

COMPOSITE RESIN COMPOSITION AND ELECTRONIC COMPONENT MOLDED
FORMED FROM COMPOSITE RESIN COMPOSITION

TECHNICAL FIELD

The present invention relates to a composite resin composition and an electronic component molded from the composite resin composition.

BACKGROUND ART

Liquid crystal polymers are thermoplastic resins having, for example, high dimensional accuracy and excellent fluidity. Because of such characteristics, the liquid crystal polymers have been conventionally used as materials for various electronic components.

In particular, due to demands in the present age associated with improvement in performance of electronic equipment in recent years, i.e., demands for connectors to be more heat resistant (for an increase in productivity by developing mounting technology), more dense (for employment of multi-core), and smaller in size, liquid crystal polymer components utilizing the above-described characteristics of liquid crystal polymers and reinforced with glass fiber have been used as connector materials.

Recently, however, connectors have been further miniaturized, which causes a lack of rigidity due to the insufficient thickness of a molded article or internal stress due to insertion of a metal terminal. As a result, warping

deformation occurs after molding or during reflow heating, which causes a problem of defects in soldering with a board. That is, in the conventional reinforcement with only glass fiber, an increase in the amount of glass fiber for increasing rigidity prevents the thin-walled portion from being filled with a resin or causes a problem of deformation of an insert terminal due to the pressure during molding.

In order to solve the problem of warping deformation, the procedure of molding has been devised, and blending of a specific plate-shaped filler has been proposed from a material aspect. That is, in the case of ordinary connectors (electronic components) widely distributed in the market, the dimensional accuracy and warp of a product can be controlled only by adjusting the gate position and design so as to maintain symmetry when molding. Furthermore, a product with less warping deformation can be prepared by using a conventionally proposed low-warping material.

However, asymmetric electronic components not having symmetry with respect to any of the XY, YZ, and XZ axial planes of the molded article have been required in association with the complication in the shape of electronic components in recent years. A typical example of the asymmetric electronic component is a memory module connector having a latch structure (having hooks for fixing at both ends), such as a DDR-DIMM connector. In particular, a memory module connector for a notebook computer has a latch structure for installation and also has notches for alignment. The connector therefore

has a highly complicated shape.

Such asymmetric electronic components not having symmetry have a limitation in reduction of warping deformation from the aspect of the molding procedure, unlike ordinary connectors (symmetric electronic components) having symmetry with respect to any of the XY, YZ, and XZ axial planes of the molded article. In a case of an asymmetric electronic component having a complicated shape, the orientation of the resin and the filler in a molded article is complicated, higher fluidity is needed, and inhibition of warping deformation is more difficult.

As technologies for solving these problems, for example, Patent Document 1 discloses an asymmetric electronic component not having symmetry with respect to any of the XY, YZ, and XZ axial planes of the molded article molded from a liquid crystal polymer composition including a specific fibrous filler and a specific plate-shaped filler at a specific blending ratio.

Patent Document 1: PCT International Publication No.
WO2008/023839

DISCLOSURE

Unfortunately, it has been revealed that there are cases that cannot be dealt with using the known liquid crystal polymer compositions, such as those disclosed in Patent Document 1, because of changes in shape associated with, for

example, a recent increase in the accumulation rate of asymmetric electronic components, in particular due to factors such as a decrease in pitch distance, a decrease in product height, and an increase in pole number. That is, conventional liquid crystal polymer compositions have insufficient heat resistance and fluidity, and asymmetric electronic components having reduced warping deformation are difficult to be molded from such liquid crystal polymer compositions.

Liquid crystal polymer compositions may cause a problem of blister occurring. Liquid crystal polyester amides, which are liquid crystal polymer, have a good high-temperature thermal stability and are, therefore, often used as materials that need a high-temperature heat treatment. However, molded articles left in a high-temperature air or liquid for a long time causes a problem that minute swollenness called blister occurs on the surface. This phenomenon is caused as follows: decomposition gases generated when the liquid crystal polyester amides are in a molten state are imported into the inside of the molded articles; then, the gases swell at the time of high-temperature heat treatment and lift the surface of the molded articles softened by heating; and the lifted parts emerge as a blister. Blister occurring can be decreased by sufficiently degassing through a vent hole at the time of melt extrusion or by refraining from staying long in a molding machine at the time of molding. However, the range of the conditions is too narrow and too insufficient to obtain molded articles in which blister occurring is suppressed, namely,

molded articles having blister resistance. Fundamental resolution of blister occurring needs improving of the quality of liquid crystal polyester amides themselves. Neither known liquid crystal polyester amides nor methods using the same are sufficient to resolve the problem of blister occurring.

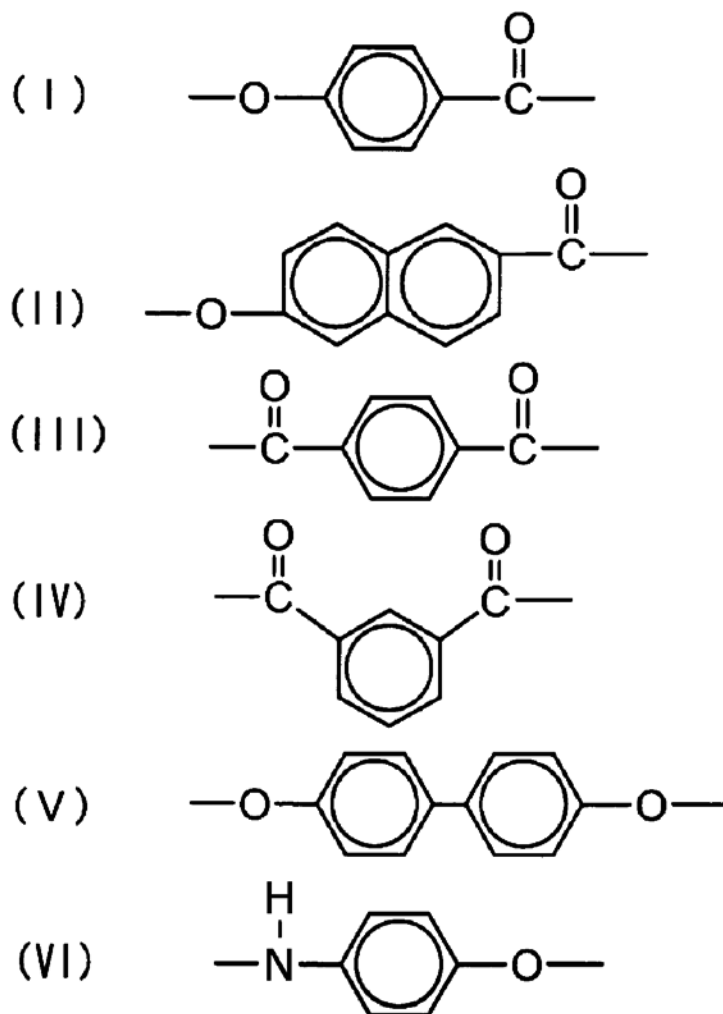
The present invention has been made in view of the foregoing circumstances, and an object of the present invention is to provide a composite resin composition that can provide an electronic component being excellent in heat resistance and having suppressed warping distortion and suppressed blister occurring, and an electronic component molded from the composite resin composition.

Embodiments provide combining a liquid crystal polymer containing predetermined amounts of specific constitutional units, a fibrous filler, and a plate-shaped filler and by setting a weight average fiber length of the fibrous filler to 250 μm or higher. Specifically, the present disclosure provides the following:

(1) A composite resin composition comprising a liquid crystalline polymer (A), a fibrous filler (B), and a plate-shaped filler (C), wherein

the liquid crystalline polymer (A) is a wholly aromatic polyester amide that exhibits optical anisotropy when melted, the wholly aromatic polyester amide consisting only of the following constituent units (I) to (VI) as essential

constitutional components:



a content of the constituent unit (I) is 50 to 70 mol% with respect to all of the constituent units;

a content of the constituent unit (II) is 0.5 mol% or higher and lower than 4.5 mol% with respect to all of the constituent units;

a content of the constituent unit (III) is 10.25 to 22.25 mol% with respect to all of the constituent units;

a content of the constituent unit (IV) is 0.5 mol% or higher and lower than 4.5 mol% with respect to all of the constituent units;

a content of the constituent unit (V) is 5.75 to 23.75 mol% with respect to all of the constituent units;

a content of the constituent unit (VI) is 1 to 7 mol% with respect to all of the constituent units;

a content of a total of the constituent unit (II) and the constituent unit (IV) is 1 mol% or higher and lower than 5 mol% with respect to all of the constituent units;

a content of a total of the constituent units (I) to (VI) is 100 mol% with respect to all of the constituent units;

a molar ratio of the constituent unit (VI) to a total of the constituent unit (V) and the constituent unit (VI) is 0.04 to 0.37;

a weight average fiber length of the fibrous filler (B) is 250 μm or higher;

the liquid crystalline polymer (A) is 37.5 to 82.5% by mass with respect to the total composite resin composition;

the fibrous filler (B) is 2.5 to 17.5% by mass with respect to the total composite resin composition;

the plate-shaped filler (C) is 15 to 45% by mass with respect to the total composite resin composition; and

a total amount of the fibrous filler (B) and the plate-shaped filler (C) is 17.5 to 62.5% by mass with respect to the total composite resin composition.

(2) The composite resin composition according to (1), wherein a mole number of a total of the constituent unit (III) and the constituent unit (IV) is 1 to 1.1 times a mole number of a total of the constituent unit (V) and the constituent

unit (VI), or a mole number of a total of the constituent unit (V) and the constituent unit (VI) is 1 to 1.1 times a mole number of a total of the constituent unit (III) and the constituent unit (IV).

(3) The composite resin composition according to (1) or (2), wherein the fibrous filler (B) is a glass fiber.

(4) The composite resin composition according to any one of (1) to (3), wherein the plate-shaped filler (C) is talc.

(5) An electronic component

molded from the composite resin composition according to any one of (1) to (4) and

having a total product length of 30 mm or more and a product height of 5 mm or more.

(6) The electronic component according to (5), wherein the electronic component is an asymmetric electronic component having no symmetry with respect to any of the axial planes of the XY axial plane, YZ axial plane, and XZ axial plane of a molded article.

(7) The electronic component according to (5) or (6), wherein

the electronic component is a connector for a memory module, and

the connector has a distance between pitches of 0.6 mm or less, a total product length of 60.0 mm or more, a product height of 10.0 mm or less, and a pole number of 200 poles or more.

The present disclosure can provide a composite resin composition that can provide an electronic component being excellent in heat resistance and having suppressed warping distortion and suppressed blister occurring, and an electronic component molded from the composite resin composition.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a diagram illustrating a DDR-DIMM connector molded in Examples. It is noted that A indicates the position of a gate.

FIG. 2 is a diagram indicating the points of measurement of warp in a DDR-DIMM connector performed in Examples.

PREFERRED MODE FOR CARRYING OUT THE INVENTION

Embodiments of the present invention will now be specifically described.

[Composite resin composition]

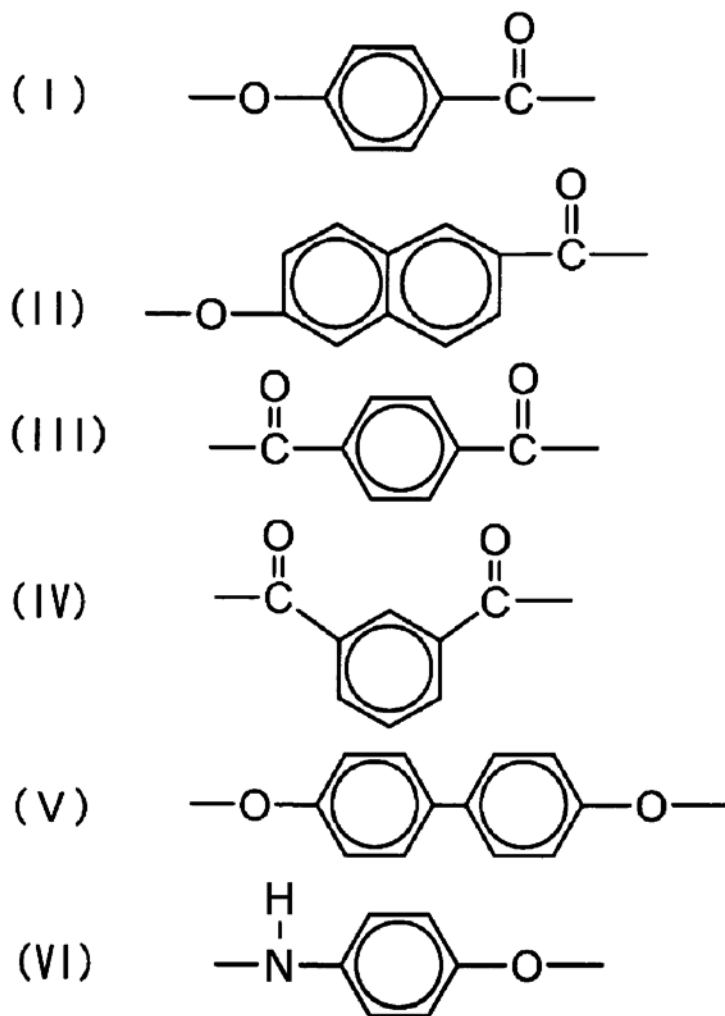
The composite resin composition of the present invention contains a specific liquid crystal polymer, a fibrous filler, and a plate-shaped filler in predetermined amounts, wherein a weight average fiber length of the fibrous filler is 250 μm or higher. Each component of the composite resin composition according to the present invention will now be described.

(Liquid crystal polymer)

The composite resin composition in the present invention contains a liquid crystal polymer which is the above wholly aromatic polyester amide. The wholly aromatic polyester amide

has a low melting point and can accordingly lower a processing temperature, thereby suppressing occurrence of decomposition gases when melted. Consequently, a molded article obtained by molding the composite resin composition containing the wholly aromatic polyester amide suppresses blister occurring and improves blister resistance. The liquid crystal polymer may be used alone or in combination of two or more thereof.

The wholly aromatic polyester amide in the present invention consists of the following constituent unit (I), the following constituent unit (II), the following constituent unit (III), the following constituent unit (IV), the following constituent unit (V) and the following constituent unit (VI).



The constituent unit (I) is derived from 4-hydroxybenzoic acid (hereinafter also referred to as "HBA"). The wholly aromatic polyester amide in the present invention includes 50 to 70 mol% of the constituent unit (I) with respect to all of the constituent units. If the content of the constituent unit (I) is lower than 50 mol% or higher than 70 mol%, at least one of melting point lowering and heat resistance easily becomes insufficient. From the viewpoint of the achievement of a balance between melting point lowering and heat resistance, the content of the constituent unit (I) is preferably 54 to 67 mol%, and more preferably 58 to 64 mol%.

The constituent unit (II) is derived from 6-hydroxy-2-naphthoic acid (hereinafter also referred to as "HNA"). The wholly aromatic polyester amide in the present invention includes 0.5 mol% or higher and lower than 4.5 mol% of the constituent unit (II) with respect to all of the constituent units. If the content of the constituent unit (II) is lower than 0.5 mol% or 4.5 mol% or higher, at least one of melting point lowering and heat resistance easily becomes insufficient. From the viewpoint of the achievement of a balance between melting point lowering and heat resistance, the content of the constituent unit (II) is preferably 0.75 to 3.75 mol%, and more preferably 1 to 3 mol%.

The constituent unit (III) is derived from 1,4-phenylene dicarboxylic acid (hereinafter also referred to as "TA"). The wholly aromatic polyester amide in the present invention includes 10.25 to 22.25 mol% of the constituent unit (III) with respect to all of the constituent units. If the content of the constituent unit (III) is lower than 10.25 mol% or higher than 22.25 mol%, at least one of melting point lowering and heat resistance easily becomes insufficient. From the viewpoint of the achievement of a balance between melting point lowering and heat resistance, the content of the constituent unit (III) is preferably 12.963 to 20.75 mol%, and more preferably 15.675 to 19.25 mol%.

The constituent unit (IV) is derived from 1,3-phenylene dicarboxylic acid (hereinafter also referred to as "IA"). The wholly aromatic polyester amide in the present invention

includes 0.5 mol% or higher and lower than 4.5 mol% of the constituent unit (IV) with respect to all of the constituent units. If the content of the constituent unit (IV) is lower than 0.5 mol%, or 4.5 mol% or higher, at least one of melting point lowering and heat resistance easily becomes insufficient. From the viewpoint of the achievement of a balance between melting point lowering and heat resistance, the content of the constituent unit (IV) is preferably 0.5 to 3.75 mol%, and more preferably 0.5 to 3 mol%.

The constituent unit (V) is derived from 4,4'-dihydroxybiphenyl (hereinafter also referred to as "BP"). The wholly aromatic polyester amide in the present invention includes 5.75 to 23.75 mol% of the constituent unit (V) with respect to all of the constituent units. If the content of the constituent unit (V) is lower than 5.75 mol% or higher than 23.75 mol%, at least one of melting point lowering and heat resistance easily becomes insufficient. From the viewpoint of the achievement of a balance between melting point lowering and heat resistance, the content of the constituent unit (V) is preferably 8.5 to 20.375 mol%, and more preferably 11.25 to 17 mol% (e.g., 11.675 to 17 mol%).

The constituent unit (VI) is derived from N-acetyl-p-aminophenol (hereinafter also referred to as "APAP"). The wholly aromatic polyester amide in the present invention includes 1 to 7 mol% of the constituent unit (VI) with respect to all of the constituent units. If the content of the constituent unit (VI) is lower than 1 mol% or higher than 7

mol%, at least one of melting point lowering and heat resistance easily becomes insufficient. From the viewpoint of the achievement of a balance between melting point lowering and heat resistance, the content of the constituent unit (VI) is preferably 1.5 to 7 mol%, and more preferably 2 to 7 mol%.

The wholly aromatic polyester amide in the present invention includes 1 mol% or higher and lower than 5 mol% of a total of the constituent unit (II) and the constituent unit (IV) with respect to all of the constituent units. In the wholly aromatic polyester amide, when the flexible constituent unit (II) having a naphthalene skeleton and the flexible constituent unit (IV) having a benzene skeleton coexist in a total amount in the above range, it is easy to sufficiently achieve a balance between melting point lowering and heat resistance. If the content of the total is lower than 1 mol%, the proportion of the flexible constituent unit excessively decreases, so that the melting point lowering easily becomes insufficient. If the content of the total is 5 mol% or higher, the proportion of the flexible constituent unit excessively increases, so that the heat resistance easily becomes insufficient. From the viewpoint of the achievement of a balance between melting point lowering and heat resistance, the content of the total is preferably 1.75 to 4.75 mol%, and more preferably 2.5 to 4.5 mol%.

In the wholly aromatic polyester amide in the present invention, a molar ratio of the constituent unit (VI) to a total of the constituent unit (V) and the constituent unit

(VI) is 0.04 to 0.37. If the molar ratio is lower than 0.04, the proportion of the constituent unit having a biphenyl skeleton increases, so that the crystallinity of the wholly aromatic polyester amide deteriorates, and thus the achievement of a balance between melting point lowering and heat resistance easily becomes insufficient. If the molar ratio is higher than 0.37, hetero bonds other than the ester bond increase, so that the crystallinity of the wholly aromatic polyester amide deteriorates, and thus the achievement of a balance between melting point lowering and heat resistance easily becomes insufficient. From the viewpoint of the achievement of a balance between melting point lowering and heat resistance, the molar ratio is preferably 0.07 to 0.36, and more preferably 0.11 to 0.35.

From the viewpoint of the achievement of a balance between melting point lowering and heat resistance, a mole number of a total of the constituent unit (III) and the constituent unit (IV) (hereinafter also referred to as "mole number 1A") is preferably 1 to 1.1 times a mole number of a total of the constituent unit (V) and the constituent unit (VI) (hereinafter also referred to as "mole number 2A"), or a mole number of a total of the constituent unit (V) and the constituent unit (VI) is preferably 1 to 1.1 times a mole number of a total of the constituent unit (III) and the constituent unit (IV). The mole number 1A is more preferably 1.02 to 1.06 times the mole number 2A, or the mole number 2A is more preferably 1.02 to 1.06 times the mole number 1A. The

mole number 1A is still more preferably 1.024 to 1.056 times the mole number 2A, or the mole number 2A is still more preferably 1.024 to 1.056 times the mole number 1A.

As mentioned above, the wholly aromatic polyester amide in the present invention includes each of specific constituent units (I) to (VI) and a total of the constituent unit (II) and the constituent unit (IV) in a specific amount with respect to all of the constituent units, and a molar ratio of the constituent unit (VI) to a total of the constituent unit (V) and the constituent unit (VI) is in a specific range, so that the achievement of a balance between melting point lowering and heat resistance is sufficient. The wholly aromatic polyester amide of the present invention includes 100 mol% of a total of the constituent units (I) to (VI) with respect to all of the constituent units.

Examples of an index representing the heat resistance include a deflection temperature under load (hereinafter also referred to as "DTUL"). DTUL is preferably 260°C or higher since the heat resistance tends to become higher. DTUL is a value measured in a state of a polyester amide resin composition obtained by melt-kneading 60% by mass of the wholly aromatic polyester amide with 40% by mass of a milled fiber having an average fiber diameter of 11 μm and an average fiber length of 75 μm at a melting point of the wholly aromatic polyester amide + 20°C, and can be measured in conformity with ISO 75-1,2. From the viewpoint of the achievement of a balance between melting point lowering and

heat resistance, DTUL is preferably 265°C or higher and 310°C or lower, and more preferably 267 to 300°C.

A method for producing a wholly aromatic polyester amide in the present invention will be described below. The wholly aromatic polyester amide in the present invention is polymerized using a direct polymerization method, a transesterification method or the like. In the case of polymerization, it is possible to use a melt polymerization method, a solution polymerization method, a slurry polymerization method, a solid phase polymerization method and the like, or a combination of two or more thereof. It is possible to preferably use a melt polymerization method, or a combination of a melt polymerization method and a solid phase polymerization method.

In the present invention, in the case of polymerization, it is possible to use an acylating agent for a polymerizable monomer or to use a terminal-activated monomer as an acid chloride derivative. Examples of the acylating agent include fatty acid anhydrides such as acetic anhydride.

In the case of polymerization, various catalysts can be used, and examples of typical ones include dialkyltin oxide, diaryltin oxide, titanium dioxide, alkoxytitanium silicates, titanium alcoholates, fatty acid metal salts, and Lewis acid salts such as BF_3 , and fatty acid metal salts are preferable. An amount used of the catalyst is generally about 0.001 to 1% by mass, and particularly preferably about 0.003 to 0.2% by mass, with respect to the total mass of the monomer.

When solution polymerization or slurry polymerization is performed, it is possible to use, as the solvent, liquid paraffin, high heat resistant synthetic oil, inert mineral oil and the like.

The reaction conditions are, for example, as follows: a reaction temperature of 200 to 380°C and a final ultimate pressure of 0.1 to 760 Torr (i.e., 13 to 101,080 Pa). Particularly in the melting reaction, for example, the reaction temperature is 260 to 380°C, and preferably 300 to 360°C, and the final ultimate pressure is 1 to 100 Torr (i.e., 133 to 13,300 Pa), and preferably 1 to 50 Torr (i.e., 133 to 6,670 Pa).

The reaction can be started after charging all of raw material monomers (HBA, HNA, TA, IA, BP, and APAP), an acylating agent, and a catalyst in the same reaction vessel (one-step system), and it is also possible to acylate hydroxy groups of raw material monomers HBA, HNA, BP, and APAP using an acylating agent, followed by reaction with carboxyl groups of TA and IA (two-step system).

After the temperature inside the reaction system reaches a predetermined temperature, pressure reduction is started and the pressure reaches a predetermined vacuum degree, and then the solution polymerization is performed. After torque of a stirrer reaches a predetermined value, an inert gas is introduced to turn from a depressurized state to a predetermined pressurized state via a normal pressure, and then the wholly aromatic polyester amide is discharged from

the reaction system.

It is possible to increase the molecular weight of the wholly aromatic polyester amide produced by the above polymerization method, by further subjection to solid phase polymerization where heating is performed under normal pressure or reduced pressure in the inert gas. Preferable conditions of the solid phase polymerization reaction are as follows: a reaction temperature is 230 to 350°C, and preferably 260 to 330°C, and a final ultimate pressure is 10 to 760 Torr (i.e., 1,330 to 101,080 Pa).

The method for producing a wholly aromatic polyester amide in the present invention preferably includes acylating 4-hydroxybenzoic acid, 6-hydroxy-2-naphthoic acid, 4,4'-dihydroxybiphenyl and N-acetyl-p-aminophenol with a fatty acid anhydride in the presence of a fatty acid metal salt and conducting transesterification with 1,4-phenylene dicarboxylic acid and 1,3-phenylene dicarboxylic acid. With respect to all of the monomers consisting of 4-hydroxybenzoic acid, 6-hydroxy-2-naphthoic acid, 1,4-phenylene dicarboxylic acid, 1,3-phenylene dicarboxylic acid, 4,4'-dihydroxybiphenyl and N-acetyl-p-aminophenol, an amount used of 4-hydroxybenzoic acid is 50 to 70 mol%, preferably 54 to 67 mol%, and more preferably 58 to 64 mol%, from the viewpoint of the achievement of a balance between melting point lowering and heat resistance, an amount used of 6-hydroxy-2-naphthoic acid is 0.5 mol% or higher and lower than 4.5 mol%, preferably 0.75 to 3.75 mol%,

and more preferably 1 to 3 mol%, from the viewpoint of the achievement of a balance between melting point lowering and heat resistance,

an amount used of 1,4-phenylene dicarboxylic acid is 10.25 to 22.25 mol%, preferably 12.963 to 20.75 mol%, and more preferably 15.675 to 19.25 mol%, from the viewpoint of the achievement of a balance between melting point lowering and heat resistance,

an amount used of 1,3-phenylene dicarboxylic acid is 0.5 mol% or higher and lower than 4.5 mol%, preferably 0.5 to 3.75 mol%, and more preferably 0.5 to 3 mol%, from the viewpoint of the achievement of a balance between melting point lowering and heat resistance,

an amount used of 4,4'-dihydroxybiphenyl is 5.75 to 23.75 mol%, preferably 8.5 to 20.375 mol%, and more preferably 11.25 to 17 mol% (e.g., 11.675 to 17 mol%), from the viewpoint of the achievement of a balance between melting point lowering and heat resistance,

an amount used of N-acetyl-p-aminophenol is 1 to 7 mol%, preferably 1.5 to 7 mol%, and more preferably 2 to 7 mol%, from the viewpoint of the achievement of a balance between melting point lowering and heat resistance,

an amount used of a total of 6-hydroxy-2-naphthoic acid and 1,3-phenylene dicarboxylic acid is 1 mol% or higher and lower than 5 mol%, preferably 1.75 to 4.75 mol%, and more preferably 2.5 to 4.5 mol%, from the viewpoint of the achievement of a balance between melting point lowering and heat resistance,

an amount used of a total of 4-hydroxybenzoic acid, 6-hydroxy-2-naphthoic acid, 1,4-phenylene dicarboxylic acid, 1,3-phenylene dicarboxylic acid, 4,4'-dihydroxybiphenyl and N-acetyl-p-aminophenol is preferably 100 mol%,

a molar ratio of an amount used of N-acetyl-p-aminophenol to an amount used of a total of 4,4'-dihydroxybiphenyl and N-acetyl-p-aminophenol is 0.04 to 0.37, preferably 0.07 to 0.36, and more preferably 0.11 to 0.35, from the viewpoint of the achievement of a balance between melting point lowering and heat resistance, and

an amount used of the fatty acid anhydride is preferably 1.02 to 1.04 times a hydroxy equivalent of a total of 4-hydroxybenzoic acid, 6-hydroxy-2-naphthoic acid, 4,4'-dihydroxybiphenyl and N-acetyl-p-aminophenol. The fatty acid metal salt is more preferably an acetic acid metal salt, and the fatty acid anhydride is more preferably acetic anhydride. A mole number of a total of 1,4-phenylene dicarboxylic acid and 1,3-phenylene dicarboxylic acid (hereinafter also referred to as "mole number 1B") is more preferably 1 to 1.1 times a mole number of a total of 4,4'-dihydroxybiphenyl and N-acetyl-p-aminophenol (hereinafter also referred to as "mole number 2B"), or a mole number of a total of 4,4'-dihydroxybiphenyl and N-acetyl-p-aminophenol is more preferably 1 to 1.1 times the a mole number of a total of 1,4-phenylene dicarboxylic acid and 1,3-phenylene dicarboxylic acid. The mole number 1B is further more preferably 1.02 to 1.06 times the mole number 2B, or the mole number 2 is further more preferably 1.02 to

1.06 times the mole number 1B. The mole number 1B is particularly preferably 1.024 to 1.056 times the mole number 2B, or the mole number 2B is particularly preferably 1.024 to 1.056 times the mole number 1B.

Properties of the wholly aromatic polyester amide will be described below. The wholly aromatic polyester amide in the present invention exhibits optical anisotropy when melted. Exhibiting optical anisotropy when melted means that the wholly aromatic polyester amide in the present invention is a liquid crystal polymer.

In the present invention, the fact that the wholly aromatic polyester amide is a liquid crystal polymer is an indispensable element for the wholly aromatic polyester amide to have both thermal stability and easy processability. Although some wholly aromatic polyester amides constituted of the structural units (I) to (VI) do not form an anisotropic melt phase depending on the constitutional component and the sequence distribution in the polymer, the polymer of the present invention is limited to a wholly aromatic polyester amide that exhibits optical anisotropy when melted.

Properties of melt anisotropy can be confirmed by a conventional polarization inspection method using an orthogonal polarizer. More specifically, confirmation of melt anisotropy can be carried out by melting a sample placed on a hot stage manufactured by Linkam Scientific Instruments Ltd. using a polarizing microscope manufactured by Olympus Corporation, and observing at a magnification of 150 times in

a nitrogen atmosphere. The liquid crystal polymer is optically anisotropic and transmits light when inserted between orthogonal polarizers. When the sample is optically anisotropic, polarized light is transmitted even in the state of, for example, a molten stationary liquid state.

A nematic liquid crystal polymer causes significant decrease in viscosity at the melting point or higher, so that it generally becomes an index of processability that liquid crystallinity is exhibited at a temperature of the melting point or higher. The melting point is preferably as high as possible from the viewpoint of the heat resistance. Taking thermal deterioration during melt processing of the polymer and heating capability of a molding machine into consideration, the melting point of 360°C or lower is a preferable rough indication. The melting point is more preferably 300 to 360°C, and still more preferably 340 to 358°C.

The melt viscosity of the wholly aromatic polyester amide as measured at a temperature that is 10 to 30°C higher than the melting point of the wholly aromatic polyester amide in the present invention and a shear rate of 1,000/sec is preferably 500 Pa·s or lower, more preferably 0.5 to 300 Pa·s, and still more preferably 1 to 100 Pa·s. If the melt viscosity is in the above range, the wholly aromatic polyester amide itself or a composition containing the wholly aromatic polyester amide easily secures fluidity during molding and the filling pressure hardly becomes excessive. As used herein, the

melt viscosity refers to a melt viscosity measured in conformity with ISO 11443.

As the index representing the heat resistance, a difference between the melting point and DTUL is also exemplified. The difference is preferably 90°C or lower since the heat resistance tends to become high. From the viewpoint of the achievement of a balance between melting point lowering and heat resistance, the difference is preferably higher than 0°C and 85°C or lower (e.g., 50°C or higher and 85°C or lower), and more preferably 55 to 79°C.

In the composite resin composition of the present invention, the content of the liquid crystal polymer is 37.5 to 82.5% by mass with respect to the total composite resin composition. If the content of the liquid crystal polymer is less than 37.5% by mass with respect to the total composite resin composition, the fluidity of the composite resin composition tends to be deteriorated, and there is a danger that warping deformation of a molded article such as an electronic component obtained from the composite resin composition becomes large. Thus, such a content is not preferred. If the content of the liquid crystal polymer is higher than 82.5% by mass with respect to the total composite resin composition, the molded article, such as an electronic component, obtained from the composite resin composition has a low bending elastic modulus and low cracking resistance. Thus, such a content is not preferred. The composite resin composition in the present invention contains the liquid

crystal polymer in an amount of preferably 44 to 75% by mass and more preferably 60 to 65% by mass with respect to the total composite resin composition.

(Fibrous filler)

The composite resin composition in the present invention contains the liquid crystal polymer and a fibrous filler, and the weight average fiber length of the fibrous filler is 250 μm or higher; and thereby a molded article molded from the composite resin composition has excellent high-temperature rigidity and reduced warping deformation. The fibrous filler may be used alone or in combination of two or more thereof. The fibrous filler in the present invention is not particularly limited, and examples thereof include a glass fiber, a milled fiber, a carbon fiber, an asbestos fiber, a silica fiber, a silica-alumina fiber, a zirconia fiber, a boron nitride fiber, a silicon nitride fiber, a boron fiber, and a potassium titanate fiber. The fibrous filler in the present invention is preferably a glass fiber because the high-temperature rigidity of the molded article obtained from the composite resin composition may be readily improved

In the composite resin composition of the present invention, the fibrous filler has a weight average fiber length of 250 μm or higher, preferably 350 μm or higher, and more preferably 450 μm or higher. When the weight average fiber length is less than 250 μm , a molded article molded from the composite resin composition is difficult to have sufficient high-temperature rigidity, and warping deformation

of the molded article can be increased. Thus, such a weight average fiber length is not preferred. The upper limit of the weight average fiber length is not particularly limited and is preferably 700 μm or less and more preferably 500 μm or less. When the weight average fiber length is 600 μm or less, the composite resin composition can have excellent fluidity, and warping deformation of a molded article can be restrained. Thus, such a weight average fiber length is preferred. Herein, a weight average fiber length of a fibrous filler means a weight average fiber length measured with an image measuring apparatus for a dispersion obtained by heating the composite resin composition at 600°C for 2 hours for incineration and dispersing the resulting incineration residue in an aqueous solution of 5% by mass of polyethylene glycol.

The fiber diameter of the fibrous filler in the present invention is not particularly limited, and the fiber diameter used is typically approximately 5 to 15 μm .

The content of the fibrous filler in the composite resin composition in the present invention is 2.5 to 17.5% by mass with respect to the total composite resin composition. When the content of the fibrous filler is less than 2.5% by mass with respect to the total composite resin composition, a molded article, such as an electronic component, molded from the composite resin composition has a low load deflection temperature and does not have sufficient high-temperature rigidity. Thus, such a content is not preferred. When the content of the fibrous filler is more than 17.5% by mass with

respect to the total composite resin composition, the composite resin composition has deteriorated fluidity, and warping deformation of a molded article can be increased. Thus, such a content is not preferred. The content of the fibrous filler in the composite resin composition in the present invention is preferably 4 to 16% by mass and more preferably 5 to 15% by mass with respect to the total composite resin composition.

(Plate-shaped filler)

The composite resin composition of the present invention further contains a plate-shaped filler. The composite resin composition of the present invention can produce a molded article having less warping deformation by containing the plate-shaped filler. The plate-shaped filler may be used alone or in combination of two or more thereof.

The content of the plate-shaped filler is 15 to 45% by mass with respect to the total composite resin composition. If the content of the plate-shaped filler is less than 15% by mass with respect to the total composite resin composition, a molded article molded from the composite resin composition, such as an electronic component, has a risk of having large warping deformation. Thus, such a content is not preferred. If the content of the plate-shaped filler is higher than 45% by mass with respect to the total composite resin composition, the composite resin composition has a risk of having deteriorated fluidity. Thus, such a content is not preferred. The plate-shaped filler in the present invention is contained

in the composite resin composition in an amount of preferably 20 to 40% by mass and more preferably 25 to 35% by mass with respect to the total composite resin composition.

Examples of the plate-shaped filler in the present invention include talc, mica, glass flakes, and various types of metal foil. The plate-shaped filler is preferably talc from the point of preventing warping deformation of the molded article molded from the composite resin composition and not deteriorating the fluidity of the composite resin composition. The plate-shaped filler may have any average particle diameter, but a smaller average particle diameter is desirable in light of the fluidity at a thin-walled portion. In contrast, in order to reduce the warping deformation of the molded article molded from the composite resin composition, such as an electronic component, the plate-shaped filler essentially maintains a certain size. Specifically, the average particle diameter is preferably 1 to 100 μm and more preferably 5 to 50 μm .

(Talc)

As the talc that can be used in the present invention, based on the total solid amount of the talc, the total content of Fe_2O_3 , Al_2O_3 , and CaO is preferably 2.5% by mass or less, the total content of Fe_2O_3 and Al_2O_3 is preferably higher than 1.0% by mass and not higher than 2.0% by mass, and the content of CaO is preferably less than 0.5% by mass. That is, the talc that can be used in the present invention may contain at least one selected from Fe_2O_3 , Al_2O_3 , and CaO within the content

ranges shown above, in addition to its main components SiO_2 and MgO .

When the total content of Fe_2O_3 , Al_2O_3 , and CaO in the talc is 2.5% by mass or less, the molding workability of the composite resin composition is hardly deteriorated, and the heat resistance of a molded article molded from the composite resin composition, such as an electronic component, is hardly deteriorated. The total content of Fe_2O_3 , Al_2O_3 , and CaO is preferably 1.0% by mass or more and 2.0% by mass or less.

In the above-described various types of talc, talc having a total content of Fe_2O_3 and Al_2O_3 of higher than 1.0% by mass is readily available. When the talc has a total content of Fe_2O_3 and Al_2O_3 of 2.0% by mass or less, the molding workability of the composite resin composition is hardly deteriorated, and the heat resistance of a molded article molded from the composite resin composition, such as an electronic component, is hardly deteriorated. The total content of Fe_2O_3 and Al_2O_3 is preferably higher than 1.0% by mass and not higher than 1.7% by mass.

When the talc has a content of CaO of less than 0.5% by mass, the molding workability of the composite resin composition is hardly deteriorated, and the heat resistance of a molded article molded from the composite resin composition, such as an electronic component, is hardly deteriorated. The content of CaO is preferably 0.01% by mass or more and 0.4% by mass or less.

The talc in the present invention preferably has a mass-

based or volume-based cumulative mean particle diameter (D_{50}) of 4.0 to 20.0 μm , more preferably 10 to 18 μm , measured by laser diffractometry, from the viewpoint of preventing warping deformation of the molded article and maintaining the fluidity of the composite resin composition.

(Mica)

Mica is a ground product of a silicate mineral containing aluminum, potassium, magnesium, sodium, iron, and so on. Examples of the mica that can be used in the present invention include muscovite, phlogopite, biotite, and micanite. Among them, muscovite is preferred because of its satisfactory hue and low cost.

Known methods of pulverizing a mineral for producing mica are classified into either a wet grinding process or a dry grinding process. In the wet grinding process, mica ore is coarsely ground with a dry mill, the resulting coarse mica is then mixed with water to form slurry, and the slurry is finely ground by wet grinding, followed by dehydration and drying. Although the dry grinding process is inexpensive, compared to the wet grinding process, and is a common process, the wet grinding process can easily grind a mineral into thin and fine particles. A thin and fine ground product can provide mica having preferred average particle diameter and thickness described below and therefore is preferably used in the present invention. Accordingly, in the present invention, mica prepared by a wet grinding process is preferably used.

In the wet grinding process, a step is required where the

grinding object is dispersed in water. Thus, in order to enhance the dispersion efficiency of the grinding object, a flocculation/sedimentation agent and/or a flocculant is usually added to the grinding object. Examples of the flocculation/sedimentation agent and flocculant that can be used in the present invention include polyaluminum chloride, aluminum sulfate, ferrous sulfate, ferric sulfate, chlorinated copperas, polyferric sulfate, polyferric chloride, iron-silica inorganic polymer coagulant, ferric chloride-silica inorganic polymer coagulant, calcium hydroxide ($\text{Ca}(\text{OH})_2$), sodium hydroxide (NaOH), and sodium carbonate (Na_2CO_3). These flocculation/sedimentation agents and flocculants have alkaline or acidic pH levels. In the present invention, when the mica is prepared by wet grinding, preferably, no flocculation/sedimentation agent and/or flocculant is used. In the use of mica that has not been treated with any flocculation/sedimentation agent and/or flocculant, the polymer in a composite resin composition is scarcely decomposed, and generation of a large amount of gas and a decrease in the molecular weight of the polymer scarcely occur. Accordingly, a resulting molded article such as an electronic component can easily maintain higher quality.

The mica that can be used in the present invention preferably has an average particle diameter of 10 to 100 μm , more preferably 20 to 80 μm , measured by microtrac laser diffractometry. When the mica has an average particle diameter of 10 μm or more, a sufficient effect of improving the

rigidity of a molded article is readily obtained. Thus, such a size is preferred. When the mica has an average particle diameter of 100 μm or less, a sufficient improvement in the rigidity of a molded article and a sufficient welding strength are readily obtained. Thus, such a size is preferred. In addition, an average particle diameter of mica of 100 μm or less can easily secure fluidity sufficient for molding, for example, an electronic component of the present invention.

The mica that can be used in the present invention preferably has a thickness of 0.01 to 1 μm , more preferably 0.03 to 0.3 μm , actually measured with an electron microscope. The mica having a thickness of 0.01 μm or more is scarcely broken in melt processing of the composite resin composition. Thus, such a thickness has a possibility of easily enhancing the rigidity of a molded article and is therefore preferred. A thickness of 1 μm or less of mica sufficiently improves the rigidity of a molded article and is therefore preferred.

The mica that can be used in the present invention may be surface-treated with, for example, a silane coupling agent and/or may be granulated into granulates with a binder.

In the composite resin composition in the present invention, a total amount of the fibrous filler and the plate-shaped filler is 17.5 to 62.5% by mass with respect to the total composite resin composition. If the total amount is less than 17.5% by mass with respect to the total composite resin composition, the molded article, such as an electronic component, obtained from the composite resin composition has a

low load deflection temperature, does not have sufficient high-temperature rigidity, and can have increased warping deformation. Thus, such a total amount is not preferred. If the total amount is higher than 62.5% by mass with respect to the total composite resin composition, the composite resin composition has deteriorated fluidity, and warping deformation of a molded article can be increased. Thus, such a total amount is not preferred. The total amount is preferably 25 to 56% by mass and more preferably 35 to 40% by mass with respect to the total composite resin composition.

(Other components)

The composite resin composition of the present invention may further contain at least one selected from nucleating agents, carbon black, pigments such as inorganic fired pigments, antioxidants, stabilizers, plasticizers, lubricants, mold release agents, flame retardants, and known inorganic fillers, in addition to the above-mentioned components.

The composite resin composition of the present invention can be prepared by any process capable of uniformly mixing the components of the composite resin composition and of setting the weight average fiber length of the fibrous filler to 250 μm or higher. The composite resin composition can be prepared by a process appropriately selected from conventionally known processes for producing resin compositions. The composite resin composition is prepared, for example, by melting and kneading the components and extruding the mixture with a melt kneader, such as a single- or twin-screw extruder, and

processing the resulting composite resin composition into a desired form, such as powder, flake, or pellet.

The composite resin composition of the present invention has excellent fluidity. Accordingly, the minimum filling pressure during molding is prevented from being excessively increased, which is preferable for forming, for example, an electronic component, in particular, a component having a complicated shape, such as an asymmetric electronic component having a latch structure, a notch, or the like. The degree of fluidity is determined by the minimum filling pressure of a connector. That is, the minimum injection filling pressure for providing a satisfactory molded article, a DDR-DIMM connector shown in FIG. 1, by injection molding was measured as the minimum filling pressure. The lower the minimum filling pressure is, the more excellent the evaluation of the fluidity is.

A composite resin composition having a melt viscosity of 1×10^5 Pa·s or less (more preferably 5 Pa·s or more and 1×10^2 Pa·s or less) measured in accordance with ISO11443 at a temperature higher than the melting point of the liquid crystal polymer by 10°C to 30°C and a shear rate of 1000/sec is preferred due to the fact that the fluidity of the composite resin composition is secured and that it does not need excessive filling pressure in molding a part having a complicated shape in an electronic component, in particular, in molding of a part having a complicated shape, such as a latch structure or a notch, of an asymmetric electronic component.

[Electronic component]

The electronic component of the present invention can be prepared by molding the composite resin composition in the present invention. The electronic component of the present invention is not particularly limited, and examples thereof include an electronic component having a total product length of 30 mm or more and a product height of 5 mm or more. Of the electronic components of the present invention, the asymmetric electronic component refers to that not having symmetry with respect to any of the XY, YZ, and XZ axial planes of the molded article.

Ordinary connectors (electronic components) widely distributed in the market have symmetry with respect to any of the XY, YZ, and XZ axial planes, and the dimensional accuracy and warp of a product can be controlled by adjusting the gate position and design so as to maintain the symmetry in the molding. Contrary to this, an asymmetric electronic component has a complicated shape and is difficult to be prevented from warping deformation through the molding procedure. The electronic component, in particular, the asymmetric electronic component, of the present invention can be prevented from warping deformation by using the composite resin composition of the present invention.

Typical examples of such an electronic component include a connector and a socket.

Examples of the connector include a memory module connector and an interface connector. Examples of the memory

module connector include a DIMM connector; and a DDR connector such as a DDR-DIMM connector, a DDR2-DIMM connector, a DDR-SO-DIMM connector, a DDR2-SO-DIMM connector, a DDR-Micro-DIMM connector, and a DDR2-Micro-DIMM connector. Examples of the interface connector include a SATA connector, a SAS connector, and an NGFF connector. Among them, preferred are a DDR connector, a SATA connector, a SAS connector, and an NGFF connector. Particularly preferred is a memory module connector having thin walls and complicated shapes for notebook personal computers, having a pitch distance of 0.6 mm or less, product total length of 60.0 mm or more, a product height of 10.0 mm or less, and a pole number of 200 or more. Such a memory module connector is subjected to an IR reflow process for surface mounting at a peak temperature of 230°C to 280°C and is required to have a warp of 0.1 mm or less before the IR reflow process and a difference in the warp between before and after the reflow of 0.05 mm or less. The present invention can satisfy such requirements.

Examples of the socket include a memory card socket such as a card bus, a CF card, a memory stick, a PC card, an SD card, a secure data access module (SDMo), a smart card, and a smart media card.

The electronic component of the present invention may be molded by any process. In order to prevent warping deformation of the electronic component, molding conditions not causing residual internal stress are preferably selected. The cylinder temperature of a molding machine is preferably equal to or

higher than the melting point of a liquid crystal polymer for reducing the filling pressure and reducing the residual internal stress of the resulting electronic component.

The mold temperature is preferably 70°C to 100°C. A mold temperature being low may cause insufficient flowing of the composite resin composition packed in a mold and is therefore not preferred. A mold temperature being high may cause problems, such as flash, and is therefore not preferred. Molding is preferably performed at an injection speed of 150 mm/sec or more. When the injection speed is low, only unfilled molded articles may be obtained; completely filled molded articles, if obtained, have a high filling pressure and a high residual internal stress; and only electronic components having large warping deformation may be obtained.

The electronic component of the present invention has reduced warping deformation. The degree of warp of an electronic component is determined as follows. That is, the heights of the DDR-DIMM connector shown in FIG. 1 are measured at the plural positions shown in FIG. 2 with the black circles. The difference between the maximum height and the minimum height from a least squares plane is defined as the warp. The electronic component of the present invention is prevented from changing in warp before and after IR reflow.

The electronic component of the present invention has reduced blister occurring. The degree of blister occurring is determined with a blister temperature. That is, it is visually observed whether blister occurring is present or not on the

surface of a molded article that has been pressed for 5 minutes with a hot press at a predetermined temperature. The highest temperature at which the number of blister occurring is zero is defined as a blister temperature. The higher the blister temperature is, the more suppressed the blister occurring is evaluated to be.

The electronic component of the present invention was excellent in heat resistance such as evaluated with high-temperature rigidity. The high-temperature rigidity can be evaluated by measuring the load deflection temperature in accordance with ISO75-1, 2.

EXAMPLES

The present invention will now be specifically described by examples, but is not limited to them.

Synthesis Example 1

The following raw material monomers, fatty acid metal salt catalyst, and acylating agent were charged in a polymerization vessel equipped with a stirrer, a reflux column, a monomer charge port, a nitrogen introducing port, and a depressurization/fluxion line, and nitrogen purging was started.

(I) 4-Hydroxybenzoic acid: 9.7 mol (58 mol%) (HBA)

(II) 6-Hydroxy-2-naphthoic acid: 0.17 mol (1 mol%) (HNA)

(III) Terephthalic acid: 3.2 mol (19.25 mol%) (TA)

(IV) Isophthalic acid: 0.25 mol (1.5 mol%) (IA)

(V) 4,4'-Dihydroxybiphenyl: 2.5 mol (15.25 mol%) (BP)

(VI) N-acetyl-p-aminophenol: 0.83 mol (5 mol%) (APAP)

Potassium acetate catalyst: 110 mg

Acetic anhydride: 1,734 g (an amount that is 1.03 times a hydroxy equivalent of a total of the HBA, HNA, BP and APAP)

After charging raw materials, the temperature of the reaction system was raised to 140°C, followed by a reaction at 140°C for 1 hour. Then, the temperature was further raised to 360°C over 5.5 hours and the pressure was reduced to 10 Torr (i.e., 1,330 Pa) over 20 minutes and, while distilling out acetic acid, excess acetic anhydride and other low boiling point components, melt polymerization was performed. After stirring torque reached a predetermined value, nitrogen was introduced to turn from a depressurized state to a pressurized state via a normal pressure, and then the polymer was discharged from the bottom of the polymerization vessel.

Evaluation

With respect to the wholly aromatic polyester amide of Synthesis Example 1, the evaluation of melting point, melt viscosity, and DTUL was performed by the following methods. The evaluation results are shown in Table 1.

[Melting Point]

After observing an endothermic peak temperature (T_{m1}) observed when a polymer is measured from room temperature under temperature rise conditions of 20°C/min using DSC (manufactured by TA Instruments), the polymer was held at a temperature of $(T_{m1} + 40)^{\circ}\text{C}$ for 2 minutes and cooled to room temperature under temperature drop conditions of 20°C/min, and

then the endothermic peak temperature observed when measured again under the temperature rise conditions of 20°C/min was measured.

[DTUL]

Using a twin-screw extruder (Model TEX30 α , manufactured by The Japan Steel Works, Ltd.), 60% by mass of a polymer and 40% by mass of a glass fiber (EFH75-01, manufactured by Central Glass Co., Ltd., milled fiber, average fiber diameter of 11 μ m, average fiber length of 75 μ m) were melt-kneaded at a cylinder temperature of the melting point of the polymer + 20°C to obtain polyester amide resin composition pellets. Using a molding machine ("SE100DU", manufactured by Sumitomo Heavy Industries, Ltd.), the polyester amide resin composition pellets were molded under the following molding conditions to obtain a test piece for measurement (4 mm $\times$ 10 mm $\times$ 80 mm). Using the test piece, deflection temperature under load was measured by the method in conformity with ISO 75-1,2. Bending stress used was 1.8 MPa. The results are shown in Table 1.

(Molding Conditions)

Cylinder temperature: melting point of polymer + 15°C

Mold temperature: 80°C

Back pressure: 2 MPa

Injection speed: 33 mm/sec

[Melt Viscosity]

Using Capilograph manufactured by TOYO SEIKI SEISAKU-SHO, LTD., a melt viscosity of a liquid crystal polymer was measured at a temperature that is 10 to 30°C higher than the

melting point of the liquid crystal polymer and a shear rate of 1,000/sec in conformity with ISO 11443, using an orifice having an inner diameter of 1 mm and a length of 20 mm. The measurement temperature was as shown in Table 1.

Synthesis Examples 2 to 18, Comparative Synthesis Examples 1 to 11

In the same manner as in Synthesis Example 1, except that types and charge ratios (mol%) of raw material monomers were changed as shown in Tables 1 to 3, polymers were obtained. In the same manner as in Synthesis Example 1, evaluation was performed. The evaluation results are shown in Tables 1 to 3.

[Table 1]

	Synthesis Example								
	1	2	3	4	5	6	7	8	9
HBA (mol%)	58	62	58	62	58	58	60	62	58
HNA (mol%)	1	1	1	1	2	1	1.5	1.5	3
TA (mol%)	19.25	17.25	17.75	15.75	18.75	17.75	17.25	16.25	18.25
IA (mol%)	1.5	1.5	3	3	1.5	3	2.25	2.25	1.5
BP (mol%)	15.25	13.25	15.25	13.25	12.75	13.25	13	12	14.25
APAP (mol%)	5	5	5	5	7	7	6	6	5
Total (mol%)	100	100	100	100	100	100	100	100	100
HNA+IA (mol%)	2.5	2.5	4	4	3.5	4	3.75	3.75	4.5
APAP/(BP+APAP)	0.25	0.27	0.25	0.27	0.35	0.35	0.32	0.33	0.26
Melting point (°C)	355	356	343	343	353	350	347	351	345
Temperature at which melt viscosity was measured (°C)	370	370	360	360	370	370	360	370	360
Melt viscosity (Pa·s)	17.9	20.8	22.6	23.7	18.0	22.2	24.0	20.3	17.8
DTUL (°C)	300	293	278	267	274	272	275	281	269
(Melting point)-DTUL	55	63	65	76	79	78	72	70	76

[Table 2]

	Synthesis Example								
	10	11	12	13	14	15	16	17	18
HBA (mol%)	64	60	58	60	62	60	60	60	60
HNA (mol%)	2.15	2.5	2	2	2	2.8	3	1.5	2.8
TA (mol%)	15.675	18	18.75	17.75	16.75	18.15	18.25	17.5	18.4
IA (mol%)	1.5	1	1.5	1.5	1.5	0.7	0.5	2	0.7
BP (mol%)	11.675	13.5	14.75	13.75	12.75	13.35	13.25	17	13.1
APAP (mol%)	5	5	5	5	5	5	5	2	5
Total (mol%)	100	100	100	100	100	100	100	100	100
HNA+IA (mol%)	3.65	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5
APAP/(BP+APAP)	0.30	0.27	0.25	0.27	0.28	0.27	0.27	0.11	0.28
Melting point (°C)	346	342	348	347	346	342	343	351	343
Temperature at which melt viscosity was measured (°C)	360	360	360	360	360	360	360	370	360
Melt viscosity (Pa·s)	23.7	20.1	23.6	24.6	19.4	21.7	21.3	15.6	19.1
DTUL (°C)	277	270	275	276	276	273	269	282	274
(Melting point)-DTUL	69	72	73	71	70	69	74	69	69

[Table 3]

	Comparative Synthesis Example										
	1	2	3	4	5	6	7	8	9	10	11
HBA (mol%)	62	58	67	70	64	50	60	48	60	62	62
HNA (mol%)	2	2	2	2	0	2.5	5	3	2	0	1
TA (mol%)	15.25	17.25	11.25	8.75	11.45	23.75	17.5	21	16.75	15.75	15.75
IA (mol%)	3	3	4.5	5.5	6.8	0	0	3.5	2.5	3.5	3
BP (mol%)	10.75	14.75	15.25	13.75	15.75	18.75	12.5	24.5	18.75	17.75	11.25
APAP (mol%)	7	5	0	0	2	5	5	0	0	1	7
Total (mol%)	100	100	100	100	100	100	100	100	100	100	100
HNA+IA (mol%)	5	5	6.5	7.5	6.8	2.5	5	6.5	4.5	3.5	4
APAP/(BP+APAP)	0.39	0.25	0	0	0.11	0.21	0.29	0	0	0.05	0.38
Melting point (°C)	352	333	332	330	327	365	336	355	367	362	357
Temperature at which melt viscosity was measured (°C)	370	350	350	350	350	380	360	380	380	380	370
Melt viscosity (Pa·s)	20.1	25.4	30.8	37.3	20.1	61.0	20.5	29.0	23.8	21.4	26.3
DTUL (°C)	254	252	237	215	258	280	258	245	236	295	261
(Melting point)-DTUL	98	81	95	115	69	85	78	110	131	67	96

Examples 1 to 12, Comparative Examples 1 to 5

In the following Examples and Comparative Examples, the liquid crystal polymer 1 is the liquid crystal polymer obtained in Synthesis Example 15. The liquid crystal polymers

2 and 3 were produced as stated below.

In this example, the melting point and melt viscosity of the pellet were measured under the following respective conditions.

[Measurement of melting point]

The melting point was measured with DSC manufactured by TA Instruments Inc. as follows: A liquid crystal polymer was heated at a temperature rise rate of 20°C/min from room temperature to observe an endothermic peak temperature (T_{m1}), was retained at a temperature of $T_{m1}+40^{\circ}\text{C}$ for 2 minutes, was then cooled at a temperature fall rate of 20°C/min to room temperature, and was heated at a temperature rise rate of 20°C/min again to observe an endothermic peak temperature; and the temperature of the endothermic peak was measured as the melting point.

[Measurement of melt viscosity]

The melt viscosity of a liquid crystal polymer was measured in accordance with ISO11443 at a temperature higher than the melting point of the liquid crystal polymer by 10°C to 30°C and a shear rate of 1000/sec with Capilograph 1B manufactured by Toyo Seiki Seisaku-sho, Ltd., using an orifice with a diameter of 1 mm and a length of 20 mm. The measuring temperatures are 360°C for the liquid crystal polymer 1, 350°C for the liquid crystal polymer 2, and 380°C for the liquid crystal polymer 3.

(Process of producing liquid crystal polymer 2)

A polymerization vessel equipped with a stirrer, a reflux

column, a monomer input port, a nitrogen inlet port, and a pressure reducing/outflow line was fed with the raw material monomers, metal catalyst, and acylating agent shown below, and nitrogen purge was started.

(I) 4-hydroxybenzoic acid: 1380 g (60 mol%) (HBA)

(II) 6-hydroxy-2-naphthoic acid: 157 g (5 mol%) (HNA)

(III) terephthalic acid: 484 g (17.5 mol%) (TA)

(IV) 4,4'-dihydroxybiphenyl: 388 g (12.5 mol%) (BP)

(V) 4-(acetoxymino)phenol: 126 g (5 mol%) (APAP)

Potassium acetate catalyst: 110 mg

Acetic anhydride: 1659 g

After feeding of the raw materials into the polymerization vessel, the temperature of the reaction system was raised to 140°C, and reaction was performed at 140°C for 1 hour. The temperature was then further raised to 340°C over 4.5 hours. Subsequently, the pressure was reduced to 10 Torr (i.e., 1330 Pa) over 15 minutes. Thus, melt polymerization was performed while acetic acid, excessive acetic anhydride, and other low boiling components were being distilled. After the stirring torque reached a predetermined value, nitrogen was introduced for increasing the pressure from the reduced state, through a normal pressure, to a pressurized state to discharge the polymer from a lower part of the polymerization vessel. The resulting strand was pelletized into a pellet. The resulting pellet had a melting point of 336°C and a melt viscosity of 19 Pa·s.

(Process of producing liquid crystal polymer 3)

A polymerization vessel equipped with a stirrer, a reflux column, a monomer input port, a nitrogen inlet port, and a pressure reducing/outflow line was fed with the raw material monomers, a metal catalyst, and acylating agent shown below, and nitrogen purge was started.

(I) 4-hydroxybenzoic acid: 1040 g (48 mol%) (HBA)

(II) 6-hydroxy-2-naphthoic acid: 89 g (3 mol%) (HNA)

(III) terephthalic acid: 547 g (21 mol%) (TA)

(IV) isophthalic acid: 91 g (3.5 mol%) (IA)

(V) 4,4'-dihydroxybiphenyl: 716 g (24.5 mol%) (BP)

Potassium acetate catalyst: 110 mg

Acetic anhydride: 1644 g

After feeding of the raw materials into the polymerization vessel, the temperature of the reaction system was raised to 140°C, and reaction was performed at 140°C for 1 hour. The temperature was then further raised to 360°C over 5.5 hours. Subsequently, the pressure was reduced to 5 Torr (i.e., 667 Pa) over 20 minutes. Thus, melt polymerization was performed while acetic acid, excessive acetic anhydride, and other low boiling components were being distilled. After the stirring torque reached a predetermined value, nitrogen was introduced for increasing the pressure from the reduced state, through a normal pressure, to a pressurized state to discharge the polymer from a lower part of the polymerization vessel. The resulting strand was pelletized into a pellet. The resulting pellet had a melting point of 355°C and a melt viscosity of 10 Pa.s.

(Components other than liquid crystal polymer)

Each liquid crystal polymer prepared above and the following components were mixed with a twin-screw extruder to prepare each composite resin composition. The blended amounts of the components are shown in Tables 4 and 5. Hereinafter, "%" in Tables represents % by mass.

Fibrous filler (B)

Glass fiber 1: ECS03T-786H, a chopped strand having a fiber diameter of 10 μm and a length of 3 mm, manufactured by Nippon Electric Glass Co., Ltd.

Glass fiber 2: ECS03T-790DE, a chopped strand having a fiber diameter of 6 μm and a length of 3 mm, manufactured by Nippon Electric Glass Co., Ltd.

Milled fiber: PF70E001, fiber diameter: 10 μm , average fiber length: 70 μm (maker nominal value), manufactured by Nitto Boseki Co., Ltd.

The maker nominal value stated above is different from 100 μm in Table 4, which is an actual measured value in the composition.

Plate-shaped filler (C)

Talc: Crown Talc PP, average particle diameter: 10 μm , manufactured by Matsumura Sangyo Co., Ltd.

The extrusion conditions for preparing the composite resin composition were as follows.

[Extrusion conditions]

Examples 1 to 12, Comparative Examples 1 to 3

The temperature of the cylinder placed at the main feed

port was set to 250°C, and those of other cylinders were set to 360°C. All of liquid crystal polymers were supplied through the main feed port. The filler was supplied through the side feed port.

Comparative Example 4

The temperature of the cylinder placed at the main feed port was set to 250°C, and those of other cylinders were set to 350°C. All of liquid crystal polymers were supplied through the main feed port. The filler was supplied through the side feed port.

Comparative Example 5

The temperature of the cylinder placed at the main feed port was set to 250°C, and those of other cylinders were set to 380°C. All of liquid crystal polymers were supplied through the main feed port. The filler was supplied through the side feed port.

The weight average fiber length of the fibrous filler in the composite resin composition was measured by the following process.

[Measurement of weight average fiber length]

5 g of the composite resin composition pellet was heated at 600°C for 2 hours for incineration. The incineration residue was thoroughly dispersed in an aqueous solution of 5% by mass of polyethylene glycol. The dispersion was transferred to a petri dish with a syringe and was subjected to observation of the fibrous filler with a microscope. At the same time, the weight average fiber length of the fibrous

filler was measured with an image measuring apparatus (LUZEXFS, manufactured by Nireco Corporation).

[Measurement of melt viscosity of composite resin composition]

The melt viscosity of a composite resin composition was measured in accordance with ISO11443 at a temperature higher than the melting point of the liquid crystal polymer by 10°C to 30°C and a shear rate of 1000/sec with Capilograph 1B manufactured by Toyo Seiki Seisaku-sho, Ltd., using an orifice with a diameter of 1 mm and a length of 20 mm. The measuring temperatures are 360°C for the composite resin composition with the liquid crystal polymer 1, 350°C for the composite resin composition with the liquid crystal polymer 2, and 380°C for the composite resin composition with the liquid crystal polymer 3. Tables 4 and 5 show the results.

The physical properties of a connector molded from the composite resin composition were measured by the following processes. Tables 4 and 5 show the results of each evaluation.
(Bending test)

A molded article with a thickness of 0.8 mm was produced by injection molding of a composite resin composition under the following molding conditions. The bending strength, fracture strain, and bending elastic modulus were measured in accordance with ASTM D790.

[Molding conditions]

Molding machine: Sumitomo Heavy Industries, Ltd., SE100DU

Cylinder temperature:

360°C (Examples 1 to 12, Comparative Examples 1 to 3)

350°C (Comparative Example 4)

370°C (Comparative Example 5)

Mold temperature: 80°C

Injection speed: 33 mm/sec

(Load deflection temperature)

A molded article was produced by injection molding of a composite resin composition under the following molding conditions. The load deflection temperature was measured in accordance with ISO75-1,2.

[Molding conditions]

Molding machine: Sumitomo Heavy Industries, Ltd., SE100DU

Cylinder temperature:

360°C (Examples 1 to 12, Comparative Examples 1 to 3)

350°C (Comparative Example 4)

370°C (Comparative Example 5)

Mold temperature: 80°C

Injection speed: 33 mm/sec

(Blister temperature)

A molded article with a weld part and a dimension of 12.5 mm × 120 mm × 0.8 mm was produced by injection molding of a composite resin composition under the following molding conditions. A piece obtained by dividing the molded article into two pieces at the weld part was used as a specimen and pressed for 5 minutes with a hot press at a predetermined temperature. Then, it was visually examined whether blister occurred or not on the surface of the specimen. The highest temperature at which the number of blister occurring was zero

was defined as a blister temperature. The predetermined temperature stated above was set for every 10°C in the range of 250 to 300°C.

[Molding conditions]

Molding machine: Sumitomo Heavy Industries, Ltd., SE100DU

Cylinder temperature:

360°C (Examples 1 to 12, Comparative Examples 1 to 3)

350°C (Comparative Example 4)

370°C (Comparative Example 5)

Mold temperature: 90°C

Injection speed: 33 mm/sec

(Warp of DDR connector)

A DDR-DIMM connector having a total size of 70.0 mm × 26.0 mm × 4.0 mm, a pitch distance of 0.6 mm, and a number of pin holes of 100 × 2, as shown in FIG. 1, was molded by injection molding (gate: tunnel gate, gate size: φ 0.75 mm) of a composite resin composition under the following molding conditions.

[Molding conditions]

Molding machine: Sumitomo Heavy Industries, Ltd., SE30DUZ

Cylinder temperature:

360°C (Examples 1 to 12, Comparative Examples 1 to 3)

350°C (Comparative Example 4)

370°C (Comparative Example 5)

Mold temperature: 80°C

Injection speed: 200 mm/sec

The resulting connector was placed on a horizontal table.

The height of the connector was measured with an image measuring apparatus, Quick Vision 404PROCNC, manufactured by Mitutoyo Corporation). The heights were measured at a plurality of positions indicated with black circles in FIG. 2. The difference between the maximum height and the minimum height from a least squares plane was defined as the warp of the DDR connector. The warp was measured before and after the IR reflow under the following conditions.

[IR reflow conditions]

Measuring apparatus: large tabletop reflow soldering equipment, RF-300 (using a far infrared heater), manufactured by Japan Pulse Laboratories, Inc.

Sample feed rate: 140 mm/sec

Time for passing through reflow furnace: 5 minutes

Temperature of preheat zone: 150°C

Temperature of reflow zone: 190°C

Peak temperature: 251°C

(Deformation amount of DDR connector)

The difference in warp between before and after the reflow measured by the above-described process was defined as the deformation amount of the DDR connector.

(Minimum filling pressure for DDR connector)

The minimum injection filling pressure for providing a satisfactory molded article, a DDR-DIMM connector shown in FIG. 1, by injection molding was measured as the minimum filling pressure.

[Table 4]

		Example				Comparative Example				
		1	2	3	4	1	2	3	4	5
Liquid crystal polymer 1	%	60	65	60	60	75	60	60		
Liquid crystal polymer 2	%								60	
Liquid crystal polymer 3	%									60
Glass fiber 1	%	10	5	15	5	15	20		10	10
Milled fiber	%							10		
Talc	%	30	30	25	35	10	20	30	30	30
Total amount of fillers	%	40	35	40	40	25	40	40	40	40
Weight average fiber length	μm	450	450	450	450	450	450	100	450	450
Melt viscosity	Pa·s	32	28	35	27	25	42	19	40	25
Bending strength	MPa	166	157	171	155	176	173	141	172	148
Fracture strain	%	2.4	2.7	2.3	2.4	3.1	2.3	2.9	2.6	1.9
Bending elastic modulus	MPa	12500	10300	12810	10500	10190	13100	11900	12600	11500
Blister temperature	°C	280	280	280	270	280	280	280	280	280
Load deflection temperature	°C	278	275	281	274	283	282	258	260	255
Warp of DDR connector (before reflow)	mm	0.043	0.045	0.055	0.039	0.082	0.081	0.100	0.045	0.044
Warp of DDR connector (after reflow)	mm	0.072	0.071	0.110	0.066	0.183	0.122	0.212	0.080	0.085
Deformation amount of DDR connector	mm	0.029	0.026	0.055	0.027	0.101	0.041	0.112	0.035	0.041
Minimum filing pressured for DDR connector	MPa	135	120	138	129	102	144	90	135	128

[Table 5]

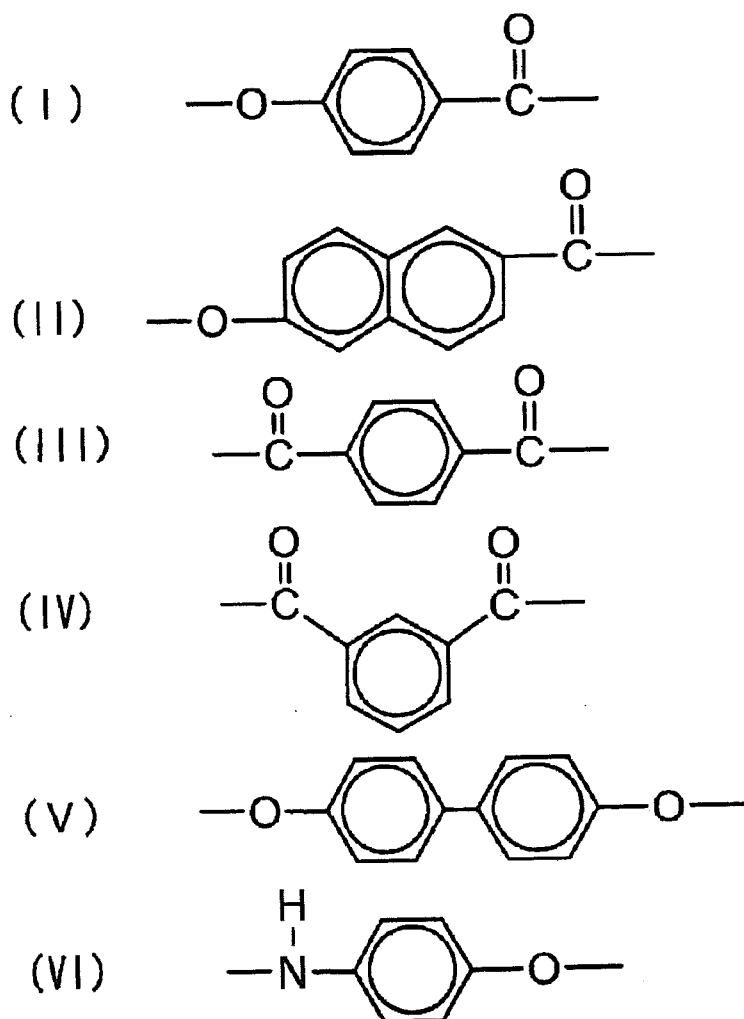
		Example							
		5	6	7	8	9	10	11	12
Liquid crystal polymer 1	%	60	65	62.5	67.5	62.5	68	72	63
Liquid crystal polymer 2	%								
Liquid crystal polymer 3	%								
Glass fiber 1	%	10	10	7.5	7.5				
Glass fiber 2	%					7.5	10	8	12
Talc	%	30	25	30	25	30	22	20	25
Total amount of fillers	%	40	35	37.5	32.5	37.5	32	28	37
Weight average fiber length	μm	362	382	531	528	424	649	488	416
Melt viscosity	Pa·s	22	17	18	16	22	18	16	19
Bending strength	MPa	162	165	154	158	159	173	167	179
Fracture strain	%	2.3	2.4	2.6	2.8	2.6	2.4	2.6	2.2
Bending elastic modulus	MPa	12900	12600	12000	11600	11900	11800	11400	13000
Blister temperature	°C	280	280	280	280	280	280	280	280
Load deflection temperature	°C	267	266	266	265	269	273	266	273
Warp of DDR connector (before reflow)	mm	0.055	0.053	0.054	0.055	0.053	0.071	0.075	0.050
Warp of DDR connector (after reflow)	mm	0.086	0.081	0.089	0.091	0.076	0.098	0.099	0.070
Deformation amount of DDR connector	mm	0.031	0.028	0.035	0.036	0.023	0.027	0.024	0.020
Minimum filing pressured for DDR connector	MPa	125	126	109	103	110	120	102	110

As shown in Tables 4 and 5, the electronic components molded from the composite resin compositions in the present invention were excellent in heat resistance and were prevented from warping deformation and blister occurring.

CLAIMS

1. A composite resin composition comprising a liquid crystalline polymer (A), a fibrous filler (B), and a plate-shaped filler (C), wherein

the liquid crystalline polymer (A) is a wholly aromatic polyester amide that exhibits optical anisotropy when melted, the wholly aromatic polyester amide consisting only of the following constituent units (I) to (VI) as essential constitutional components:



a content of the constituent unit (I) is 50 to 70 mol%

with respect to all of the constituent units;

a content of the constituent unit (II) is 0.5 mol% or higher and lower than 4.5 mol% with respect to all of the constituent units;

a content of the constituent unit (III) is 10.25 to 22.25 mol% with respect to all of the constituent units;

a content of the constituent unit (IV) is 0.5 mol% or higher and lower than 4.5 mol% with respect to all of the constituent units;

a content of the constituent unit (V) is 5.75 to 23.75 mol% with respect to all of the constituent units;

a content of the constituent unit (VI) is 1 to 7 mol% with respect to all of the constituent units;

a content of a total of the constituent unit (II) and the constituent unit (IV) is 1 mol% or higher and lower than 5 mol% with respect to all of the constituent units;

a content of a total of the constituent units (I) to (VI) is 100 mol% with respect to all of the constituent units;

a molar ratio of the constituent unit (VI) to a total of the constituent unit (V) and the constituent unit (VI) is 0.04 to 0.37;

a weight average fiber length of the fibrous filler (B) is 250 μm or higher;

the liquid crystalline polymer (A) is 37.5 to 82.5% by mass with respect to the total composite resin composition;

the fibrous filler (B) is 2.5 to 17.5% by mass with respect to the total composite resin composition;

the plate-shaped filler (C) is 15 to 45% by mass with respect to the total composite resin composition; and

a total amount of the fibrous filler (B) and the plate-shaped filler (C) is 17.5 to 62.5% by mass with respect to the total composite resin composition.

2. The composite resin composition according to claim 1, wherein a mole number of a total of the constituent unit (III) and the constituent unit (IV) is 1 to 1.1 times a mole number of a total of the constituent unit (V) and the constituent unit (VI), or a mole number of a total of the constituent unit (V) and the constituent unit (VI) is 1 to 1.1 times a mole number of a total of the constituent unit (III) and the constituent unit (IV).

3. The composite resin composition according to claim 1 or 2, wherein the fibrous filler (B) is a glass fiber.

4. The composite resin composition according to any one of claims 1 to 3, wherein the plate-shaped filler (C) is talc.

5. An electronic component

molded from the composite resin composition according to any one of claims 1 to 4 and

having a total product length of 30 mm or more and a product height of 5 mm or more.

6. The electronic component according to claim 5, wherein the electronic component is an asymmetric electronic component having no symmetry with respect to any of the axial planes of the XY axial plane, YZ axial plane, and XZ axial plane of a molded article.

7. The electronic component according to claim 5 or 6, wherein

the electronic component is a connector for a memory module, and

the connector has a distance between pitches of 0.6 mm or less, a total product length of 60.0 mm or more, a product height of 10.0 mm or less, and a pole number of 200 poles or more.