POLYCARBONATE RESIN COMPOSITION HAVING EXCELLENT WEAR RESISTANCE AND ELECTRIC CONDUCTIVITY, AND METHOD OF PREPARING THE SAME

CROSS-REFERENCE TO RELATED APPLICATIONS

This application claims priority from Korea Patent Application No. 2009-0134952, filed on December 30, 2009, in the Korean Intellectual Property Office, the disclosure of which is incorporated herein by reference in its entirety.

FIELD OF THE INVENTION

The present invention relates to a polycarbonate resin composition having excellent wear resistance and electric conductivity, and method of preparing the same. Particularly, the present invention relates to a polycarbonate resin composition having excellent wear resistance and electric conductivity, which is prepared by mixing (A) a polycarbonate, (B) a styrene copolymer resin, (C) a carbon nano-tube and (D) a carbon black, and method of preparing the same.

BACKGROUND OF THE INVENTION

A tray to transfer items such as wafer, IC chip and electronic components and the like requires that the tray contain antistatic properties. Therefore, traditionally, plastic material, for example, in order to impart conductive property, was made by mixing ABS resin with antistatic agents, carbon black, carbon fiber, carbon nano-tube and the like. However, these trays have the following associated problems as follows.

Antistatic agents are affected easily by humidity because of ion conductivity and deterioration of antistatic properties coming from dropping out of antistatic agents through long time use or washing. In addition, mixing mass antistatic agents has

problems associated with deteriorating physical properties such as heat resistance.

Using a carbon black is not affected by humidity, washing and the like. However, adding mass carbon blacks is required to impart conductive property. Accordingly, the surface of the plastic article becomes weak to scratches and abrasion and, therefore, there is a problem in that abrasion loss or dropping out of the carbon particles may occur easily.

On the contrary, using carbon fiber resin influences electrical parts since the particles easily fall off through the protruding exterior of the plastic article and the resin per se has strong strength. Additionally, during the process of treating a head or an IC chip with ultrasonic waves, the products get damaged by debris of the carbon fiber per se and resin debris of the carbon fiber surface, which are induced by contacts between particles.

SUMMARY OF THE INVENTION

An object of the present invention is to provide a polycarbonate resin composition having excellent wear resistance and method of preparing the same.

Another object of the invention is to provide a polycarbonate resin composition having excellent electric conductivity and method of preparing the same.

Another object of the invention is to provide a polycarbonate resin composition having both excellent wear resistance and excellent electric conductivity, and method of preparing the same.

It is a feature of an embodiment of the present invention to provide a

polycarbonate resin composition comprising a polycarbonate (A), a styrene copolymer resin (B), a carbon nano-tube (C) and a carbon black (D).

In an embodiment of the present invention, the carbon nano-tube (C) and the carbon black (D) form the dimensional network structures.

In another embodiment of the present invention, the carbon black (D) is conductive globular carbon black having a particle size of about 1 to about 100 nm.

In another embodiment of the present invention, the styrene copolymer resin (B) includes about 60 to about 90 % by weight of a styrene monomer and about 10 to about 40 % by weight of an unsaturated nitrile monomer.

In another embodiment of the present invention, the polycarbonate resin composition includes about 0.1 to about 5 parts by weight of the carbon nano-tube (C) and about 1 to about 20 parts by weight of the carbon black (D), based on 100 parts by weight of base resin comprising about 45 to about 95 % by weight of the polycarbonate (A) and about 5 to about 55 % by weight of the styrene copolymer resin (B).

In another embodiment of the present invention, the polycarbonate resin composition which is extruded at 280°C has surface resistance of about E+5 or less according to ASTM D257.

In another embodiment of the present invention, the polycarbonate resin composition which is extruded at 280°C has an abrasion loss of about 30 mg or less measured under a condition of at a pressure of 3 Kgf, 1000rpm, at 200°C for 4 hours and a half.

It is another feature of an embodiment of the present invention to provide a method for preparing a polycarbonate resin composition having excellent wear resistance and electric conductivity which is prepared by mixing polycarbonate (A), a

styrene copolymer resin (B), a carbon nano-tube (C) and a carbon black (D).

In another embodiment of the method for preparing a polycarbonate resin composition, the carbon nano-tube (C) and the carbon black (D) form three-dimensional network structures.

It is another feature of an embodiment of the present invention to provide a plastic article prepared by the polycarbonate resin composition.

In another embodiment of the present invention, the plastic article is anti-charged tray.

BRIEF DESCRIPTION OF THE DRAWINGS

The above and other features and advantages of the present invention will become more apparent to those of ordinary skill in the art by describing in detail exemplary embodiments thereof with reference to the attached drawings, in which:

Fig. 1-4 below analyzes the forms of the polycarbonate resin composition according to the present invention observed by using the FE-TEM (Field Electron Transmission Electron Microscope) manufactured by Jeol Ltd. and exhibits the observations of the surface of sliced tensile specimens.

Fig. 1 illustrates a transmission electron microscope (TEM) photograph observing a surface of respective Examples 1, 2 and 3.

Fig. 2 illustrates a transmission electron microscope (TEM) photograph, which enlarges a surface of Example 1, observing a network formed by carbon fiber and carbon black.

Fig. 3 illustrates a transmission electron microscope (TEM) photograph, which enlarges a surface of Example 2, observing a network formed by carbon fiber and carbon black.

Fig. 4 illustrates a transmission electron microscope (TEM) photograph,

which enlarges a surface of Example 3, observing a network formed by carbon fiber and carbon black.

DETAILED DESCRIPTION OF THE INVENTION

The present invention will be described more fully hereinafter in the following detailed description of the invention, in which some, but not all embodiments of the invention are described. Indeed, this invention may be embodied in many different forms and should not be construed as limited to the embodiments set forth herein; rather, these embodiments are provided so that this disclosure will satisfy applicable legal requirements.

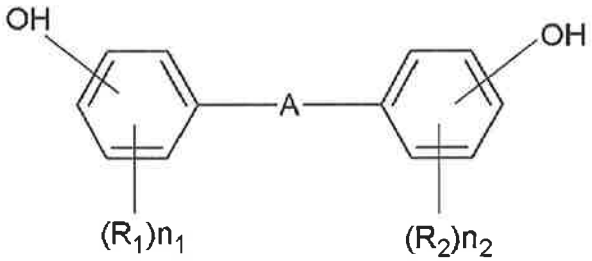
The present invention provides a polycarbonate resin composition comprising a polycarbonate (A), a styrene copolymer resin (B), a carbon nano-tube (C) and carbon black (D).

In an embodiment of the present invention, the polycarbonate resin composition comprises about 45 to about 95 % by weight of the polycarbonate (A), about 5 to about 55 % by weight of the styrene copolymer resin (B), about 0.1 to about 5 % by weight of the carbon nano-tube (C) and about 1 to about 20 % by weight of the carbon black (D).

(A) Polycarbonate resin

A polycarbonate resin of the present invention may be prepared by reacting diphenols represented by Chemical Formula 1 with a compound selected from the group consisting of a phosgene, a halogen formate, a carbonate diester and a combination thereof.

[Formula 1]



(A is a single bond, a substituted or unsubstituted C1 to C30 alkylene which are linear or branched, a substituted or unsubstituted C2 to C5 alkenylene, a substituted or unsubstituted C2 to C5 alkylidene, a substituted or unsubstituted C1 to C30 haloalkylene which are linear or branched, a substituted or unsubstituted C5 to C6 cycloalkylene, a substituted or unsubstituted C5 to C6 cycloalkenylene, a substituted or unsubstituted C5 to C10 cycloalkylidene, a substituted or unsubstituted C6 to C30 arylene, a substituted or unsubstituted C1 to C20 alkoxylene which are linear or branched, halogene acid ester, carbonic acid ester, CO, S or SO_2, and

Each of R_1 and R_2 is independently a substituted or unsubstituted C1 to C30 alkyl or a substituted or unsubstituted C6 to C30 aryl, and

n_1 and n_2 are independently integers ranging from 0 to 4.)

Examples of diphenols of Chemical Formula 1 may include without limitation hydroquinol, resocinol, 4,4'-dihydroxy diphenyl, 2,2-bis-(4-hydroxyphenyl)-propane, 2,4-bis-(4-hydroxyphenyl)-2-methyl buthane, bis-(4-hydroxyphenyl)methane, 1,1-bis-(4-hydroxyphenyl)-cyclohexane, 2,2-bis-(3-chloro-4-hyroxyphenyl)-propane, 2,2-bis-(3,5-dichloro-4-hydroxyphenyl)-propane, 2,2-bis-(3,5-dichloro-4-hydroxyphenyl)propane, 2,2-bis-(4-hydroxyphenyl)ketone, bis(4-hydroxyphenyl)ether and the like, and mixtures thereof.

From among these, 2,2-bis-(4-hydroxyphenyl)-propane, 2,2-bis-(3,5-

dichloro-4-hydroxyphenyl)-propane, 1,1-bis-(4-hydroxyphenyl)-cyclohexane and the like is preferable. Further, the 2,2-bis-(4-hydroxyphenyl)-propane (also referred to as bisphenol-A, BPA) is the most preferable.

The polycarbonate resin according to the present invention may have without limitation a weight average molecular weight (Mw) of about 10,000 to about 200,000 g/mol, for example about 15,000 to about 80,000 g/mol.

The polycarbonate resin may be a mixture of copolymers prepared by two or more kinds of the diphenols. Also the polycarbonate resin is linear polycarbonate resin, branched polycarbonate resin, polyestercarbonate copolymer resin and the like.

Examples of the linear polycarbonate resin include bisphenol-A polycarbonate resin and the like. The branched polycarbonate resin may be prepared by reacting multifunctional aromatic compound such as trimellitic anhydride, trimelliticaicd and the like with diphenols and carbonate compound. The multifunctional aromatic compound may include about 0.05 to about 2 % by mole, per total amount of the branched polycarbonate resin. The polyester-carbonate copolymer resin may be prepared by reacting bifunctional carboxylic acid with diphenols and carbonate. Examples of the carbonate are diarylcarbonate such as diphenylcarbonate, ethylene carbonate and the like.

The polycarbonate of the present invention may be prepared without limitation by interfacial polymerization or melt method using ester exchange reaction which react dihydroxy compound with dicarbonate compound.

In an embodiment of the present invention, the amount of the polycarbonate is about 45 to about 95 % by weight per total amount of the composition.

(B) Styrene copolymer resin

A styrene copolymer resin (B) of the present invention is a resin prepared by copolymerizing styrene monomer and unsaturated nitrile monomer. The styrene monomer may include without limitation styrene, α-methyl styrene, p-methyl styrene, 4-tert butyl styrene, 2,5-dimethyl styrene, vinyl toluene and the like. The unsaturated nitrile monomer may include without limitation methacrylronitrile and acrylronitrile and the like.

In an embodiment, the styrene copolymer resin may be prepared by one of well-known methods selected from a group consisting of emulsion polymerization, suspension polymerization, bulk polymerization and the like. It is preferred that about 60 to about 90 % by weight of the styrene monomer and about 10 to about 40 % by weight of the unsaturated nitrile monomer is used. If the amount of the unsaturated nitrile monomer is less than about 10 % by weight, conductive fillers (carbon fiber and carbon black) in polycarbonate is difficult to disperse and form networks as the carbon fiber (C) and the carbon black (D) may flow towards styrene copolymer resin due to having small amounts of unsaturated nitrile monomer. Accordingly, if the amount of the unsaturated nitrile monomer is less 10 % by weight, electrical conductivity thereof becomes deteriorative.

In an embodiment, the amount of the styrene copolymer resin (B) may be about 5 to about 55 % by weight per total weight of the composition. The conductive fillers of the present invention are located in polycarbonate phase. If the amount of the styrene copolymer resin (B) is more that 55 % by weight, the resin composition get lower conductivity because the amount of the polycarbonate including conductive fillers decreases. However, if the amount of the styrene copolymer resin (B) is less than 5% by weight, an abrasion may decline. As the styrene copolymer

resin (B) of the present invention has excellent physical property, it performs a role to enhance an abrasion of the polycarbonate resin composition.

(C) Carbon nano-tube

In an embodiment of the present invention, the carbon nano-tube is the one selected from the group consisting of single wall carbon nano-tube, double wall carbon nano-tube, multi wall carbon nano-tube, a cup-stacked carbon nano-fiber shaped in a hollow form with an interior that has multiple layers of truncated cone graphenes stacked therein and a combination thereof.

Also, the carbon nano-tube and carbon nano-fiber may be coated by metal materials such as Ni, NiP3, Cu, Fe, Au, Ag, Pb, Co, Sn.

Since it is difficult to disperse in process, as an aspect ratio(ratio to length and diameter of tube) of the carbon nano-tube is larger, it is preferred that multi wall carbon nano-tube having a diameter of about 1 to about 30 nm and length of 50μm or less is used.

The amount of the carbon nano-tube is about 0.01 to about 5 parts by weight per 100 parts by weight of a base resin, for example about 0.1 to about 1 part by weight. If the carbon nano-tube is used in such the amounts, it is suitable to form an electrical percolation for achieving conductivity of a conductive polyamide complex composition and it may maintain physical properties such as heat stability and machinery strength for example tensile strength and the like because of having proper process time to obtain homogeneous dispersion of carbon nano-tube within a polycarbonate resin composition.

(D) Carbon black

In an embodiment of the present invention, the carbon black may be selected from a group consisting of ketjen black, acetylene black, furnace black, channel black and a combination thereof. The carbon black is preferably ketjen black which can implement excellent conductivity.

The carbon black is a particle having particle size of about 10 to 100 nm, wherein the carbon black having particle size of about 10 μm represented by Figure 3 is connected continuously to implement conductivity. The conductive carbon black may be used preferably, which has particle size of about 20 to 50 nm and globular shape continuously.

Although the carbon black has an excellent electrical conductivity, it has a defect that massive abrasions occur since carbon particles may easily break away by scratches or friction. However, when the carbon black is employed with the carbon nano-tube, a substantial electrical conductivity may be obtained while decreasing the amount of addition of the carbon black. Further, it was found that a microscopic electrical conductive three dimension network structure may be formed between the carbon fibril of the carbon nano-tube so that the surface resistance and particle shed may be stabilized. That is, since the amount of carbon black inducing massive abrasion decreases and the structures of carbon fiber and carbon black becomes stabilized through network, particles are prevented from shedding and, therefore, the abrasion resistance of the resin composition strikingly improves.

Comparative abrasion of a carbon nano-tube, a carbon black, and a carbon nano-tube forming a network and a carbon black is in the following.

Solo existence of a carbon black > Solo existence of a carbon nano-tube > a network formed by a carbon nano-tube and a carbon black

The amount of the carbon black according to the present invention may include about 1 to about 20 parts by weight per 100 parts by weight of base resin. When the amount of the carbon black is less than 1 part by weight, form of network is difficult so that electric conductivity and an abrasion resistance may be declined. When the amount of the carbon black is more than 20 parts by weight, an abrasion resistance may be declined because of containing a lot of carbon black having much abrasion loss.

The polycarbonate resin composition prepared as above described is extruded through a conventional twin screw extruder (L/D=35, Φ=45 mm) into pellets. The resin pellets are molded into a test specimen using a 10 oz injection molding machine at 280°C of injection temperature and then the specimen has a surface resistance of E+5 or less measured according to ASTM D257. Also, the pellets which is extruded at 280°C has an abrasion loss of about 30 mg or less measured under a condition of at a pressure of 3 Kgf, 1000rpm, at 200°C for 4 hours and a half.

Because the polycarbonate resin composition of the present invention have excellent electric conductivity and abrasion resistance as above mentioned, the polycarbonate resin composition is suitable to use for material of plastic article using in environment which static electricity is easily generated and abrasion is readily induced, preferably use for wafer, IC chip, tray material to transfer electric parts.

The polyamide resin composition of the present invention is used in anyone requiring electric conductivity and abrasion resistance as well as anti-static tray. For example, it is used in any kinds of electric parts, machinery parts, housing materials and the like.

The invention may be better understood by reference to the following examples which are intended for the purpose of illustration and are not to be construed as in any way limiting the scope of the present invention, which is defined in the claims appended hereto.

EXAMPLE

The polycarbonate resin, the styrene copolymer resin, the carbon fiber and carbon black used in following examples and comparative examples are given below;

(A) Polycarbonate

PANLITE L-1225WXwith a weight average molecular weight of 22,000g/mol manufactured by Teijin Ltd. is used.

(B) Styrene copolymer resin

The styrene copolymer resin with a weight average molecular weight of 130,000g/mol including 71 parts by weight of styrene and 29 parts by weight of acrylonitrile is used.

(C) Carbon nano-tube

The product name NC-7000, a multi-walled carbon nano-tube with an average external diameter of 5~30 nm and average length of 1~25 μm manufactured by Nanocyl Ltd. is used.

(D) Conductive carbon black

The product name ENSACO 250G, a conductive carbon black which is a globular particle with an average diameter of 20~50 nm and is connected to each other to develop structure, manufactured by TIMCAL Ltd. is used.

The components as shown in Table 1 and 2 were mixed with antioxidant and heat stabilizer into each thermoplastic resin composition, and then each thermoplastic resin composition was extruded through a conventional twin extruder (L/D=35, Φ=45 mm) into pellets. The resin pellets were molded into a test specimen using a 10 oz injection molding machine at 280°C to measure the electrical conductivity and various physical properties. After exposure at 23°C and 50% of a relative humidity for 28 hours, the electrical conductivity and the physical properties of the test specimens were measured according to ASTM which is a standard method of measurement of America and the results were shown in Table 1 and 2 below.

A detailed explanation of each component of the present invention is as follows.

1) Surface resistance (Ω/sq): The surface resistance of each specimen is measured according to ASTM D257 using SRM-100 of Wolfgang Warmbier Ltd.

2) Abrasion loss: a specimen is measured under a condition of pressure at 3 Kgf, 1000 rpm, at 200°C for 4 hours and a half by using a machine measuring abrasion resistance Produced by Cheil Industrial Inc.

[Table 1]

Component	Classification	Examples				
		1	2	3	4	5
Composition	(A) Polycarbonate resin	90	90	70	50	70
	(B) Styrene copolymer resin	10	10	30	50	30
	(C) Carbon nano-tube	0.1	0.5	0.5	0.5	3
	(D)Conductive carbon black	20	10	10	10	1

Physical properties	Surface resistance (Ω/sq.)	E+4	E+4	E+4	E+4	E+4
	Abrasion (mg)	25	20	12	8	15

[Table 2]

Component	Classification	Comparative Examples					
		1	2	3	4	5	6
Composition	(A) Polycarbonate resin	100	100	100	40	90	70
	(B) Styrene copolymer resin	-	-	-	60	10	30
	(C) Carbon nano-tube	-	-	0.5	0.5	-	0.5
	(D) Conductive carbon black	10	20	10	10	10	-
Physical properties	Surface resistance (Ω/sq.)	E+12	E+4	E+4	E+10	E+12	E+12
	Abrasion (mg)	100	197	105	8	35	18

As shown in Tables 1 and 2, Examples 1-5 show prominent improvement of electrical conductivity and wear resistance as having low surface resistance and little abrasion loss. Meanwhile, Comparatives 5, 6 which do not include carbon nano-tube or carbon black show high surface resistance and lots of abrasion loss. Further, Comparative 3 which does not include a styrene copolymer resin shows excellent electrical conductivity, but it shows deterioration of abrasion resistance. In addition, Comparative 4 comprising polycarbonate and styrene copolymer resin which has an amount beyond the scope of the present inventions show deterioration of electrical conductivity because of small amounts of polycarbonate including conductive filler. In addition, Comparative 1 and 2 not including both styrene copolymer resin and carbon nano-tube show deterioration of electrical conductivity and abrasion resistance.

Many modifications and other embodiments of the invention will come to

mind to one skilled in the art to which this invention pertains having the benefit of the teachings presented in the foregoing descriptions. Therefore, it is to be understood that the invention is not to be limited to the specific embodiments disclosed and that modifications and other embodiments are intended to be included within the scope of the appended claims. Although specific terms are employed herein, they are used in a generic and descriptive sense only and not for purposes of limitation, the scope of the invention being defined in the claims.

What is claimed is:

1. A polycarbonate resin composition comprising: (A) Polycarbonate, (B) styrene copolymer resin, (C) carbon nano-tube, and (D) carbon black.

2. The polycarbonate resin composition of claim 1, wherein the carbon nano-tube and the carbon black has three dimensional network structures forming.

3. The polycarbonate resin composition of claim 1,wherein the carbon nano-tube is selected from the group consisting of single wall carbon nano-tube, double wall carbon nano-tube, multi wall carbon nano-tube, a cup-stacked carbon nano-fiber shaped in a hollow form with an interior that has multiple layers of truncated cone graphenes stacked therein and combinations thereof.

4. The polycarbonate resin composition of claim 1, wherein the carbon black is conductive globular carbon black having a particle size of about 1 to about 100 nm.

5. The polycarbonate resin composition of claim 4, wherein the carbon black is conductive rectangular carbon black which does not have gaps between globular shapes.

6. The polycarbonate resin composition of claim 1, wherein the styrene copolymer resin includes about 60 to about 90% by weight of styrene based monomer and about 10 to about 40% by weight of unsaturated-nitrile based monomer.

7. The polycarbonate resin composition of claim 1, wherein the polycarbonate

resin composition comprises about 0.1 to about 5 parts by weight of the carbon nano-tube (C) and about 1 to about 20 parts by weight of the carbon black (D), based on 100 parts by weight of base resin including about 45 to about 95% by weight of the polycarbonate (A) and about 5 to about 55% by weight of the styrene copolymer resin.

8. The polycarbonate resin composition of claim 1, wherein the pellets have a surface resistance of E+5 or less measured according to ASTM D257, which are prepared by extruding the polycarbonate and are molded at 280°C of injection temperature.

9. The polycarbonate resin composition of claim 1, wherein the pellets have an abrasion loss of about 30 mg or less measured under a condition of pressure at3 Kgf, 1000 rpm, at 200°C for 4 hours and a half, which are prepared by extruding the polycarbonate and are molded at 280°C of injection temperature.

10. A method for preparing the polycarbonate resin composition having excellent wear resistance and electric conductivity by mixing (A) a polycarbonate, (B) styrene copolymer resin, (C) carbon nano-tube, and (D) carbon black.

11. A plastic article prepared from the polycarbonate resin composition as in one of claims 1-9.

12. The plastic article of claim 11, wherein the plastic article is an anti-charged tray.