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DESCRIPTION

SEMICONDUCTIVE RESIN COMPOSITION AND FORMED ARTICLE

TECHNICAL FIELD OF THE INVENTION:

This invention relates to a liquid crystalline polymer composition containing graphite, a fibrous conductive filler and a fibrous non-conductive filler, and more particularly, it relates to a semiconductive liquid crystalline polymer composition which is suitably used for forming electronic parts in which an antistatic property is required.

BACKGROUND ART:

Liquid crystalline polymers capable of forming an anisotropic molten phase have been known as materials which have excellent dimensional accuracy, vibration-damping property, and fluidity, and hardly cause flash during molding. Conventionally, taking these advantages, glass fiber-reinforced liquid crystalline polymer compositions have been frequently used as materials for electronic parts. However, in recent years, a problem arises in that such electronic parts are electrostatically charged due to contact or sliding during assembling operations, thereby causing electrostatic damage. To prevent such electrostatic damage, an attempt is made at imparting an antistatic property to a molded article in itself by blending a conductive filler with a plastic

material of the molded article.

For example, in JP-A-62-131067, an attempt at improving conductivity has been made by blending conductive carbon black with a liquid crystalline polymer. According to such a method, conductivity is improved but volume resistivity is reduced to $1 \times 10^1 \Omega \cdot \text{cm}$ or less, and as a result, a resultant molded article has electrical conductivity in itself while having an antistatic effect so that it is not possible to use such a molded article in a part where insulation should be provided. In such a case where conductive carbon black is used, it is difficult to control volume resistivity in a range of 1×10^4 to $1 \times 10^{11} \Omega \cdot \text{cm}$ so that the molded article can have an antistatic effect without having electrical conductivity. Further, in JP-A-6-207083 and JP-A-2000-281885, attempts at improving an antistatic property have been made by blending graphite as a conductive filler. When only graphite is used as a conductive filler, while surface resistivity is excellently controlled, a necessary amount of graphite and the like for attaining an antistatic property becomes excessive. As a result, fluidity and mechanical properties are lowered, thus resulting in lack of practicability. Furthermore, in JP-A-63-146959, JP-A-4-311758, JP-A-6-93173, and JP-A-6-172619, attempts at improving slidability have been made by blending graphite and/or pitch-based carbon fibers. In these cases, while an improvement in slidability can be confirmed, it is difficult to control volume resistivity, thus resulting in

occurrence of wide variations in volume resistivity among molded articles. Consequently, a material which can overcome all the problems described above has not been existed until now.

DISCLOSURE OF THE INVENTION

In view of the foregoing problems, the present inventors have conducted extensive research and study on materials having an excellent antistatic property, and as a result, have found that it is possible to impart a stable antistatic property to a liquid crystalline polymer without significantly lowering the mechanical properties thereof, by blending the liquid crystalline polymer with specific graphite, a fibrous conductive filler, and a fibrous non-conductive filler in a specific amount, respectively, thus leading to completion of the present invention.

That is, the present invention provides a semiconductive resin composition having a volume resistivity in a range of 1×10^4 to $1 \times 10^{11} \Omega\cdot\text{cm}$ by blending 100 parts by weight of a liquid crystalline polymer (A) with 1 to 50 parts by weight of graphite (B) having not less than 95wt% of fixed carbon, 1 to 50 parts by weight of a fibrous electrically conductive filler (C), and 1 to 50 parts by weight of a fibrous non-conductive filler (D) in such a manner that the total blended amount of the components (B), (C), and (D) with respect to 100 parts by weight of (A) is 25-100 parts by weight, and that the ratio of (B):(C) is from

1:3 to 4:1 and the ratio of [(B)+(C)]:(D) is from 1:2 to 2:1.

DETAILED DESCRIPTION OF THE INVENTION:

The present invention will be described in detail below. A liquid crystalline polymer (A) for use in the present invention refers to a melt-fabricable polymer having properties capable of forming an optically anisotropic molten phase. The characteristics of an anisotropic molten phase can be confirmed by a conventional polarization inspection method in which crossed polarizers are used. More specifically, an anisotropic molten phase can be confirmed using a Leitz polarizing microscope by observing a molten sample placed on a Leitz hot stage, at a magnification of 40 times in an atmosphere of nitrogen. The liquid crystalline polymer for use in the present invention generally transmits polarized light even in the case where it is in a static molten state when inspected between the crossed polarizers to exhibit optical anisotropy.

Such a liquid crystalline polymer (A) as described above is not limited to any specific one, but is preferably aromatic polyester or aromatic polyesteramide. Also included in the above liquid crystalline polymer is polyester which partially contains aromatic polyester or aromatic polyesteramide in the same molecular chain. Preferably, those having an inherent viscosity (I. V.) of at least about 2.0 dl/g, more preferably in a range of 2.0 to 10.0 dl/g, when dissolved in pentafluorophenol at a concentration of

0.1wt% at 60°C are used.

Among such aromatic polyester or aromatic polyesteramide for use as a liquid crystalline polymer (A) which is applicable to the present invention, aromatic polyester or aromatic polyesteramide having at least one compound selected from the group consisting of aromatic hydroxycarboxylic acid, aromatic hydroxylamine, and aromatic diamine, as a constituent is particularly preferable.

More specifically, they include:

(1) polyester mainly comprising one or two or more of aromatic hydroxycarboxylic acid and derivatives thereof;

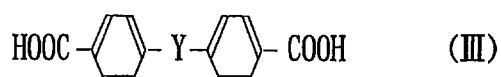
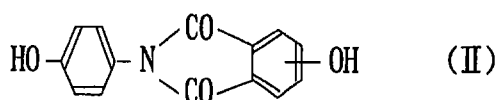
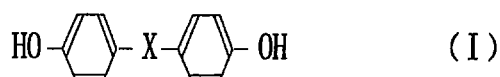
(2) polyester mainly comprising (a) one or two or more of aromatic hydroxycarboxylic acid and derivatives thereof, (b) one or two or more of aromatic dicarboxylic acid, alicyclic dicarboxylic acid, and derivatives thereof, and (c) one or two or more of aromatic diol, alicyclic diol, aliphatic diol, and derivatives thereof;

(3) polyesteramide mainly comprising (a) one or two or more of aromatic hydroxycarboxylic acid and derivatives thereof, (b) one or two or more of aromatic hydroxylamine, aromatic diamine, and derivatives thereof, and (c) one or two or more of aromatic dicarboxylic acid, alicyclic dicarboxylic acid, and derivatives thereof; and

(4) polyesteramide mainly comprising (a) one or two or more of aromatic hydroxycarboxylic acid and derivatives thereof, (b) one or two or more of aromatic hydroxylamine, aromatic diamine, and derivatives thereof, (c) one or two or

more of aromatic dicarboxylic acid, alicyclic dicarboxylic acid, and derivatives thereof, and (d) one or two or more of aromatic diol, alicyclic diol, aliphatic diol, and derivatives thereof. If necessary, a molecular weight modifier may be used with the constituents mentioned above.

Preferred examples of a compound constituting the liquid crystalline polymer (A) applicable to the present invention include: aromatic hydroxycarboxylic acid such as p-hydroxybenzoic acid or 6-hydroxy-2-naphthoic acid; aromatic diol such as 2,6-dihydroxynaphthalene, 1,4-dihydroxynaphthalene, 4,4'-dihydroxybiphenyl, hydroquinone, resorcin, or compounds represented by the following formulas (I) and (II); aromatic dicarboxylic acid such as terephthalic acid, isophthalic acid, 4,4'-diphenyldicarboxylic acid, 2,6-naphthalenedicarboxylic acid, or compounds represented by the following formula (III); and aromatic amines such as p-aminophenol or p-phenylenediamine.



[wherein X denotes a group selected from alkylene (C1~C4), alkylydene, -O-, -SO-, -SO₂-, -S-, -CO-; and Y denotes a group selected from -(CH₂)_n- (in which, n is 1 to 4), -O(CH₂)_nO- (in which, n is 1 to 4)].

Among them, aromatic polyester containing p-hydroxybenzoic acid or 6-hydroxy-2-naphthoic acid as a main constituent unit is particularly preferable as a liquid crystalline polymer (A) for use in the present invention.

To achieve the object of the present invention, that is, to impart an antistatic property to the liquid crystalline polymer without significantly lowering the mechanical properties thereof, 100 parts by weight of the liquid crystalline polymer (A) should be blended with 1 to 50 parts by weight of graphite (B) having not less than 95wt% of fixed carbon, 1 to 50 parts by weight of a fibrous electrically conductive filler (C), and 1 to 50 parts by weight of a fibrous non-conductive filler (D) in such a manner that the total blended amount of the components (B), (C), and (D) with respect to 100 parts by weight of the component (A) is 25-100 parts by weight, and that the ratio of (B):(C) is from 1:3 to 4:1 and the ratio of [(B)+(C)]:(D) is from 1:2 to 2:1.

As for the graphite (B), although various kinds of graphite such as synthetic graphite and natural graphite (e.g., laminate graphite, flake graphite, or amorphous graphite) can be used in the present invention, graphite containing 95wt% or more, preferably 98wt% or more of fixed carbon should be used to impart conductivity to the liquid crystalline polymer so that it can have an antistatic property. Among such graphite, artificial graphite having a high fixed carbon content, or flake graphite or vein graphite

which can easily form a structure in a resultant molded article is preferable from the viewpoint of performance.

Next, as for the fibrous conductive filler (C), conductive fibers such as carbon fibers or metal fibers, or glass fibers, whiskers, inorganic fibers, mineral-based fibers, or the like respectively coated with metal such as nickel or copper for attaining conductivity can be used in the present invention.

As for the carbon fibers, PAN-based fibers made of polyacrylonitrile or pitch-based fibers made of pitch can be used.

As for the metal fibers, fibers made of soft steel, stainless steel, steel and alloys thereof, brass, aluminum and alloys thereof or lead, or the like can be used. If necessary, these metal fibers may be respectively coated with another metal according to their conductivity so that the conductivity thereof can be improved.

As for the whiskers to which metal coating is applied when used, silicon nitride whiskers, silicon trinitride whiskers, basic magnesium sulfate whiskers, barium titanate whiskers, silicon carbide whiskers, boron whiskers, or the like can be used. As for the inorganic fibers to which metal coating is applied when used, various fibers such as fibers made of rockwool, zirconia, alumina-silica, potassium titanate, barium titanate, titanium oxide, silicon carbide, alumina, silica or blast-furnace slag can be used. As for the mineral-based fibers to which metal coating is

applied when used, asbestos or the like can be used. Among them, carbon fibers are preferable in terms of performance.

Then, as for the fibrous non-conductive filler (D) for used in the present invention, glass fibers, whiskers, inorganic fibers, mineral fibers, or the like can be mentioned. Examples of these fillers are the same as those of the fibrous conductive filler (C) to which metal coating is applied when used, as mentioned above. Among them, glass fibers are preferable in terms of performance.

Further, the weight average fiber length of the fibrous non-conductive filler (D) in a molded article of the semiconductive polymer composition is preferably about 600 μm or less. If the weight average fiber length exceeds 600 μm , there is a case that the molded article can not have a flame resistance of V-0 level.

In the present invention, the amount of the graphite (B), fibrous conductive filler (C), and fibrous non-conductive filler (D) to be blended is important to impart a stable antistatic property as well as excellent extrudability, moldability, and mechanical properties. That is, the amount of each of the components and the total amount of these components to be blended should lie in a specific range, respectively.

Specifically, if the blended amount of the graphite (B) is too large, extrudability and moldability are deteriorated, and mechanical strength is also lowered. On the other hand, if the blended amount of the graphite (B) is

too small, conductivity is not developed, thus resulting in poor antistatic effect. In this case, when an attempt at developing conductivity is made by increasing the blending amount of the fibrous conductive filler (C), large variations in conductivity occur so that a stable antistatic effect can not be obtained. Thus, the amount of the graphite (B) to be blended with respect to 100 parts by weight of the liquid crystalline polymer (A) should lie in a range of 1 to 50 parts by weight, preferably 10 to 30 parts by weight.

If the blended amount of the fibrous conductive filler (C) is too large, mechanical properties are improved but extrudability and moldability are deteriorated. In addition, excessively high conductivity is developed, thus resulting in the case that electrical continuity is established. On the other hand, if the blended amount of the fibrous conductive filler (C) is too small, conductivity is not developed, thus resulting in a poor antistatic effect. In this case, when an attempt at developing conductivity is made by increasing the blending amount of the graphite (B), extrudability and moldability are deteriorated, and further mechanical properties are lowered, as described above. Therefore, the amount of the fibrous conductive filler (C) to be blended with respect to 100 parts by weight of the liquid crystalline polymer (A) should lie in a range of 1 to 50 parts by weight, preferably 5 to 25 parts by weight.

The blending ratio of the graphite (B) to the fibrous conductive filler (C) is important. That is, the

blending ratio of (B) to (C) should lie in a range of 1:3 to 4:1. If the ratio of the component (B) exceeds the upper limit value, a desired conductivity can not be developed. On the other hand, the ratio of the component (B) is less than the lower limit value, excessively high conductivity is developed, thus resulting in the case that electrical continuity is undesirably established.

In the present invention, the effect obtained by blending the fibrous non-conductive filler (D) is especially important. Specifically, when the fibrous filler is added to the liquid crystalline polymer, a resultant molded article has roughness in its surface, and as a result, slidability is lowered. However, the effect of maintaining stable conductivity can be obtained. In the case where an attempt at obtaining such an effect is made by using the fibrous conductive filler (C), the blending amount of the fibrous conductive filler (C) is increased, thereby causing a problem in that electrical continuity is established, as described above. Therefore, it is necessary to blend a specific amount of the fibrous non-conductive filler (D). In this case, if the blended amount of the fibrous non-conductive filler (D) is too large, conductivity becomes stable but extrudability and moldability are deteriorated. On the other hand, if the blended amount of the fibrous non-conductive filler (D) is too small, stable conductivity can not be obtained, and further mechanical strength is lowered. For this reason, the amount of the fibrous non-conductive filler (D) to be blended

with respect to 100 parts by weight of the liquid crystalline polymer (A) should lie in a range of 1 to 50 parts by weight, preferably 10 to 40 parts by weight, and the blending ratio of [(B)+(C)] to (D) also should lie in a range of 1:2 to 2:1.

Further, if the total blended amount of the components (B), (C), and (D) is too large, extrudability and moldability are deteriorated. On the other hand, if the total blended amount of them is too small, stable conductivity can not be obtained, and further mechanical strength is lowered. Therefore, the total amount of the components (B), (C), and (D) to be blended with respect to 100 parts by weight of the liquid crystalline polymer (A) should lie in a range of 25 to 100 parts by weight, preferably in a range of 40 to 80 parts by weight, and more preferably in a range of 50 to 70 parts by weight.

Further, a non-fibrous filler comprised of particles or flakes may be blended in the semiconductive resin composition of the present invention within such a range as not impairing the antistatic property thereof, that is, the object of the present invention. Examples of a material of the non-fibrous filler include: silicates such as talc, mica, kaolin, clay, graphite, vermiculite, calcium silicate, aluminum silicate, feldspar powder, acid clay, agalmatolite clay, sericite, sillimanite, bentonite, glass flake, slate powder, and silane; carbonates such as calcium carbonate, chalk, barium carbonate, magnesium carbonate, and dolomite; sulfates such as barite powder, blanc fixe, precipitating

calcium sulfate, baked gypsum, and barium sulfate; hydroxides such as alumina hydrate; oxides such as alumina, antimony oxide, magnesia, titanium oxide, zinc white, silica, silicic sand, quartz, white carbon, and diatomaceous earth; sulfides such as molybdenum disulfide; and metal powder.

In the present invention, although the graphite, the fibrous conductive filler, and the fibrous non-conductive filler may be used as they are, they may be used in combination with a known surface treatment agent or a binder commonly used.

It is to be noted that compositions to which desired properties are imparted by adding additives such as nucleating agent, carbon black, pigment such as inorganic baked pigment, antioxidant, stabilizer, plasticizer, lubricant, releasing agent and flame retardant to a liquid crystalline polymer composition are also included in the liquid crystalline polymer composition of the present invention.

In the present invention, by using two or more kinds of conductive fillers and one or more kinds of non-conductive fillers so as to compensate for their drawbacks with each other, it is possible to obtain a liquid crystalline polymer composition having an excellent antistatic property, without impairing the mechanical properties thereof. A molded article made of such a liquid crystalline polymer composition exhibits high performance in a state where each of the components is uniformly dispersed wherein the graphite exists

among fibrous fillers.

Such a liquid crystalline polymer composition can be manufactured by blending both the fillers at the ratio mentioned above and kneading them. In general, they are kneaded in an extruder and then extruded into pellets for use in injection molding. However, kneading is not particularly limited to one using an extruder.

EXAMPLES

Hereinbelow, the present invention will be described in detail based on examples, but the present invention is not limited thereto. In this regard, it is to be noted that measurements of physical properties and tests for the examples were made as follows.

(1) Volume resistivity

According to ASTM D257, volume resistivity was measured using a $\phi 100 \times 3$ t plate specimen. Measurement was made for five specimens, and an average of the measurement values was practically used as volume resistivity. In this regard, it is to be noted that the average was obtained as a logarithmic mean. Further, evaluation was made for variations in measurement values among five specimens.

(2) Tensile property test

Tensile strength and tensile elongation were measured using an ASTM type I dumbbell specimen according to ASTM D638.

(3) Flexural property test

Flexural strength and flexural modulus of elasticity were measured using a specimen having a size of 130 × 13 × 0.8 mm according to ASTM D790.

(4) Method of measuring fiber length of glass fibers (GF)

About 2 g of pellet was heated in an electric furnace at about 700°C for 4 hours to burn all of resin, graphite, and carbon fibers. Then, a residual glass fibers as ash were dispersed in a 5% aqueous polyethyleneglycol solution, and the right amount of it was placed on a glass plate. This was observed under magnification using a microscope, and 500 to 1,000 of the fibers were measured using an image processing unit to obtain weight average fiber length.

(5) Combustion test

Flammability was measured using a specimen having a size of 130 × 13 × 0.8 mm according to UL-94.

Examples 1 to 5 and Comparative Example 1 to 12

In each of the examples and comparative examples, each of the fillers shown in Table 1 or 2 was dry blended with 100 parts by weight of a liquid crystalline polyester (LCP; Vectra A950 made by Polyplastics Co., Ltd.) at the ratios shown in Table 1 or 2, and then they were molten and kneaded using a twin extruder (PCM-30 model manufactured by Ikegai Tekko K.K.) to pelletize. The thus obtained pellets were subjected to an injection molding machine to prepare test specimens for the tests described above. Evaluations were made using these test specimens, and the results are

shown in Tables 1 and 2.

Table 1

	Composition (parts by weight)							GF weight average fiber length (μ m)	
	(A) ICP	(B) GP		(C) CF		(D) GF			
	Amount	Kind	Amount	Amount	Amount	Amount			
Ex.	1	100	GP1	25	10	25	2.5:1	1.4:1	485
	2	100	GP1	25	10	25	2.5:1	1.4:1	786
	3	100	GP1	15	15	30	1:1	1:1	560
	4	100	GP1	10	20	25	1:2	1.2:1	453
	5	100	GP2	25	10	25	2.5:1	1.4:1	521

Table 1 (continued)

	Physical properties							Flammability
	Volume resistivity ($\Omega \cdot \text{cm}$)		Tensile strength (MPa)	Tensile elongation (%)	Flexural strength (MPa)	Flexural modulus (MPa)	UL-94	
	Average	R						
Ex.	1	5.8×10^5	$4.2 \times 10^5 \sim 7.1 \times 10^5$	196	2.2	230	14600	V-0
	2	4.2×10^5	$1.2 \times 10^4 \sim 5.4 \times 10^5$	197	2.1	235	15100	V-1
	3	6.5×10^4	$3.8 \times 10^4 \sim 2.2 \times 10^5$	195	2.1	225	14600	V-0
	4	5.3×10^4	$1.8 \times 10^4 \sim 8.9 \times 10^4$	192	2.2	232	14500	V-0
	5	3.6×10^6	$8.7 \times 10^5 \sim 7.6 \times 10^6$	190	2.1	221	15000	V-0

Table 2

	Composition (parts by weight)							(B) : (C)	[(B) + (C)] : (D)	GF weight average fiber length (μm)
	(A)	(B)		(C)		(D)				
	LCP	GP	CF	GF						
	Amount	Kind	Amount	Amount	Amount					
Com. Ex.	1	100	GP1	5	5	10	10	1:1	1:1	832
	2	100	GP1	30	10			3:1	—	—
	3	100	GP1	30		25		—	1.2:1	730
	4	100	GP2	20		20		—	1:1	815
	5	100	GP2	30	20			1.5:1	—	—
	6	100	GP2	30				—	—	—
	7	100	GP2	50				—	—	—
	8	100	GP3	30				—	—	—
	9	100	GP1	5	20	25		1:4	1:1	560
	10	100	GP1	15	3	25		5:1	1:1.4	538
	11	100	GP1	5	5	30		1:1	1:3	713
	12	100	GP1	10	10	5		1:1	4:1	892

Table 2 (continued)

	Physical properties							Flammability
	Volume resistivity (Ω·cm)		Tensile strength (MPa)	Tensile elongation (%)	Flexural strength (MPa)	Flexural modulus (MPa)		
	Average	R						
Com. Ex.	1	7.6×10 ¹⁶	4.5×10 ¹⁶ ~1.0×10 ¹⁷	185	2.0	193	13000	V-1
	2	5.4×10 ⁶	2.5×10 ⁵ ~3.8×10 ¹⁰	189	2.2	202	13700	—
	3	3.8×10 ¹⁴	9.8×10 ¹³ ~5.2×10 ¹⁴	183	2.0	188	12200	V-1
	4	5.6×10 ¹⁶	9.8×10 ¹⁵ ~8.3×10 ¹⁶	178	2.5	181	11700	V-1
	5	4.0×10 ³	1.3×10 ² ~3.8×10 ⁵	195	2.1	228	14100	—
	6	1.0×10 ¹⁶	9.3×10 ¹⁵ ~1.1×10 ¹⁶	162	6.0	145	10500	—
	7	8.0×10 ¹³	5.1×10 ¹² ~7.5×10 ¹⁴	148	5.2	135	9500	—
	8	1.3×10 ¹⁷	9.5×10 ¹⁶ ~2.1×10 ¹⁷	150	4.2	140	9800	—
	9	3.1×10 ⁵	5.3×10 ² ~4.7×10 ⁶	180	3.2	205	16200	V-0
	10	6.3×10 ¹⁶	1.2×10 ¹⁶ ~8.7×10 ¹⁶	179	2.9	198	14100	V-0
	11	5.3×10 ¹⁶	8.7×10 ¹⁵ ~7.9×10 ¹⁶	189	2.5	193	14300	V-1
	12	8.8×10 ¹⁰	7.7×10 ⁶ ~3.2×10 ¹⁶	185	2.3	175	13500	V-1

Com.
Ex.

GP; graphite

GP1; synthetic graphite (HAG-15, manufactured by Nippon Graphite Industries, Ltd.; fixed carbon content: 98.5wt%)

GP2; flake graphite (CP, manufactured by Nippon Graphite Industries, Ltd.; fixed carbon content: 97.0wt%)

GP3; amorphous graphite (AOP, manufactures by Nippon Graphite Industries, Ltd.; fixed carbon content: 93.0wt%)

CF; chopped carbon fibers (PAN-based fibers; diameter: 7 μm ; length: 6 mm)

GF; chopped glass fibers (diameter: 10 μm ; length: 3 mm)

Claims:

1. A semiconductive resin composition having a volume resistivity of from 1×10^4 to $1 \times 10^{11} \Omega \cdot \text{cm}$, which is obtained by blending 100 parts by weight of a liquid crystalline polymer (A) with 1-50 part(s) by weight of graphite (B) having not less than 95% by weight of fixed carbon, 1-50 part(s) by weight of a fibrous electrically conductive filler (C) and 1-50 part(s) by weight of a fibrous non-conductive filler (D) in such a manner that the total compounding amount of the components (B), (C) and (D) to 100 parts by weight of (A) is 25-100 parts by weight and that the ratio of (B):(C) is from 1:3 to 4:1 and the ratio of [(B) + (C)]:(D) is from 1:2 to 2:1.

2. The composition according to claim 1, wherein the fibrous non-conductive filler (D) is dispersed in the composition in a weight-average fiber length of not more than 600 μm .

3. The composition according to claim 1 or 2, wherein the fibrous electrically conductive filler (C) is a carbon fiber of a PAN type.

4. The composition according to any of claims 1 to 3, wherein the fibrous non-conductive filler (D) is a glass fiber.

5. A molded article which is manufactured from the composition mentioned in any of claims 1 to 4.