tubes form an aggregate in which the individual tubes are substantially electrically-isolated from one another. The polymeric wrappings around the tubes may be cross-linked by introduction of a linking agent, forming a different material in which individual, electrically-isolated SWNT are permanently suspended in a solid cross-linked polymeric matrix. Smalley et al (U.S. Pat. No. 7,008,563) disclose polymer wrapped single wall carbon nanotubes, however these wrapped nanotubes are used to make dielectric materials because the polymer wrapping prevents nanotube to nanotube contact.

Patel et al. (U.S. Patent 6,528,572) discloses compounding a polymeric resin, electrically conductive filler, antistatic agent and any other additives to form a substantially uniform conductive resin composition. Surface resistivity was measured for compositions containing a polymer resin (acrylonitrile-butadiene-styrene resin or a polyphenylene ether-high impact polystyrene resin), an antistatic agent, and carbon fibers. Both the surface and volume resistivity decrease as the weight percent of the conductive component (carbon fibers and antistatic agent) are increased.

Hirai et al. (U.S. Patent 5,227,238) discusses carbon fiber reinforced thermoplastics prepared by the use of milled fiber of an extremely short fiber length has inferior characteristics in comparison with one prepared by using carbon fiber chopped strands because of the short length of the milled fiber. As such, Hirai et al. discloses carbon fiber chopped strands suitable for use in production of a composite with a matrix material wherein the carbon fiber filaments are bundled by a sizing agent and having a length from 1 to 10 mm and a diameter from 30 to 20,000 μm.

SUMMARY ~~OF THE INVENTION~~

Embodiments of the present ~~invention~~disclosure include compositions comprising a polymer melt, an amount of nanotubes, and an amount of finely milled carbon fibers extrusion compounded together, the amount of the nanotubes and the amount of the finely milled carbon fibers dispersed in the polymer melt form a composite material. In some embodiments of the present ~~invention~~disclosure, compositions can be made in a single melt extrusion step without additional melt extrusion cycle steps. In some embodiments of the present ~~invention~~disclosure, the compositions consists or consists essentially of a polymer melt, an amount of nanotubes and an amount of finely milled carbon fibers extrusion compounded together. Compositions in embodiments of the present ~~invention~~disclosure can be made in a single melt extrusion step without additional melt extrusion cycle steps. The compositions in

versions of the present ~~invention~~disclosure do not involve coagulation or casting and can be made free of solvent or process steps such as solvent removal, filtration, and drying.

Embodiments of the ~~invention~~present disclosure include compositions comprising a polymer melt, an amount of nanotubes, and an amount of finely milled carbon fibers extrusion compounded together, where it is contemplated that the amount of the nanotubes and the amount of the finely milled carbon fibers dispersed in the polymer melt form a composition that has a storage modulus G′ that is substantially invariant with further extrusion compounding of the composition. In some embodiments of the present ~~invention~~disclosure, it is contemplated the composition is substantially invariant to an increase in storage modulus and/or to a decrease in resistivity after one or more extrusion cycles. Compositions in embodiments of the present ~~invention~~disclosure can be made in a single melt extrusion step without additional melt extrusion cycle steps.

In some embodiments of the present ~~invention~~disclosure, the compositions consists or consists essentially of a polymer melt, an amount of nanotubes, and an amount of finely milled carbon fibers extrusion compounded together, where it is contemplated that the amount of the nanotubes and the amount of the finely milled carbon fibers dispersed in the polymer melt to form a composition that has a storage modulus G′ that can be substantially invariant with further extrusion compounding of the composition. In some embodiments of the present ~~invention~~disclosure, it is contemplated that the storage modulus does not increase with further extrusion compounding. Compositions in embodiments of the present ~~invention~~disclosure can be made in a single melt extrusion step without additional melt extrusion cycle steps.

The compositions in versions of the present ~~invention~~disclosure do not involve coagulation or casting and can be made free of solvent or process steps such as solvent removal, filtration, and drying.

In some embodiments, the polymer melt with dispersed nanotubes and finely milled carbon fibers comprises high temperature, high strength thermoplastic polymers. In some embodiments these polymers can be poly ether ether ketone (PEEK), polyimides (PI), or polyetherimide (PEI); in other embodiments the polymer comprises PEEK or PEI; in still other embodiments the polymer comprises PEEK; in some embodiments the polymer can be a blend of any of these polymers.

In some embodiments, the nanotubes are single walled carbon nanotubes (SWNTs), multiwalled carbon nanotubes (MWNTs), tungsten disulfide nanotubes, or

other commercially available nanotubes, ropes of these, or a combination of these where the amount of the nanotubes in the polymer can be less than about 5% by weight, in some embodiments about 4% or less by weight, in some embodiments about 3% or less by weight, and in still some other embodiments less than about 2% by weight. In some embodiments of the ~~invention~~present disclosure the amount of nanotubes in the polymer may range from about 0% to about 5% by weight, in some embodiments about 0.5% to about 4% by weight, in some embodiments about 1% to about 3% by weight, and in still other embodiments about 1.25% to about 2.5% by weight. The nanotubes are at least partially deagglomerated or dispersed in a network compared to their initial state such as before extrusion compounding.

In some embodiments, the finely milled carbon fibers are initially provided as carbon fibers having an aspect ratio greater than about 10, such as about 20, and then undergo a process to modify or otherwise change the aspect ratio until the aspect ratio is greater than 1 and less than about 5, in some embodiments between about 1.5 and about 5, and in still other embodiments between about 2 and about 4. In some embodiments, in order to modify the aspect ratio, the carbon fibers are milled, pulverized, ground, chopped, broken under shear force, or the like. It should be understood herein, that the term "finely milled carbon fibers" refers to the resulting carbon fibers having a reduced length and/or diameter such that the aspect ratio (length/diameter), irrespective of the process used to modify them, has an aspect ratio greater than 1 and less than about 5, in some embodiments between about 1.5 and about 5, and in still other embodiments between about 2 and about 4. In some embodiments, before undergoing the modification process, the carbon fibers are about 5 microns to about 20 microns in diameter and about 100 microns to about 25,000 microns in length with longer lengths contemplated, and the resulting finely milled carbon fibers have an aspect ratio greater than 1 and less than about 5, in some embodiments between about 1.5 and about 5, and in still other embodiments between about 2 and about 4. In some embodiments, before undergoing the modification process, the carbon fibers are about 6 microns to about 18 microns in diameter and about 110 microns to about 2,500 microns in length with longer lengths contemplated, and the resulting finely milled carbon fibers have an aspect ratio greater than 1 and less than about 5, in some embodiments between about 1.5 and about 5, and in still other embodiments between about 2 and about 4. In some embodiments, after undergoing the modification

process, the carbon fibers have an average diameter between about 5 microns and about 12 microns and an average length between about 10 microns and about 40 microns.

In some embodiments, the carbon fibers as initially provided are finely milled carbon fibers having an aspect ratio greater than 1 and less than about 5, in some embodiments between about 1.5 and about 5, and in still other embodiments between about 2 and about 4, wherein the initially provided carbon fibers do not need to undergo any processing to modify or change the length and/or diameter of the carbon fibers. It should be understood herein, that the term "finely milled carbon fibers" thus also refers to the carbon fibers having an initial or original length and diameter such that the aspect ratio (length/diameter) is greater than 1 and less than about 5, in some embodiments between about 1.5 and about 5, and in still other embodiments between about 2 and about 4. In some embodiments, the carbon fibers have an average diameter between about 5 microns and about 12 microns and an average length between about 10 microns and about 40 microns and an aspect ratio greater than 1 and less than about 5. In some embodiments, the carbon fibers have an average diameter between about 6 microns and about 10 microns and an average length between about 10 microns and about 30 microns and an aspect ratio greater than 1 and less than about 5.

In some embodiments, the finely milled carbon tubes in the polymer can be greater than about 20% by weight, in some embodiments greater than about 25% by weight, in some embodiments greater than about 30% by weight, in some embodiments greater than about 35% by weight, in some embodiments greater than about 40% by weight, in some embodiments greater than about 45% by weight, and in still some other embodiments less than about 50% by weight. In some embodiments of the present ~~invention~~disclosure, the amount of the finely milled carbon fibers in the polymer can be between about 20% to about 50% by weight, in some embodiments about 25% to about 45% by weight, in some embodiments about 30% to about 40% by weight, and in still other embodiments about 33% to about 38% by weight. In some embodiments, the finely milled carbon fibers are not agglomerated in their initial state, such as before extrusion compounding.

In some embodiments of the present ~~invention~~disclosure, the compositions or articles have an electrical resistivity of less than about 10^{13} ohm/sq; some compositions or articles have a resistivity of less than about 10^{11} ohm/sq; some compositions or articles have a resistivity of less than about 10^{9} ohm/sq; some compositions or articles have a resistivity of less than

about 10^7 ohm/sq; and other embodiments of compositions or articles are contemplated to have an electrical resistivity of less than about 10^5 ohm/sq. In some embodiments, the electrical resistivity of the compositions or articles may be tunable by varying the amount of the nanotubes and/or the amount of the finely dispersed carbon fibers in the polymer.

Another embodiment of the ~~invention~~present disclosure is a first composition comprising a polymer melt as a continuous phase and an amount of nanotubes and an amount of finely milled carbon fibers extrusion compounded together, such that the composition is contemplated to have a storage modulus G' that is substantially invariant, or does not increase, with further extrusion compounding of the composition. The composition is contemplated to have an axial force measured in a squeeze flow test of the composition that is greater than an axial force measured on a second extrusion compounded polymer composition comprising the same type of nanotubes and finely milled carbon fibers dispersed into an extruded melt of the polymer. In the second extrusion compounded polymer, at least the nanotubes and optionally the finely milled carbon fibers are added into an extruded melt of the polymer at a location equal to or greater than half the length of an extruder used to make the first composition. The contemplated high value of the storage modulus would indicate that the nanotubes and finely milled carbon fibers are dispersed, and an essentially constant value of the storage modulus would indicate that the polymer matrix is not degraded by the initial dispersion and or distribution of the nanotubes and finely milled carbon fibers into the polymer matrix.

Nanotubes and in particular SWNTs are difficult to disperse due to the high van der Waal interaction between the nanotubes. Efforts have been made to overcome these forces by dispersion of the nanotubes in a solvent and casting with a soluble polymer, co-polymerization of solvated nanotube with monomer, coagulation dispersion, surface functionalization, polymer wrapping and other methods. A process, and in some versions a continuous process as disclosed in U.S. Patent Application Publication 2010/0267883, which is incorporated in its entirety by reference, is used for dispersing the nanotubes and/or the finely milled carbon fibers in various polymer matrices to prepare compositions with a high dispersion or distribution of nanotubes and finely milled carbon fibers in the continuous polymer matrix. These compositions include a network or dispersion of the nanotubes and finely milled carbon fibers in the continuous polymer matrix such that the compositions have an increased storage modulus over the starting polymer and where the storage modulus of the composition depends on the amount of nanotubes and finely milled

carbon fibers dispersed in the matrix. Further, the storage modulus is contemplated to be essentially invariant, or does not increase, with continued extrusion cycles of the material. The compositions in embodiments of the present ~~invention~~disclosure can be molded to form articles and products with various molding processes. Further, compared to compositions with only nanotubes dispersed in the polymer, the compositions of the present ~~invention~~disclosure are less process sensitive such that varying the shear flow conditions of the molding process will not substantially affect the electrical resistance of the molded article.

In some embodiments of the present ~~invention~~disclosure, a dispersion of MWNTs and finely milled carbon fibers in a melt processable polymer without dispersion additives forms an electrically dissipative article when melt processed (extrusion, injection molding, compression mold, coining) under shear flow conditions. The shear conditions maintain a network or dispersion of MWNTs and finely milled carbon fibers in the polymer such that the average surface resistance of the resulting product is between about 10^6 ohms and about 10^8 ohms.

In some embodiments, the dispersion of nanotubes and finely milled carbon fibers is in PEEK, PEI, PI, combinations or blends of these, or co-polymers including any of these. The dispersion of the nanotubes and finely milled carbon fibers in the melted polymer can be formed into various articles with different degrees of interconnecting networks of the nanotubes and finely milled carbon fibers based on the shear flow conditions used to process the dry mixed melted mixture of nanotubes and finely milled carbon fibers with the polymer. Articles with different electrical dissipative characteristics can be made based on varying the amount of the nanotubes and/or the amount of finely milled carbon fibers dispersed in the polymer.

Embodiments of the present ~~invention~~disclosure provide composite materials having substantially uniform surface resistivity across a sample or article made from the composite materials. In some embodiments, the substantial uniform surface resistivity of any point on the surface of a sample of the composite of nanotubes and finely mille carbon fibers in the polymer is within a factor of 100 and in some embodiments within a factor of 10 from any other test point on the sample. This is advantageous in electrostatic discharge applications of the composites in articles such as chip trays, reticle and wafer carriers, wafer shippers, test sockets and the like.

In a first aspect, there is provided a composition comprising:

a thermoplastic polymer melt, an amount of carbon nanotubes, and an amount of carbon fibers extrusion compounded together in the composition, the amount of carbon nanotubes and the amount of carbon fibers dispersed in the polymer melt, wherein the carbon fibers have an aspect ratio greater than 1 and less than about 5.

In a second aspect, there is provided an article comprising a molded composition according to the first aspect.

In a third aspect, there is provided a composition comprising:

a thermoplastic polymer;

a network of nanotubes dispersed in the thermoplastic polymer; and

a network of carbon fibers having an aspect ratio greater than 1 and less than about 5 dispersed in the thermoplastic polymer;

wherein an amount of the nanotubes in the composition is greater than about 0.0 wt-% and less than about 5.0 wt-% and an amount of the carbon fibers is greater than about 20 wt-%.

In a fourth aspect, there is provided a fluid handling article comprising the composition according to the third aspect.

In a fifth aspect, there is provided a carrier comprising the composition according to the third aspect.

In a sixth aspect, there is provided a housing comprising the composition according to the third aspect.

In a seventh aspect, there is provided a molded article comprising the composition according to the third aspect.

In an eighth aspect, there is provided a method of forming a composite for the manufacturing of an article, the method comprising

providing an extruder;

feeding an amount of a thermoplastic polymer into the extruder;

feeding an amount of nanotubes into the extruder;

feeding an amount of carbon fibers having an aspect ratio greater than 1 and less than about 5 into the extruder; and

applying shear to blend the nanotubes, the carbon fibers, and the polymer,

wherein a thermoplastic polymer melt is formed having the amount of carbon nanotubes and the amount of carbon fibers dispersed in the polymer melt.

In a ninth aspect, there is provided a composite composition consisting essentially of a polymer, 1% to 3% by weight nanotubes, and 20% to 50% by weight carbon fibers having an aspect ratio greater than 1 and less than about 5 as described herein.

In a tenth aspect, there is provided an article formed from a composite composition consisting essentially of a polymer, 1% to 3% by weight nanotubes, and 20% to 50% by weight carbon fibers having an aspect ratio greater than 1 and less than about 5 as described herein.

In an eleventh aspect, there is provided a method of manufacturing an article having a composite composition consisting essentially of a polymer, 1% to 3% by weight nanotubes, and 20% to 50% by weight carbon fibers having an aspect ratio greater than 1 and less than about 5 as described herein.

Advantageously embodiments of the present compositions and methods for making them eliminates the cost, waste, and time used to remove solvent from cast dispersions of nanotubes and/or carbon fibers in dissolved polymers. These embodiments of the compositions can be formed free or essentially free of additives, solvents, without sidewall or end functionalization of the nanotubes or ropes, or any combination of these. These compositions can be formed free of nanotubes or ropes chemically bonded through a linker, either through their side or an end to the polymer. The dispersions can be made free of cross linking agent. Further, by eliminating excess solvent, compositions of the present ~~invention~~disclosure will have a low solvent outgassing and molecular contamination, which may be determined by Gas Chromatography Mass Spectroscopy (GCMS), Inductively Coupled Plasma Mass Spectroscopy (ICPMS), ICMS thermal gravimetric analysis and or TG-MS. This can be an important property for such materials where low levels of contamination, for example part per million or less, part per billion or less, or part per trillion or less of outgassing vapors can adsorb onto and be detrimental to materials such as bare and coated wafers, reticles, lens, or other substrates as well as processes used in semiconductor and pharmaceutical applications. Lower levels of outgassing or gas permeability in compositions of the present ~~invention~~disclosure are advantageous in reducing defects caused by for example but not limited to reticle haze, adsorption of gases such as hydrocarbons on substrates, or adsorption of contaminants which can alter the refractive index of optical components.

Advantageously embodiments of the present compositions and methods for making them also allow for high carbon loading levels while simultaneously providing reduced electrical resistivity at lower nanotube loading than traditionally available, which also reduces costs of the composition and resulting articles. Also, the high carbon loading levels can be achieved while reducing or eliminating the detrimental particle-particle interactions or particle-base polymer interactions that are often encountered with other small-sized carbon fillers (i.e., carbon black, carbon nanofibers, and carbon nanotubes), which results in lower maximum loading carbon levels. Further, embodiments of the present compositions and methods for making them also retain the relatively larger filler size of the carbon fibers such that the rheological properties of the base resin are substantially retained or more similar than compared to other smaller-sized carbon fillers. Still further, embodiments of the present compositions and methods for making them isotropic where anisotropy is substantially reduced or eliminated, including shrink

variability and warpage issues, of finished articles that is traditionally observed due to the non-random orientation of carbon fibers that is often dependent upon the carbon fibers orienting in a manner that depends upon the local flow field, which results in local variability in shrink and therefore contributes to warping of finished articles. Yet still further, embodiments of the present compositions and methods for making them also provide for polymer blends that flow easily and similar to the base polymer during processing.

Polymer compositions comprising dispersed or distributed nanotubes and finely milled carbon fibers in embodiments of the present ~~invention~~disclosure are contemplated to have a storage modulus and electrical resistivity that do not appreciably change with additional melt extrusion melting cycles. This is advantageous over other processes where repeated melt processing resulted in a change in the properties of a SWNT polymer composite. Embodiments of the present ~~invention~~disclosure can provide polymer composites with consistent electrical and mechanical properties that enable tighter process control over articles such but not limited to chip carriers, reticle domes, wafer carriers or other housing or fluid contacting articles. Electrically dissipative polymer articles can be made from embodiments of the present ~~invention~~disclosure without stretch aligning films of SWNTs in a polymer.

Compositions and articles made from them in embodiments of the present ~~invention~~disclosure may be used in a variety of engineering and structural plastics. These plastics may be used to make electrically dissipative materials for example but not limited to substrate carriers such as but not limited to wafer carriers, reticle pods, shippers, chip trays, test sockets, head trays (read and or write); fluid tubing, chemical containers, and the like. Compositions of the present ~~invention~~disclosure may be used to make fire retardant plastics and structural materials for use in applications that benefit from increased thermal conductance (heat exchangers, sensors, light weight automotive parts). The nanotubes and/or finely milled carbon fibers can be part of composite materials to elicit specific physical, chemical or mechanical properties in those materials such as but not limited to electrical and/or thermal conductivity, chemical inertness, mechanical toughness, and combinations of these. The carbon nanotubes themselves and materials and structures comprising carbon nanotubes such as SWNTs may also be useful as supports for catalysts used in industrial and chemical devices and processes such as fuel cells, hydrogenation, reforming and cracking.

Advantageously carbon nanotubes and carbon fibers are stronger than carbon particles, for applications where reduction or elimination of particle shedding is important, the use of finely milled carbon fibers and carbon nanotubes would provide less particles. SWNTs and carbon fibers are cleaner than carbon powders. Because lower nanotube loading can be utilized while maintaining a high carbon loading level with the finely milled carbon fibers in order to achieve the flame retardant or electrically dissipative properties and a continuous process can used to prepare the polymer/nanotube/finely milled carbon fiber dispersion in embodiments of the present ~~invention~~disclosure, composites and articles made from them in embodiments of the present ~~invention~~disclosure can be less expensive per pound compared to traditional multiwall nanotube polymer composites, traditional singlewall nanotube polymer composites, and traditional carbon fiber polymer composites.

BRIEF DESCRIPTION OF THE DRAWINGS

The present invention may be more completely understood in consideration of the following detailed description of various embodiments of the invention in connection with the accompanying drawings, in which:

FIGS. 1A-1H are SEM images of various types of carbon. FIGS. 1A and 1B are SEM images of SWNTs with the scale bar being 1 micron and 100 nm, respectively. Under normal circumstances as shown in the SEM images, SWNTs exist in bundles of different sizes and not usually as individuals. FIGS. 1C and 1D are SEM images of MWNTs with the scale bar being 1 micron and 100 nm, respectively. Under normal circumstances as shown in the SEM images, MWNTs exist as individuals of different sizes. FIGS. 1E and 1F are SEM images of carbon powder with the scale bar being 1 micron and 100 nm, respectively. Under normal circumstances as shown in the SEM images, carbon powder particles form large agglomerates. FIGS. 1G and 1H are SEM images of carbon fibers with an aspect ratio greater than 10 and prior to any processing with the scale bar being 1 micron and 10 microns, respectively. Under normal circumstances as shown in the SEM images, carbon fibers are more than about 100 times larger than the other types of carbon shown in FIGS. 1A-1F;

FIG. 2 is an optical microscope image of carbon fiber with the scale bar being 50 microns;

FIG. 3 is an optical microscope image of the finely milled carbon fiber according to an embodiment of the present invention with the scale bar being 50 microns;