was measured.

[0089] From the results of the measurement, a case where the maximum value of the skew values at the eight points was less than 2.5 ps/100-mm was evaluated as $\odot$, a case where

the value was 2.5 ps/100-mm or more and less than 3.5 ps/100-mm was evaluated as ○, and a case where the value was 3.5 ps/100-mm or more was evaluated as ×.

[0090] (Example 2)

In this Example, a surface-treated opened glass cloth and a copper-clad laminate were obtained in exactly the same manner as in Example 1 except that a glass cloth corresponding to IPC4412 standard #1280 (used yarn: D500 (fiber diameter: 5.0 μm , yarn weight: 10.1 g/1000-m), warp weaving density: 59 yarn/25-mm, weft weaving density: 59 yarn/25-mm, weight per unit area: 48 g/m²) was produced.

[0091] Then, in exactly the same manner as in Example 1, the yarn widths of the warp and the weft, the strand thicknesses, and the skew were measured to calculate the average warp width, the average weft width, the opening area rate S, the warp yarn width opening rate Lt, the weft yarn width opening rate Ly, the ratio σ_t/σ_y of a standard deviation σ_t of the glass strand thickness of the warp to a standard deviation σ_y of the glass strand thickness of the weft, and a ratio Rt/Ry of a maximum-minimum difference Rt in the glass strand thickness of the warp to a maximum-minimum difference Ry in the glass strand thickness of the weft, and to evaluate the skew. Table 1 shows the results.

[0092] (Example 3)

In this Example, a surface-treated opened glass cloth and a copper-clad laminate were obtained in exactly the same manner as in Example 1 except that: the glass cloth was produced by using a glass fiber (a glass strand) composed by bundling 200 glass filaments having a relative dielectric constant of 4.5 (measurement frequency: 10 GHz); and the opening treatment was a water pressure opening with a jet spray at a water pressure of 5.0 MPa.

[0093] Then, in exactly the same manner as in Example 1, the yarn widths of the warp and the weft, the strand thicknesses, and the skew were measured to calculate the average warp width, the average weft width, the opening area rate S, the warp yarn width opening rate Lt, the weft yarn width opening rate Ly, the ratio σ_t/σ_y of a standard deviation σ_t of the glass strand thickness of the warp to a standard deviation σ_y of the glass strand thickness of the weft, and a ratio Rt/Ry of a maximum-minimum difference Rt in the glass strand

thickness of the warp to a maximum-minimum difference R_y in the glass strand thickness of the weft, and to evaluate the skew. Table 1 shows the results.

[0094] (Example 4)

In this Example, a surface-treated opened glass cloth and a copper-clad laminate were obtained in exactly the same manner as in Example 3 except that: a yarn dried without contact in a chamber at a temperature held at 120°C in the warping step was used as the warp of the glass cloth; and the opening treatment was a water pressure opening with a jet spray at a water pressure of 7.0 MPa

[0095] Then, in exactly the same manner as in Example 1, the yarn widths of the warp and the weft, the strand thicknesses, and the skew were measured to calculate the average warp width, the average weft width, the opening area rate S , the warp yarn width opening rate L_t , the weft yarn width opening rate L_y , the ratio σ_t/σ_y of a standard deviation σ_t of the glass strand thickness of the warp to a standard deviation σ_y of the glass strand thickness of the weft, and a ratio R_t/R_y of a maximum-minimum difference R_t in the glass strand thickness of the warp to a maximum-minimum difference R_y in the glass strand thickness of the weft, and to evaluate the skew. Table 1 shows the results.

[0096] (Example 5)

In this Example, a surface-treated opened glass cloth and a copper-clad laminate were obtained in exactly the same manner as in Example 1 except that a glass cloth corresponding to IPC4412 standard #2116 (used yarn: E250 (fiber diameter: 7.0 μm , yarn weight: 20.2 g/1000-m), warp weaving density: 59 yarn/25-mm, weft weaving density: 57 yarn/25-mm, weight per unit area: 95 g/m²) was produced.

[0097] Then, in exactly the same manner as in Example 1, the yarn widths of the warp and the weft, the strand thicknesses, and the skew were measured to calculate the average warp width, the average weft width, the opening area rate S , the warp yarn width opening rate L_t , the weft yarn width opening rate L_y , the ratio σ_t/σ_y of a standard deviation σ_t of the glass strand thickness of the warp to a standard deviation σ_y of the glass strand thickness of the weft, and a ratio R_t/R_y of a maximum-minimum difference R_t in the glass strand thickness of the warp to a maximum-minimum difference R_y in the glass strand thickness of the weft, and to evaluate the skew. Table 1 shows the results.

[0098] (Comparative Example 1)

In this Comparative Example, a surface-treated glass cloth and a copper-clad laminate were obtained in exactly the same manner as in Example 1 except that the opening treatment was not performed at all.

[0099] Then, in exactly the same manner as in Example 1, the yarn widths of the warp and the weft, the strand thicknesses, and the skew were measured to calculate the average warp width, the average weft width, the opening area rate S , the warp yarn width opening rate L_t , the weft yarn width opening rate L_y , the ratio σ_t/σ_y of a standard deviation σ_t of the glass strand thickness of the warp to a standard deviation σ_y of the glass strand thickness of the weft, and a ratio R_t/R_y of a maximum-minimum difference R_t in the glass strand thickness of the warp to a maximum-minimum difference R_y in the glass strand thickness of the weft, and to evaluate the skew. Table 1 shows the results.

[0100] In this Comparative Example, the opening area rate S , the warp yarn width opening rate L_t , and the weft yarn width opening rate L_y were calculated by using yarn widths of warp and weft that were not subjected to the opening treatment.

[0101] (Comparative Example 2)

In this Comparative Example, a surface-treated opened glass cloth and a copper-clad laminate were obtained in exactly the same manner as in Example 1 except that the opening treatment of the glass cloth was performed by water pressure opening with a fan-shaped spray at a water pressure of 6.0 MPa.

[0102] Then, in exactly the same manner as in Example 1, the yarn widths of the warp and the weft, the strand thicknesses, and the skew were measured to calculate the average warp width, the average weft width, the opening area rate S , the warp yarn width opening rate L_t , the weft yarn width opening rate L_y , the ratio σ_t/σ_y of a standard deviation σ_t of the glass strand thickness of the warp to a standard deviation σ_y of the glass strand thickness of the weft, and a ratio R_t/R_y of a maximum-minimum difference R_t in the glass strand thickness of the warp to a maximum-minimum difference R_y in the glass strand thickness of the weft, and to evaluate the skew. Table 1 shows the results.

[0103] (Comparative Example 3)

In this Comparative Example, a surface-treated opened glass cloth and a copper-clad laminate were obtained in exactly the same manner as in Example 1 except that the opening treatment of the glass cloth was performed with a contactless ultrasonic-wave opening treatment by passing the glass cloth through water liquid vibrated with an ultrasonic-wave vibrator at 60 Hz.

[0104] Then, in exactly the same manner as in Example 1, the yarn widths of the warp and the weft, the strand thicknesses, and the skew were measured to calculate the average warp width, the average weft width, the opening area rate S , the warp yarn width opening rate L_t , the weft yarn width opening rate L_y , the ratio σ_t/σ_y of a standard deviation σ_t of the glass strand thickness of the warp to a standard deviation σ_y of the glass strand thickness of the weft, and a ratio R_t/R_y of a maximum-minimum difference R_t in the glass strand thickness of the warp to a maximum-minimum difference R_y in the glass strand thickness of the weft, and to evaluate the skew. Table 1 shows the results.

[0105] (Table 1)

	Example 1	Example 2	Example 3	Example 4	Example 5	Comparative Example 1	Comparative Example 2	Comparative Example 3
Warp filament diameter (μm)	5	5	5	5	7	5	5	5
Number of warp filaments	200	200	200	200	200	200	200	200
Weaving density of warp Wt (yam/25-mm)	53	59	53	53	59	53	53	53
Weft filament diameter (μm)	5	5	5	5	7	5	5	5
Number of weft filaments	200	200	200	200	200	200	200	200
Weaving density of weft Wy (yam/25-mm)	53	59	53	53	57	53	53	53
Cloth thickness (μm)	43.2	44.5	43.3	43.0	89.9	57.0	52.0	45.5
Relative dielectric constant of glass	4.7	4.7	4.5	4.5	4.7	4.7	4.7	4.7
Relative dielectric constant of resin	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
Average yarn width of warp Bt (μm)	334	301	300	304	350	189	224	396
Average yarn width of weft By (μm)	463	419	453	451	418	323	465	432
Average thickness of warp strand (μm)	25.8	30.5	29.3	26.4	55.6	40.5	39.3	26.6
Maximum value of warp strand thickness (μm)	28.3	34.4	32.2	31.0	57.8	47.8	47.7	29.3
Minimum value of warp strand thickness (μm)	23.4	28.2	25.2	22.7	53.2	33.2	34.0	23.2
Maximum-minimum difference in warp strand thickness Rt (μm)	4.8	6.2	6.9	8.3	4.6	14.6	13.8	6.1
Standard deviation of warp strand thickness σ_t (μm)	1.48	1.62	1.70	2.05	1.03	3.58	3.05	1.98
Average thickness of weft strand (μm)	20.3	23.6	20.3	19.3	49.5	29.6	24.1	22.9
Maximum value of weft strand thickness (μm)	24.6	28.3	26.7	24.1	54.1	35.6	30.3	26.6
Minimum value of weft strand thickness (μm)	17.4	18.9	15.4	14.4	44.0	25.1	19.3	20.2
Maximum-minimum difference in weft strand thickness Ry (μm)	7.3	9.5	11.3	9.6	10.1	10.5	11.0	6.4
Standard deviation of weft strand thickness σ_y (μm)	2.08	2.55	2.84	2.83	2.77	2.72	2.44	1.97
Rt/Ry	0.67	0.66	0.61	0.86	0.45	1.39	1.25	0.95
σ_t/σ_y	0.71	0.64	0.60	0.72	0.37	1.32	1.25	1.01
Opening area rate S (%)	99.5	99.7	98.6	98.4	99.2	81.1	99.3	98.6
Warp yarn width opening rate Lt (%)	70.8	71.0	63.6	64.4	82.6	40.1	47.5	84.0
Weft yarn width opening rate Ly (%)	98.2	98.9	96.0	95.6	95.3	68.5	98.6	91.6
Skew evaluation	⊙	⊙	⊙	○	⊙	×	×	×

[0106] It is obvious from Table 1 that the glass cloths of Examples 1 to 5 having the ratio σ_t/σ_y of the standard deviation σ_t of the glass strand thickness of the warp to the standard deviation σ_y of the glass strand thickness of the weft within a range of 0.3 to 0.9 can reduce the skew when used for the printed wiring board.

[0107] Meanwhile, it is obvious that the glass cloths of Comparative Examples 1 to 3 having the ratio σ_t/σ_y of the standard deviation σ_t of the glass strand thickness of the warp

to the standard deviation σ_y of the glass strand thickness of the weft of more than 0.9 cannot reduce the skew when used for the printed wiring board.

Claims

[Claim 1]

A glass cloth, comprising glass fibers as warp and weft,
wherein a ratio σ_t/σ_y of a standard deviation σ_t of a glass strand thickness of the warp to a standard deviation σ_y of a glass strand thickness of the weft of the glass cloth is within a range of 0.3 to 0.9.

[Claim 2]

The glass cloth according to claim 1, wherein the glass cloth has an opening area rate S within a range of 90 to 100%, wherein the opening area rate S is determined by a following expression (1) from a weaving density Wt of the warp, an average yarn width Bt of the warp, a weaving density Wy of the weft, and an average yarn width By of the weft.

(Expression 1)

$$S = \frac{\left(\frac{25000}{Wt}\right) \times \left(\frac{25000}{Wy}\right) - \left(\left(\frac{25000}{Wt}\right) - Bt\right) \times \left(\left(\frac{25000}{Wy}\right) - By\right)}{\left(\frac{25000}{Wt}\right) \times \left(\frac{25000}{Wy}\right)} \times 100 \quad \cdot \cdot \cdot (1)$$

[Claim 3]

The glass cloth according to claim 1, wherein the glass cloth has a ratio Rt/Ry within a range of 0.3 to 0.9, wherein Rt/Ry is a ratio of a maximum-minimum difference Rt being a difference between a maximum value and a minimum value of the glass strand thickness of the warp to a maximum-minimum difference Ry being a difference between a maximum value and a minimum value of the glass strand thickness of the weft.

[Claim 4]

The glass cloth according to claim 1, wherein the glass cloth has a yarn width opening rate Lt of the warp determined by a following expression (2) within a range of 60 to 83%, and has a yarn width opening rate Ly of the weft determined by a following expression (3) within a range of 85% or more.

(Expression 2)

$$Lt = \frac{Bt}{\left(\frac{25000}{Wt}\right)} \times 100 \quad \cdot \cdot \cdot (2)$$

(Expression 3)

$$L_y = \frac{By}{\left(\frac{25000}{W_y}\right)} \times 100 \quad \cdot \cdot \cdot (3)$$

[Claim 5]

The glass cloth according to claim 1, wherein the glass cloth has a thickness within a range of 18 to 100 μm .

[Claim 6]

A prepreg, comprising the glass cloth according to any one of claims 1 to 5.

[Claim 7]

The prepreg according to claim 6, wherein a difference between a relative dielectric constant of the glass cloth and a relative dielectric constant of a matrix resin of the prepreg is within a range of 1.5 to 3.0.

[Claim 8]

A printed wiring board, comprising the prepreg according to claim 6.