

## NANOTUBE POLYMER COMPOSITE COMPOSITIONS AND METHODS OF MAKING

### CROSS REFERENCE TO RELATED APPLICATIONS

This application claims the benefit of to U.S. Provisional Patent Application No. 60/775,569, filed on February 22, 2006 which is incorporated herein by reference in its entirety.

### BACKGROUND

Nanocomposites are compositions in which a continuous phase has dispersed or distributed in it at least one additional constituent such as particles, rods, or tubes where the additional constituent has one or more dimensions, such as length, width or thickness, in the nanometer or molecular size range. In order to effectively improve the physical or mechanical properties of the composite it is important to disperse these additional constituents throughout the polymer in order to promote more interfaces and enhance the affinity between the additional constituents and polymer. If the added constituent is uniformly dispersed throughout the polymer, less material may be added to the nanocomposite composition without adversely affecting the physical properties of the nanocomposite.

Nanotubes are an example of nanometer or molecular size materials that may be used as an additional constituent in a nanocomposite. These nanotubes may be may be doped with conductive atoms; in some cases the dopants may be inside the tube. Examples of nanotubes are single-walled carbon nanotubes (SWNTs), multiwalled carbon nanotubes (MWNTs), and tungsten disulfide nanotubes. Individual SWNT and ropes of single-wall carbon nanotubes exhibit high strength, metallic conductivity, and high thermal conductivity. Nanotubes and ropes of nanotubes may be useful in applications where an electrical conductor is needed, for example as an additive in electrically conductive polymeric materials, paints or in coatings. Because of van der Waals attraction between nanotubes, SWNTs tend to exist as aggregates or ropes rather than tubes. During processing to form composites with other materials, SWNTs also tend to form aggregates which can inhibit the formation of electrically conductive nanotube networks or rheological networks in the composite. In polymers, single-wall carbon nanotubes have substantial potential for enhancing the polymers' strength, toughness, electrical conductivity, and thermal conductivity.

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However, achieving the full potential of the properties of single-wall carbon nanotubes in polymers has been hampered by the difficulty of dispersing the nanotubes.

Approaches to promote more affinity between nanotubes and the polymer at the interface and provide a uniform dispersion of the nanotubes within the polymer include the use of dispersing agents or modifying the surface chemistry of the nanotubes. Dispersing agents such as surfactants, or nanotube surfaces modified with carboxylic, amide groups, or surface bound polymers have been used to facilitate nanotube incorporation into a polymer. These treatments add impurities and additional steps to the process which increase the costs of the nanocomposite. Other approaches include dispersing the nanotubes in a solvent and mixing this dispersion with a polymer that is also dissolved in a solvent. The solution can be cast into films following removal of the solvent. The additional dispersal, casting, and solvent removal steps to enhance the affinity between the nanotubes and the polymer at the interface add time, generate waste, and increase the cost of such nanocomposite. Barraza et al, NANO Letters, vol. 2, pp. 797-802 state that the literature discloses that solution casting methods have limited applicability for producing highly conductive films because SWNT composites tend to saturate at 1-2% nanotube content as the excess nanotubes aggregate. This limits the compositions that can be formed by this method.

Haggenmuller observed progressive improvement in nanotube dispersion, with mixing cycles, 20 or more, (see pp 221, Chemical Physics letters vol. 330 (2000), pp 219- 225). Haggenmuller formed a solution of the polymer in a solvent and dispersed SWNTs into it with sonication, the mixtures were cast and the solvent evaporated. In a second method, cast films were broken and hot pressed- this melt mixing repeated up to 25 times. It was reported that the dispersion increased with each additional melt mixing cycle. Elkovitch et al, U.S. Patent Application Publication No.: 20050029498 discloses that highly pure SWNT cannot be separated from the ropes as easily as less pure SWNT and that the shear forces developed during the extrusion process are not as effective at breaking up the aggregates of SWNTs formed by highly pure SWNTs. SWNT polymer compositions disclosed by Elkovitch include levels of iron for example that can vary from a few tenths of a percent to greater than 10%. Further, Elkovitch et al (U.S. Pat. Publication No.: 20050029498) disclose that production related impurities facilitate the dispersion of ropes of carbon nanotubes within a matrix of an organic polymer and that compositions prepared with carbon nanotubes have a surface resistivity that varies with the amount of energy imparted over time to a composition of polymer and nanotubes during mixing. Elkovitch observed a decrease in resistivity for some impurity containing SWNT polymer samples during mixing and a decrease and then an increase in other impurity containing SWNT polymer

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samples during mixing. Smalley, U.S. Pat. No.: 6,936,233 discloses a method for the purification of as produced single wall carbon nanotubes to remove production related impurities.

Du et al (Macromolecules 2004, 37, pp 9048) describe the dispersion of SWNTs in a polymer formed by coagulation. In the coagulation method a polymer is dissolved in a solvent (Du et. al J. Polym. Sci., Part B: Polym. Phys. (2003), vol. 41, pp 3333-3338.) purified nanotubes are added to a solvent and sonicated for 24 hours to disperse the SWNTs in the solvent. A polymer was dissolved in the SWNT solvent mixture or solution or suspension. This suspension was dripped into a non-solvent in a blender, the precipitating polymer chains entrapped the SWNTs and prevented them from bundling again. The precipitate was filtered and dried in vacuum. Coagulation is a method that can be sensitive to the purification method used to treat the nanotubes and creates waste solvent. Fibers of the precipitate were subsequently melt spun.

Andrews dissolved pitch in a solvent, added and dispersed purified nanotubes to the hot pitch solution and sonicated the mixture. Vacuum distillation was used to remove solvent and prepare suspensions of SWNTs. This pitch suspension could be cooled to a solid and subsequently compression molded or extruded to form a thread. The compression molded article or thread was then oxidatively stabilized by heating and then subsequently carbonized at 1100 C. Petroleum pitch is a residue from heat treatment and distillation of petroleum fractions. It is a solid at room temperature, consists of a complex mixture of numerous predominantly aromatic and alkyl-substituted aromatic hydrocarbons, and exhibits a broad softening point range instead of a defined melting point. Pitch is soluble in some organic solvents which need to be removed and disposed of to form suspensions of the nanotubes. Pitch is an unacceptable material for many high purity applications and those requiring high wear resistance. Andrews et al report (Macromol. Mater. Eng. Vol. 287, pp. 395-403, (2002)) on the effect of shear mixing on MWNT lengths and reported that tube length decreases from about 20 micron to about 5 microns with increasing energy input into the mixing system.

Potschke et al (Polymer, vol. 43, pp. 3247-3255, (2002) prepared multiwalled nanotube composites compression molded in polycarbonate. At a concentration between 1 and 2% MWNTs, a reduction in resistivity from about  $10^{13}$  ohm/sq to about  $10^3$  ohm/sq was observed. At a frequency of about 0.1 rad/s the polycarbonate had a  $G'$  of about 2 (extrapolated) while 1% wt MWNT had a  $G'$  of about 20 (extrapolated) and a 5 wt % MWNT had a  $G'$  of about 20,000. Sennett et al (Mat. Res. Soc. Symp. Proc. Vol. 706, pp. 97-102, (2002) prepared MWNT and SWNT composites in polycarbonate by conical twin screw extrusion. The authors reported that MWNTs were degraded at processing times used to partially disperse SWNTs (ropes still present).

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They also reported that SWNTs appeared to be more difficult to disperse than MWNTs and that complete dispersion of SWNTs was not achieved at the processing times studied.

Kawagashi et al. (Macromol. Rapid Commun. (2002), 23, 761-765) prepared melt blended MWNTs in polypropylene by first forming a polypropylene melt and then adding MWNTs. These composite materials were evaluated for their fire retardancy.

Smalley et al. U.S. Patent Application Publication No. 2002/0046872 discloses polymer-coated and polymer wrapped single-wall nanotubes (SWNTs), small ropes of polymer-coated and polymer-wrapped SWNTs, and materials comprising them. According to the disclosure nanotubes are solubilized or suspended, optionally with a surfactant, in a liquid by associating them robustly with linear polymers compatible with the liquid used, for example, polyvinyl pyrrolidone and polystyrene sulfonate. The wrapped nanotubes are removed from solution, the polymer wrapping remains, and the 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.

A composition with nanotubes dispersed or distributed in a continuous matrix would provide composite materials with improved electrical and thermal conductivity and or flame retardancy. A continuous process for making such materials would provide cost reduction and an increase in manufacturing throughput for such materials.

## SUMMARY

Embodiments of the invention include compositions comprising a polymer melt and an amount of nanotubes extrusion compounded together, the amount of the nanotubes 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 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 can be made in a single melt extrusion step without additional melt extrusion cycle steps. In some embodiments of the invention the compositions consists or consists essentially of a polymer melt and an amount of nanotubes extrusion compounded together, the amount of the nanotubes

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dispersed in the polymer melt form a composition that has a storage modulus  $G'$  that can be substantially invariant with further extrusion compounding of the composition; in some embodiments the storage modulus does not increase with further extrusion compounding. Compositions in embodiments of the present invention can be made in a single melt extrusion step without additional melt extrusion cycle steps. The compositions in versions of the present invention do not involve coagulation or casting and can be made free of solvent or process steps such as solvent removal, filtration, and drying.

The dispersion or distribution of the nanotubes in the polymer provides a composition whose structure and properties can be modified with the molding shear flow rate of the composition. For example, in some embodiments of the composition, the higher the shear flow rate of the molding process, the higher the electrical resistivity of an article molded from the composition.

In some embodiments of the invention, molding the composition comprising the nanotubes dispersed in the polymer provides an article that is electrically dissipative. The conductivity, surface resistivity, or volume resistivity of the article can be modified by extensional flow. In other embodiments of the invention, molding the composition comprising the nanotubes dispersed in the polymer provides an article that is flame retardant and or can maintain its shape and prevent dripping of polymer. In still other embodiments of the invention, molding the composition comprising the nanotubes dispersed in the polymer provides an article that is electrically dissipative and flame retardant.

In some embodiments the polymer melt with dispersed nanotubes 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.

Embodiments of the invention can comprise a molded article of the composition that is electrically dissipative. Some embodiments of the invention can comprise a molded article of the composition that is electrically insulating and wherein the molded article can become electrically dissipative with heating or thermal conditioning of the sample.

In some embodiments the nanotubes are single walled carbon nanotubes, ropes of these, or a combination of these where the amount of single walled carbon nanotubes in the polymer can be less than about 10% by weight, in some embodiments about 7% or less by weight, in some embodiments about 5% or less by weight, in some embodiments less than about 2% by weight, in

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some embodiments less than about 1% by weight, and in still other embodiments less than about 0.5% by weight. In some embodiments of the invention the amount of single walled carbon nanotubes in the polymer can range from 0.5% to 7% by weight. The single walled carbon nanotubes are at least partially deagglomerated or dispersed in a network compared to their initial state such as before extrusion compounding.

Some embodiments of the invention include compositions or articles with an electrical 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 have an electrical resistivity of less than about  $10^4$  ohm/sq.

Another embodiment of the invention is a first composition comprising a polymer melt as a continuous phase and an amount of nanotubes extrusion compounded together, such that the composition has a storage modulus  $G'$  that is substantially invariant, or does not increase, with further extrusion compounding of the composition. The composition has 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 dispersed into an extruded melt of the polymer. In the second extrusion compounded polymer, the nanotubes 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 high value of the storage modulus indicates that the nanotubes are dispersed, the essentially constant value of the storage modulus indicates that the polymer matrix is not degraded by the initial dispersion and or distribution of the nanotubes into the polymer matrix.

One embodiment of the invention is a composition comprising a polymer melt and an amount of single walled carbon nanotubes extrusion compounded together in the composition, the amount of the nanotubes dispersed in the polymer melt forms an electrically dissipative solid in a low shear flow molding process, the electrical resistivity of an article molded from the composition increases with increasing molding shear flow rate.

In some embodiments of the invention the composite comprising a polymer melt and an amount of nanotubes, preferably single walled carbon nanotubes, extrusion compounded together has a storage modulus at low frequency of the composition that is at least about 90 times the storage modulus at low frequency of the polymer in a liquid, non-solid, or melted state of the composition when the amount of nanotubes dispersed in the composition is 0.5% wt.

One embodiment of the invention is method comprising extrusion compounding an amount of nanotubes, preferably single walled carbon nanotubes, with a polymer to form a composition.

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The extrusion compounding disperses the nanotubes in the polymer forming a composition that has a storage modulus  $G'$  that is substantially invariant, or does not increase, with further extrusion compounding of the composition.

Nanotubes and in particular SWNTs are difficult to disperse due to the high van der Waal interaction between the tubes. 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. Surprisingly, the inventors have discovered a process, and in some versions a continuous process, for dispersing nanotubes in various polymer matrices to prepare compositions with a high dispersion or distribution of nanotubes in the continuous polymer matrix. These compositions include a network or dispersion of the nanotubes 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 dispersed in the matrix. Further it has been found that the storage modulus is essentially invariant, or does not increase, with continued extrusion cycles of the material. The compositions in embodiments of the invention can be molded to form articles and the properties of the articles can be varied with the shear flow conditions of the molding process. For example, in some embodiments with electrically conductive singled walled carbon nanotubes dispersed in a continuous polymer matrix, the electrical resistance of the molded article increases with increasing shear flow of the composition.

One embodiment of the invention is a dispersion of SWNTs in a melt processable polymer without dispersion additives that can be used to form electrically dissipative articles when melt processed (extrusion, injection molding, compression mold, coining) under low shear flow conditions. The low shear conditions maintain a network or dispersion of SWNTs in the polymer such that the conductance is above the electrical percolation threshold (resistivity less than about  $10^{12}$  ohm/sq). In some embodiments, the dispersion of SWNTs in the polymer forms articles above the electrical percolation threshold at a weight percent of SWNTs in the polymer of 7% or less, in some versions less than 5 % by weight, in some embodiments less than 2 % by weight, in some embodiments less than 1% by weight, and in still other embodiments less than 0.5% by weight. In some embodiments the surface resistivity for a low flow shear processed composition or article of the dispersed SWNT in the polymer is less than or equal to about  $10^9$  ohm/sq, in some versions less than about  $10^6$  ohm/sq, in some versions less than about  $10^5$  ohm/sq, and in some embodiments less or equal to about  $10^4$  ohm/sq for samples comprising SWNTs in the polymer of

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7 % by weight or less, in some embodiments less than 5 % by weight, in some embodiments less than 1% by weight, and in still other embodiments less than 0.5% by weight.

In some embodiments, the dispersion of SWNTs is in PEEK, PEI, PI, combinations or blends of these, or co-polymers including any of these. The dispersion can be processed to form articles above the electrical percolation threshold at a weight percent of SWNTs in the polymer of less than 10 % by weight, in some embodiments less than 2 % by weight, in some embodiments less than 1% by weight, and in still other embodiments less than 0.5% by weight. The dispersion of the SWNTs in the melted polymer forms a first composition that has a storage modulus  $G'$  that is substantially invariant, or one that does not increase, with further extrusion compounding of the composition. The first composition is electrically dissipative when molded in a low shear molding process, and where the composition has an axial force measured in a squeeze flow test above the glass transition or melting point of the composition that is greater than an axial force measured on a second extrusion compounded polymer composition comprising the same type of SWNTs dispersed into an extruded melt of the polymer. In the second extrusion compounded polymer, the nanotubes 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 dispersion of the SNWTs in the melted polymer can be formed into various articles with different degrees of interconnecting networks of the SWNTs based on the shear flow conditions used to process the dry mixed melted mixture of SWNTs and polymer. Articles with different electrical dissipative characteristics can be made based on the shear flow conditions used to process the melted dispersion.

Embodiments of the present invention 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 single walled nanotube and 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.

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 nanotube 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

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dispersions can be made free of cross linking agent. Further, by eliminating excess solvent, compositions of the present invention will have a low solvent outgassing, 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 microgram per gram or less, 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 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.

Polymer compositions comprising dispersed or distributed SWNTs in embodiments of the present invention 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 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 without stretch aligning films of SWNTs in a polymer. Advantageously, compositions in embodiments of the invention can utilize the shear flow rate or thermal treatment to prepare articles with a range of resistivities in a continuous process. For example, processing compositions of SWNT comprising material dispersed in an extrusion melted polymer under high shear flow in an injection molding process can be used to form intricate moldings which are an initially insulating article that can then be subsequently heat relaxation treated to form electrically dissipative articles. The time and temperature of the relaxation treatment may be used to control the electrical resistivity of the relaxation treated sample. Advantageously, embodiments of the present invention can be formed into stock pieces and articles having a thickness much greater than cast films while providing the network structure of the nanotubes in the polymer as characterized by the storage modulus value and slope of the storage modulus with frequency as described herein.

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Compositions and articles made from them in embodiments of the present invention 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. Compositions of the present invention may be used to make fire retardant plastics and structural materials for use in applications that benefit from increase thermal conductance (heat exchangers, sensors, light weight automotive parts). The nanotubes 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 SWNT are stronger than carbon particles, for applications where reduction or elimination of particle shedding is important, the use of SWNT would provide less particles. SWNTs are cleaner than carbon powders. Because lower nanotube loading can be utilized to achieve the flame retardant or electrically dissipative properties and a continuous process can used to prepare the polymer/SWNT dispersion in embodiments of the invention, composites and articles made from them in embodiments of the present invention can be less expensive per pound compared to multiwall nanotube polymer composites.

#### BRIEF DESCRIPTION OF THE DRAWINGS

The file of this patent contains at least one figure executed in color. Copies of this patent with color figures will be provided by the Office upon request and payment of the necessary fee.

FIG. 1A and FIG. 1B are SEMs of electrically dissipative molded samples of single walled nanotubes and ropes of SWNTs dispersed in a continuous polymer phase of PEEK in embodiments of the invention. SWNTs or ropes of them up to several hundred nanometers are visible. In the scanning electron micrograph (SEM) of FIG. 1A, SWNTs 100 are shown dispersed in the PEEK polymer matrix, the SEM is of a dispersion of SWNTs in PEEK from an electrically dissipative sample of an injection molded composite; SWNTs of from about 0.1 to about 1 micron are visible. FIG. 1B is an SEM of an electrically dissipative sample  $10^4$  to  $10^{10}$  ohm/sq illustrating SWNTs 110 dispersed in the polymer to form an embodiment of the invention.

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FIG. 2 is a Table illustrating the thermal properties of as extruded and pelletized resin. Samples in embodiments of the invention include varying amounts of SWNT nanotubes dispersed in the polymer.

FIG. 3 illustrates how processing conditions can be used to affect the resistivity of a solid form of the extrusion dispersed SWNTs in the thermoplastic. The thicker extruded end portions 320 of the sample in the photograph are formed under low shear flow and are electrically dissipative, the center portion 310 (hand drawn) which is thinner was formed under higher shear flow conditions and is less electrically conductive. The hand drawn portion 310 illustrates how the uptake rate can be used to modify the electrical properties of extruded composites.

FIG. 4 Schematically illustrates an embodiment of the invention where an insulating article 410 (can be solid, tape, tube, or other form of a composite material in an embodiment of the invention) formed by high shear flow processing of the dispersion of conductive nanotubes, for example SWNTs, in the polymer can subsequently be thermally treated in a step 420 to form an electrically dissipative or conductive article 430. The thermal or heat treatment can be a low shear flow method such as but not limited to a hot press treatment, compression molding, or other similar method.

FIG. 5 is a graph showing the storage modulus of nanocomposites at various SWNT tube loadings performed on a melt or non-solid form of the composition, for example at 380 °C. Compared with the unfilled polymer PEEK, the nanotubes dispersed in the PEEK polymer in the melt show an increase in the storage modulus  $G'$  at low frequency 0.1 (rad/s) of about 90x or more for SWNTs of 0.5% by weight; of about 2000x or more for SWNTs of 1% by weight; of about 9000x or more for SWNTs of 2% by weight; of about 90,000x or more for SWNTs of 5% by weight. Results show an about 80-100x or more increase in  $G'$  with nanotube loading of SWNTs of 0.5% by weight to SWNTs of 2% by weight. FIG. 5 illustrates that the storage modulus at low frequency of the composition when the amount of single walled nanotubes dispersed in the composition is 0.5% wt is at least about 90 times a storage modulus at low frequency of the polymer. As shown in FIG. 5, at a loading of 0.5% SWNTs the storage modulus is about 20 [Pa] or more at a frequency of 0.1 rad/sec; at a loading of 1% SWNTs the storage modulus is about 80 [Pa] or more at a frequency of 0.1 rad/sec; at a loading of 2% SWNTs the storage modulus is about 2000 [Pa] or more at a frequency of 0.1 rad/sec; at a loading of 5% SWNTs the storage modulus is about 20,000 [Pa] or more at a frequency of 0.1 rad/sec; as shown in FIG. 17b, at a loading of 7% SWNTs the storage modulus is about 30,000 [Pa] or more at a frequency of 0.1 rad/sec; at a frequency of 0.1 rad/sec the storage modulus for PEEK is about 0.2 [Pa].

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FIG. 6 is a graph of the squeeze flow (normal force) properties of nanotubes (SWNTs 5 wt %) and polymer (PEEK) that were contemporaneously combined in a twin screw extruder (NT4). The graph compares the squeeze flow or normal force with a second extrusion compounded polymer composition (NT1) where the (SWNTs 5 wt %) and polymer were not contemporaneously combined. The NT1 composition comprises nanotubes dispersed into an extruded melt of the polymer, however the nanotubes were added into to the extruded melt of the polymer at a location equal to or greater than half the length of the extruder used to make the composition NT4; for example see FIG. 11B.

FIG. 7 illustrates the frequency response of the storage modulus for extrusion compounded compositions comprising 2 wt % SWNTs in PEEK that were formed into articles by injection molding; curve (A) with a higher  $G'$  illustrates the storage modulus of an injection molded sample with thermal relaxation treatment; curve (B) with a lower  $G'$  illustrates the storage modulus of an injection molded sample without thermal relaxation treatment. Relaxation treatment can modify the storage modulus by a factor of three or more.

FIG. 8 is an SEM of a solidified sample of SWNTs dispersed in a polymer, the nanotubes were added into to the extruded melt of the polymer by extrusion compounding at a location equal to or greater than half the length of an extruder as schematically shown in the apparatus of FIG. 11(B).

FIG. 9 is an SEM of a solidified sample of SWNTs dispersed in a polymer, the nanotubes and the polymer extrusion compounded in an essentially contemporaneous manner as for example but not limited to the process schematically illustrated by the apparatus in FIGs. 10(A-B); the finer morphology and absence of individual SWNT nanotube or ropes indicates the improved dispersion of the nanotubes in this polymer sample compared to the sample of FIG 8.

FIG. 10(A) schematically illustrates a non-limiting apparatus for a processes for dispersion mixing polymer 1010A and nanotubes 1030A; the extrusion can occur in an essentially contemporaneous manner which can be flood feeding of dry nanotubes 1030A through hopper 1026A and polymer 1010A through hopper 1014A; twin screw extruders 1018A and 1022A extrusion combine the materials to form a material 1034A in the extruder 1050A. The extruded composition 1038A can be removed from die 1060A. The extruder 1050A can be heated above the melting point of the polymer using one or more heating zones or heating gradient (not shown).

FIG. 10(B) schematically illustrate non-limiting apparatus for a processes for dispersion mixing polymer 1010B and nanotubes 1030B; the extrusion compounding can optionally use a pre-blended mix of nanotubes and polymer with a single hopper 1014B feed to twin screw

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extruders 1018B and 1022B to extrusion combine the materials to form material 1034B in the extruder 1050B. The extruded composition 1038B can be removed from die 1060B. The extruder 1050B can be heated above the melting point of the polymer using one or more heating zones or heating gradient (not shown).

FIG. 11 (A) illustrates cycled extrusion compounding (1110A) of an extrusion dispersed mixture of nanotubes and polymer (not shown), the material 1134A formed in the extruder 1150A can be removed (1138A) from die 1160A and analyzed for storage modulus or resistivity and then fed back into the extruder as 1110A; FIG. 11 (B) illustrates forming a melt of the polymer 1110B from hopper 1114B and extrusion screws 1118B and 1122B, nanotubes 1130B can be added into to the extruded melt of the polymer 1134B for extrusion compounding at a location of hopper 1126B equal to or greater than half the length ( $D/2$ ) of an extruder 1150B of length ( $D$ ) to form material 1138B which can be removed at die 1160B as material 1142B.

FIG. 12 illustrates articles prepared from a shear flow sensitive composition of nanotubes dispersed in a polymer by extrusion compounding in embodiments of the invention. The articles are prepared under different shear flow conditions (compression molded), extruded and hand drawn. Dissipative extruded portions 1210 can have a surface resistivity of  $10^5$  ohms/sq; nondissipative portions can include hand drawn portion 1220 with surface resistivity  $10^{13}$  ohms/sq; compression molded sample 1230 that is electrically dissipative with surface resistivity of about  $10^4$  ohms/sq; or compression molded sample 1240 that is electrically dissipative with surface resistivity of about  $10^5$  ohms/sq.

FIG. 13 illustrates articles prepared from a shear flow sensitive composition of nanotubes dispersed in a polymer by extrusion compounding, the articles are prepared under different shear flow conditions (compression molded, extruded, and injection molded). The compression molded sample 1310 can have electrically dissipative behavior (ESD behavior) with a surface resistivity of about  $10^5$  ohms/sq; an extruded sample 1320 with a surface resistivity of about  $10^{13}$  ohms/sq; an injection molded sample 1330 with a surface resistivity of about  $10^{13}$  ohms/sq.

FIG. 14 illustrates that composite materials of the present invention have a storage modulus proportional to frequency according to  $G' = K\omega^z$  where  $K$  is a proportionality constant,  $\omega$  is the frequency between 0.01 and 1 rad/sec, where  $z$  is less than or equal to 1.7; for the polymer alone  $z$  is greater than 1.7. Curve fits were made between 0.1 rad/sec and 10 rad/sec on data taken from FIG. 5 for PEEK, 0.5 wt % SWNTs in PEEK, and 2 wt% SWNTs in PEEK. For PEEK between 0.1 and 10 rad/sec a curve fit of the data to the function  $G' = K\omega^z$  gives  $K = 11.8$  and  $z = 1.79$  with  $R^2 = 0.99$ ; for 0.5 wt% SWNTs dispersed in PEEK, a curve fit of the data between 0.1

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and 1 rad/sec to the function  $G' = K\omega^z$  gives  $K = 66.7$  and  $z = 0.46$  with  $R^2 = 0.97$ ; for 2 wt% SWNTs in PEEK a curve fit between 0.1 and 1 rad/sec of the data to the function  $G' = K\omega^z$  gives  $K = 28630$  and  $z = 0.16$  with  $R^2 = 0.99$ .

FIG. 15a details rheological measurements, the shear dependent viscosity and storage modulus, as a function of frequency [rad/s] for polyether imide (PEI)/SWNT composites dispersed with 0.5 wt %, 1 wt%, and 2 wt% SWNTs in embodiments of the invention. The storage modulus curves for the (PEI)/SWNT composites for the 0.5 wt%, 1 wt%, and 2 wt% SWNTs are given by the curves 1510, 1520, and 1530 respectively; the viscosity curves for the (PEI)/SWNT composites for the 0.5 wt %, 1 wt%, and 2 wt% SWNTs are given by the curves 1540, 1550, and 1560 respectively. Between 0.1 and 1 [rad/s] a curve fit of the data for 1510 to the function  $G' = K\omega^z$  gives  $K = 1219.6$  and  $z = 0.29$ ; a curve fit of the data for 1520 to the function  $G' = K\omega^z$  gives  $K = 1666.1$  and  $z = 0.25$ ; a curve fit of the data for 1530 to the function  $G' = K\omega^z$  gives  $K = 16396$  and  $z = 0.19$ . FIG. 15b is a plot of force gap tests for (PEI)/SWNT composites for 0.5 wt % (1580), 1 wt% (1582), 2 wt% (1584), and 5 wt% (1586) SWNTs. The results show that for 0.5wt% (1580) and 1 wt% (1582) that the normal force is greater than 20-30 g for a gap of 1.2 mm or less, for 2 wt% (1584) the normal force is greater than about 100 g for a gap of 1.2mm or less, and for 5 wt% SWNTs (1586) the normal force is greater than about 1000 g for a gap of 1.2 mm or less. The gap for each of the samples forms the superimposed points in the trace 1572-1578.

FIG. 16a shows the normal force [g] as a function of time in a force gap or squeeze flow measurement on a non-solid sample of 2.5wt% SWNT in a polymer blend of 20 wt% PEI and 77.5 wt% PEEK; the normal force 1610 and gap 1620 are plotted as a function of time. In this embodiment the normal force is greater than about 150 g at a gap of less than 1.2 mm and preferably about 1 mm. FIG. 16b is a plot of storage modulus 1630 and viscosity 1640 as a function of Freq [rad/s] on a non solid sample of 2.5wt% SWNT in a polymer blend of 20 wt% PEI and 77.5 wt% PEEK, a curve fit of this data between 0.1 and 1 [rad/s] to a function  $G' = K\omega^z$  gives  $K = 22257$  and  $z = 0.26$  with  $R^2 = 0.99$ . The storage modulus at 0.1[rad/sec] is greater than 10,000 [dynes/cm<sup>2</sup>].

FIG. 17 a-b illustrates gap for test results and storage modulus for 7% SWNTs in PEEK. In FIG. 17a the normal force 1710 and gap 1720 are plotted as a function of time. In this embodiment the normal force is greater than about 1500 g at a gap of less than 1.2 mm. FIG. 17b is a plot of storage modulus 1730 and viscosity 1740 as a function of Freq [rad/s] on a non-solid sample of 7wt% SWNT in PEEK, a curve fit of this data between 0.1 and 1 [rad/sec] to a function

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$G' = K\omega^z$  gives  $K = 42323$  and  $z = 0.12$  with  $R^2 = 0.99$ ;  $G'$  at low frequency 0.1 rad/s is about 33,000[Pa].

FIG. 18 shows plots of strain and permittivity as a function of time for 0.5wt% SWNTs in PEEK with pre-shear of 1/sec for various compositions. The graphs illustrate that the permittivity in embodiments of the invention can be increased with pre-shear, for example 1810 and 1820 and further increased at higher temperatures 1820 (380 °C) compared to 1810 at (360 °C). Scans 1830 (360 °C, no pre-shear), 1840 (380 °C, no pre-shear), and air 1850 are also shown.

FIG. 19a shows a plot of strain and permittivity as a function of time at 380°C (non-solid) for 0.5wt% SWNTs in PEEK. Strain steps 1910 were 20, 40, 60, 80, 100, 150, 200%, and 1% and the measured permittivity 1920 as a function of time at 360°C and the measured permittivity 1930 as a function of time at 380 °C are plotted. Embodiments of the invention show a decrease in permittivity with increasing strain and increase in permittivity with increasing temperature. FIG. 19b shows DES measurements of the permittivity as a function of time for single point strain data for 20% (s1), 60% (s2), 100% (s3), and 200% (s4). The permittivity for 2% SWNTs (a-d), 1% SWNTs (e-h), and 0.5% SWNTs (j-m) are given; air permittivity (i) is also shown. The permittivity of the sample decreases when the strain is increased at the point, for example (s2), and then recovers when the strain is released (one rotation of rheometer plates). With sufficient time, the recovery is substantially the starting permittivity value, especially for higher amounts of SWNTs such as 2wt% or greater.

FIG. 20a is an overlay plot of storage modulus  $G'$  at 380 °C for SWNT 2wt% in PEEK with different shear histories, passes or cycles, through the extruder with 1.8 min residence time in the extruder. The shear history included 1 cycle (2010), 5 cycles (2020), 10 cycles (2030), 15 cycles (2040), and 20 cycles (2050). FIG. 20b shows the SWNT contribution to the plateau modulus as a function of the number of shear histories or residence time from FIG. 20a. The relative modulus  $G'r$  was determined from data at 0.1 rad/s by the equation  $G'r = [(composition\ G'/PEEK\ G') - 1]$ .

FIG. 21 shows the change in storage modulus for PEEK with different shear histories, passes or cycles through the extruder with 1.8 min residence time in the extruder for 1 cycle (2110), 5 cycles (2120), 10 cycles (2130), 15 cycles (2140), and 20 cycles (2150).

FIG. 22 (a) illustrates resistance measurement test points (1-9) on discs 2204 and a rectangular plaque 2208. FIG. 22(b) illustrates resistance of disc 2220 (circles) and rectangular plaques 2210 (triangles) molded from 5 wt% SWNTs in PEEK. The error bars represent  $\pm 1$  standard deviation based on 3 measurements. FIG. 22(c) illustrates resistance test results for 5

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wt% SWNTs in PEEK 2230. Small error bars represent  $\pm 3$  standard deviations of 15 measurements (5 samples x 3 measurements/sample using PRS-801). Large error bars (wide) represent measurement reproducibility ( $\pm 3$  standard deviations) based on replicate measurements on one sample (9 positions x 10 measurements/position using PRS-801). The results show that variation in resistance can be a factor of 100 or less and in some embodiments the variation in resistance can be a factor of 10 or less within a sample or for multiple samples.

### DESCRIPTION

Before the present compositions and methods are described, it is to be understood that this invention is not limited to the particular molecules, compositions, methodologies or protocols described, as these may vary. It is also to be understood that the terminology used in the description is for the purpose of describing the particular versions or embodiments only, and is not intended to limit the scope of the present invention which will be limited only by the appended claims.

It must also be noted that as used herein and in the appended claims, the singular forms "a", "an", and "the" include plural reference unless the context clearly dictates otherwise. Thus, for example, reference to a "nanotube" is a reference to one or more nanotubes and equivalents thereof known to those skilled in the art, and so forth. Unless defined otherwise, all technical and scientific terms used herein have the same meanings as commonly understood by one of ordinary skill in the art. Although any methods and materials similar or equivalent to those described herein can be used in the practice or testing of embodiments of the present invention, the preferred methods, devices, and materials are now described. All publications mentioned herein are incorporated by reference. Nothing herein is to be construed as an admission that the invention is not entitled to antedate such disclosure by virtue of prior invention. "Optional" or "optionally" means that the subsequently described event or circumstance may or may not occur, and that the description includes instances where the event occurs and instances where it does not. All numeric values are herein assumed to be modified by the term "about," whether or not explicitly indicated. The term "about" generally refers to a range of numbers that one of skill in the art would consider equivalent to the recited value (i.e., having the same function or result). In some embodiments the term "about" refers to  $\pm 10\%$  of the stated value, in other embodiments the term "about" refers to  $\pm 2\%$  of the stated value. In other embodiments of the invention essentially or substantially invariant resistivity and or storage modulus  $G'$  includes changes of less than  $\pm 40\%$ , in some embodiments less than  $\pm 25\%$ , in some embodiments less than  $\pm 10\%$ , and in still other embodiments less than  $\pm 5\%$  of  $G'$  and or resistivity as measured on a sample of the composite of

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polymer and SWNTs. In some embodiments the sample may have been extruded more than once by the process used to make the composition, and in some embodiments extruded less than five times by the process used to make the composition. In some embodiments compositions of the present invention are substantially invariant to an increase in the storage modulus and or to a decrease in resistivity of the composition with further extrusion cycles. The  $G'$  is substantially invariant to an increase in the storage modulus and or decrease in resistivity because no improvement in the dispersion with more extrusion process cycles or time is observed. Without wishing to be bound by theory, further extrusion processing of the composite reduces  $G'$  because the dispersion may deteriorate because for example the SWNT's are undergoing aggregation. Embodiments of the composite material of polymer and SWNT have reached the maxima for the storage modulus and with further induction of stress, the dispersion declines. As would be known to one skilled in the art, the shear modulus can also be referred to as the storage modulus.

While compositions and methods are described in terms of "comprising" various components or steps (interpreted as meaning "including, but not limited to"), the compositions and methods can also "consist essentially of" or "consist of" the various components and steps, such terminology should be interpreted as defining essentially closed-member groups.

Embodiments of the invention include nanotubes, for example some versions include SWNTs or nanotubes comprising SWNTs, distributed in a melt of thermoplastic that forms an electrically conductive or viscoelastic material from the melt on solidification. In the case of SWNT, the ropes or tubes form a network or matrix in the continuous phase of the polymer; this contrasts with individual polymer coated SWNTs prepared by a suspending individual SWNTs in a solvent and associating them with a linear polymer.

One embodiment of the invention is a composition comprising a thermoplastic polymer, the polymer is not a foam or an elastomer, and the thermoplastic polymer includes a network of single walled carbon nanotubes dispersed in the thermoplastic polymer. A melt or non-solid heated sample of said composition has a storage modulus proportional to frequency according to the relationship  $G' = K\omega^z$  where  $K$  is a proportionality constant,  $\omega$  is the frequency between 0.01 and 1 rad/sec, and  $z$  is less than or equal to 1. The amount of single walled carbon nanotube in the composition is greater than 0.5 wt% and the storage modulus at a fixed frequency can be substantially invariant with further extrusion compounding of the composition or can be substantially invariant to a further increase in storage modulus with further extrusion compounding. In some embodiments the amount of single walled carbon nanotubes is between 0.5 and 10 wt%. In some embodiments the composition does not comprise added carbon powders.

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In some embodiments the metal extractables of the composition is less than 200 microgram/gram of iron as determined by acid digestion of the composition. In some embodiments the single walled carbon nanotubes have an aspect ratio of 100 or more. In some embodiments the L/D can be 1000 or more with diameters of 1-3.5 nm or 4 nm (roping) and lengths of 1000 nm or more. The composition is made by a melt mixing, for example an extrusion process and advantageously is free of solvents used to disperse nanotubes or to dissolve the polymer. Under reduce pressure conditions the composition outgasses less than 0.01 micrograms per gram or 100 parts per billion (v/v) of a solvent vapor where the solvent is one that can dissolve the polymer or that was used in forming the nanotube dispersion. In some embodiments the composite outgasses less than 0.01 microgram/gram of sample based on the test method FGTM-1350. The outgassing of composites of the present invention and those made by solvent casting or other similar methods can also be determined by this method or the methods disclosed by Zabka et al in U.S. Pat. Application Publication No.: 20030066780, filed October 4, 2001 and published April 10, 2003, the contents of which are incorporated herein by reference in their entirety.

In some embodiments of the compositions of the invention, aqueous leachable anions from the sample can be about 510 ng/g or less and aqueous leachable cations from the sample can be about 59 ng/g or less and acid leachable metals from the sample can be about 510 ng/g or less and outgassing organics from the sample can be less than about 0.010 micrograms/g.

Advantageously the single walled carbon nanotubes in the composition are not polymer wrapped single walled carbon nanotubes. This reduces the costs of such compositions and allows the metallic, semi-metallic, semi conductive, or any combination of such single walled carbon nanotubes to form an electrically percolating network in the composition. In some embodiments the composition has a surface resistivity less than  $10^{13}$  ohm/sq in other embodiments less than  $10^{10}$  ohm/sq and in still other embodiments less than  $10^5$  ohm/sq. In some embodiments of the composition, prepared under varying shear flow conditions, the volume resistivity or surface resistivity can be decreased with heat treatment.

In some embodiments the network is characterized by a storage modulus that is at least 800 times greater than the storage modulus of the polymer at a frequency of 1 rad/sec or less when the amount of single walled carbon nanotubes is between 2 and 7 wt %. In other embodiments the network or nanotube dispersion is characterized by a storage modulus that is at least 150 times greater, in some cases 2000 times greater, than the storage modulus of the polymer at a frequency of 0.1 rad/sec when the amount of single walled carbon nanotubes is greater than 1 wt%.

The composition can be formed into various articles for fluid handling, a carrier for various substrates like wafers, reticle masks, and finished goods like computer chips and disk drive and other similar types of read heads, a housing or body or components for various devices such as membrane filters, valves, or flow controllers.

Embodiments of the present invention can include materials and compositions that comprise a dispersion of SWNTs in a thermoplastic melt as determined by the slope of the storage modulus of the composition at low frequency (below about 1 rad/sec). In some embodiments the SWNTs can be oriented, in other embodiments the SWNTs form a network in the thermoplastic. In some embodiments the network of carbon nanotubes can be described as an isotropic orientation of the carbon nanotubes or SWNTs in the polymer matrix. Isotropic embodiments of the present invention differ from compositions with relatively more aligned carbon nanotubes because the isotropic compositions for the same weight percent of carbon nanotubes in the polymer have a higher shear modulus  $G'$  and generally a smaller value of  $z$  in the expression  $G' = K\omega^z$ . On solidification, these materials become viscoelastic materials and may also be or become electrically dissipative materials with or without further treatment like molding under various shear flow conditions, heat treatment, drawing, or any combination of these. In some embodiments the electrical and rheological properties of solid compositions of SWNTs dispersed in the thermoplastic polymer can be modified by heating.

The SWNTs and polymer are blended together to yield a composite melt composition that can be molded into articles or drawn into films whose electrical resistivity depends on the molding shear flow conditions or drawing conditions. Such compositions can be made when the polymer and nanotubes are compounded together at a distance less than about  $D/2$  of the extruder screw length where  $D$  is the length of the extruder screw used to make a dispersion of the SNWTs in the melted polymer that has a storage modulus  $G'$  that is substantially invariant, or a storage modulus that does not increase, with further extrusion compounding of the composition and where the dispersion of SWNTs and polymer forms an electrically dissipative article when molded in a low shear molding process. Such compositions can also be made when the polymer and nanotubes are compounded together as illustrated in FIG. 10A or FIG. 10B. For example, the extruder can have length of about 95-100 cm and an  $L/D$  in the range of about 32-42.

Embodiments of compositions in the present invention can be formed into stock pieces and articles having a thickness much greater than cast films while retaining the network structure of the nanotubes in the polymer as characterized by the storage modulus value and storage modulus slope with frequency. While there are no limitations on the thickness of compositions or portions

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of structures of articles including compositions in embodiments of the invention, in some embodiments the composition or article can have a smallest dimension or a thickness of greater than about 1 mm, in some embodiments greater than about 10 mm, and in other embodiments greater than 10 cm or more. Thicker compositions and articles can be used for structural applications such as partitions, laboratory blast shields, laboratory hood windows, tubing, filter housing manifolds, valve body blocks, wafer and reticle carrier supports. These thick materials are more difficult to form directly by film casting or which may require additional processing steps such as hot pressing cast film pieces together to form thicker pieces.

Embodiments of the present invention are advantageous over carbon powder or other filler based polymer composites of MWNTs which can break down with high shear in the polymer. SWNT composites in compositions of the present invention minimize this problem which is advantageous for injection and extrusion molding because the process can be run at lower temperatures and higher shear for increased product output, recycling, and energy savings.

SWNT polymer composites in embodiments of the invention exhibit unique rheological and electrical properties; their behavior is a function of SWNT orientation in the continuous polymer matrix. The inventors have discovered that when some embodiments of extrusion compounded composites of SWNTs and a thermoplastic of the present invention are formed into articles by precision injection molding, that these molded articles exhibit insulative behavior and then upon heating become electrical conductive. Without wishing to be bound by theory, this behavior may be a result of a relaxation phenomenon in the SWNT composite. In the high shear flow molded article, the well-dispersed SWNT in the polymer matrix tend to align such that they are not in contact with each other and are farther than the minimum required distance, about 5 nm, to achieve electrical percolation through electron hopping. Upon heating, it may become possible for the SWNT to touch each other or locate at a distance less than or equal to about 5 nm from each other to create an electrically percolating material.

The inventors have also surprisingly discovered for single wall carbon nanotubes dispersed or distributed in the polymer in embodiments of the invention, that the orientation of the SWNTs may be modified by the molding process and shear flow conditions to change the conductivity of the resulting molded material. Compression molded samples show conductivity while injection molded samples out of the same resin are more resistive or insulating (resin includes dispersed or distributed nanotubes in the polymer where the resin is characterized by a low slope shear modulus at low frequency, below about 1 rad/sec and in some cases about 0.1 rad/sec, of  $\omega^2$  for  $z$  less than about 1.7). The conductivity, surface resistivity, or volume resistivity of electrically

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dissipative molded articles can be turned off or modified by extensional flow (pulling the resin) as illustrated in FIG. 12 where the extruded portion of the material has a surface resistivity of about  $10^5$  ohm/sq and the drawn portion of the material has a surface resistivity of about  $10^{13}$  ohm/sq. The surface resistivity in this embodiment was modified by about  $10^8$  ohm/sq; in other embodiments the surface resistivity can be modified by a factor of  $10^n$ , where  $n$  can be a rational or irrational number of about 10 or less. When the sample is re-heated to its melt temperature, the conductivity returns. This property can be used in a process like coining for injection molding to maintain the conductivity of samples while obtaining high process throughput. Coining is process where the material is shot into an open mold and then the mold is closed onto the material to reduce shear flow (the process can be used to make lenses) and achieve conductivity in injection molded parts.

The measure of the mixing of the nanotube or ropes of nanotubes may be characterized by the degree of distribution, dispersion, and uniformity in the degree of mixing throughout the continuous phase material. The amount of mixing or dispersion of the nanotubes, for example SWNT ropes and nanotubes can depend upon the level of shear applied to the polymer and nanotubes. The degree of dispersion can be determined visually, for example the SEM of FIG 9 illustrates better nanotube dispersion than in FIG. 8. The degree of dispersion can also be determined by the low frequency slope of  $G'$  vs frequency ( $\omega$ ) which approaches zero as the dispersion becomes better. Additionally, a higher the value of  $G'$  at low frequency, especially compared to the  $G'$  of the continuous polymer phase alone, indicates a better dispersion of nanotubes in the continuous phase. Dispersed nanotubes in polymers in embodiments of the invention refers to compositions where compared with the unfilled polymer, the nanotubes dispersed in the polymer in the melt or non-solid form show an increase in the storage modulus  $G'$  at low frequency above the melting point or glass transition temperature such as 0.1 (rad/s) of about 90x or more for SWNTs of 0.5% by weight; of about 400x or more for SWNTs of 1% by weight; of about 9,000x or more for SWNTs of 2% by weight; of about 90,000x or more for SWNTs of 5% by weight as illustrated in FIG. 5, of up to about 150,000x or more for SWNTs of 7% by weight as illustrated in FIG. 17b. These compositions also have a low slope shear modulus at low frequency, below about 1 rad/sec, of  $\omega^z$  for  $z$  less than about 2, in some embodiments less than about 1.7, in other embodiments less than about 1, and in still other embodiments the low frequency slope is less than about 0.5. The higher  $G'$  and the lower the slope indicating a better dispersion of the nanotubes in the polymer. In some embodiments the storage modulus curve of the polymer alone is characteristic of a bimodal distribution of molecular weights. Compositions

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of SWNTs dispersed in such a polymer utilizing the methods and materials of the invention can result in an increase in  $G'$  for the composition that is greater than the polymer alone. In some embodiments with 0.5% SWNTs or more dispersed into such a polymer, a  $G'$  value at 0.1 rad/sec can be about 50 times greater, or more, than the  $G'$  for the polymer alone. In other embodiments, a dispersion of 1% SWNTs or more into such a polymer can result in a  $G'$  value at 0.1 rad/sec that can be about 70 times greater, or more, than  $G'$  for the polymer alone. In still other embodiments, a dispersion of 2% SWNTs or more into the polymer can result in a  $G'$  value at 0.1 rad/sec that can be about 800 times greater, or more, than  $G'$  for the polymer alone. These composites can be characterized as having  $z$  of about 0.35 or less for the storage modulus fit to function  $G' = K\omega^z$ . In some embodiments the polymer can be a blend of polymers with different molecular weight distributions. Compared to the storage modulus for either of the polymers alone at 0.1 rad/s, SWNTs dispersed in this polymer blend utilizing the method and materials herein can result in an increase in  $G'$  compared to the polymers alone or their blend. In some embodiments a composite with 2.5% or more SWNTs dispersed in a blend of polymers, the  $G'$  increase can range from about 1,000 or more to about 50,000 or more compared to the  $G'$  for the neat polymers alone or the  $G'$  for their blend.

In various embodiments the storage modulus can be measured on a sample of the material in the rheometer at the processing or the average processing temperature used to make the composite material in the extruder. In some embodiments the temperature results in a melt flow rate that can range from about 3 to about 60 (g/min) and in still other embodiments the temperature can result in a melt flow of from about 16-20 (g/min).

Embodiments of the invention include or comprise SWNTs dispersed and or distributed in a polymer in an amount and for a time that reaches the rheological percolation threshold. This threshold can be characterized by the storage modulus having a low slope shear modulus at low frequency, below about 1 rad/sec, of  $\omega^z$  for  $z$  less than about 2. At this amount of dispersed SWNTs, the motion of the polymer chains are impeded by the dispersed nanotubes. Materials at this threshold of SWNTs could be molded into articles useful for fire retardant materials. While there is no particular limitation on the time the SWNTs and polymer can be in the extruder together to form the disperse network of SWNTs in the thermoplastic in embodiments of the invention, in some embodiments the residence time in the extruder can be about 2 minutes, in other embodiments the residence time of the nanotubes in the extruder can be less than about 2 minutes, for example 1.8 minutes. In other embodiments the residence time can range from about 1 to about 3 minutes, in some embodiments less than about 6 minutes (FIG. 1B), and in still other

embodiments less than about 10 minutes. Shorter processing times improves throughput and reduces the chance for damage to the polymer or nanotubes.

Electrical percolation threshold for a sample is sufficient proximity of conductive fibers, conductive particles, ropes of two or more conductive nanotubes, individual conductive nanotubes, or any combination of these to form an electrically conductive pathway through the continuous polymer matrix of the composition. For example, for SWNTs the percolation threshold may be where a sufficient number of ropes of nanotubes or nanotubes are within a distance for charge carriers in the sample to move in response to an applied electric field. In some embodiment the distance between some portion of adjacent tubes or ropes can be about 5 nm or less.

Electrically dissipative or conductive refers to molded materials from compositions in embodiments of the present invention with surface resistivities of less than about  $10^{14}$  ohm/sq, in some embodiment less than  $10^{10}$  ohm/sq; in some embodiments the resistivity can be less than about  $10^7$  ohm/sq; in some embodiments the resistivity can be less than about  $10^6$  ohm/sq; in some embodiments the resistivity can be less than about  $10^5$  ohm/sq; in some embodiments the surface resistivity can be less than about  $10^4$  ohm/sq.

Nanotubes are an example of nanometer or molecular size materials that may be used as a constituent in the compositions in embodiments of the present invention. These nanotubes may be doped with conductive atoms; in some cases the dopants may be inside the tube or the dopants may be supplied with functionalized surfaces. Examples of nanotubes are single-walled carbon nanotubes (SWNTs), multiwalled carbon nanotubes (MWNTs), or tungsten disulfide nanotubes. In some embodiments the composition comprises nanotubes that are SWNTs or ropes of them dispersed in the polymer which are not functionalized or oxidized. In some embodiments the composition consists essentially of nanotubes that are SWNTs or ropes of them dispersed in the polymer. In some embodiments the composition consists of nanotubes that are SWNTs or ropes of them dispersed in the polymer. In some embodiments the SWNTs may comprise other nanotubes, for example MWNTs, or other conductive particles such as carbon. In some compositions, the nanotubes can be used without further purification. In other embodiments the nanotubes may be purified to remove deleterious metals and catalyst that could be extracted in some applications of molded articles of the invention. In some embodiments the composition of SWNTs and polymer is absent or free of catalyst, support or any combination of these from the SWNTs that would lead to extractables by acid digestion of the sample of greater than about 2000  $\mu\text{g}$  (metal/gram of sample) of metals listed in Table 2; in some embodiments less than 200  $\mu\text{g}$  Fe/g

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of sample. The amount of the metals can be determined by acid digestion of the composite composition having the nanotube dispersed in the continuous polymer phase as described in embodiments of the present invention. In some embodiments the SWNTs are not oxidized and are absent surface functional groups.

Nanotubes in embodiments of the present invention can refer to both individual tubes, aggregates of tubes also referred to as ropes, or a combination of these. The extrusion compounding of the nanotubes can disperse aggregates of nanotubes into smaller aggregates, into individual tubes, or it can form a mixture of individual tubes and ropes. The aggregated nanotubes and individual tubes can be distributed or dispersed in the continuous phase of the polymer matrix.

A dispersion or distribution of nanotubes, ropes, or aggregates of these in a polymer matrix in embodiments of the present invention form a composition whose structure can be characterized by the storage modulus of the composition. A dispersion of the nanotubes in the polymer gives an approximate power law relationship of the storage modulus  $G'$  with frequency of the approximate form  $\omega^z$  where  $z$  is less than about 2, preferably less than about 1.7, and more preferably less than 0.5. A dispersion or distribution of nanotubes or aggregates of nanotubes gives a value of  $G'$  that is greater than the value of  $G'$  for the neat continuous phase; a higher value of  $G'$  indicating a better dispersion of the nanotubes where other characteristics of the composition such as but not limited to aspect ratio, nanotube length, and polymer molecular weight are about the same. A dispersion or distribution of nanotubes in a polymer matrix in embodiments of the invention forms a composition that has a storage modulus  $G'$  that is substantially invariant with further extrusion compounding of the composition, in some embodiments the storage modulus  $G'$  does not increase, rather it decreases, with further extrusion compounding.

A greater dispersion provides a denser network of the nanotubes in the continuous phase which imparts improved flame retardancy to the composition or molded article, the article exhibits less dripping of polymer and has a greater normal load when exposed to a flame, and also provides reduced electrical resistivity at lower nanotube loading which reduces costs.

In some embodiments the nanotubes are neat without added chemical functionalization on the ends and or sides of the tubes. In other embodiments, the nanotubes may be chemically functionalized to aid in their extrusion compounding, dispersion, or distribution in the polymer matrix. The nanotubes may in some embodiments comprise a mixture of functionalized and unfunctionalized nanotubes. In some embodiments the nanotubes do not include or are free from functional groups, groups formed by nanotube oxidation, and in particular organic functional

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groups, linked or bonded to carbon atoms of the nanotubes. This reduces the costs of the nanotubes and compositions made from them in embodiments of the invention.

Nanotubes, as ropes, tubes, or a combination of these can be used in the compositions in various embodiments of the invention. The term nanotube can refer to any of these, ropes, tubes, or their combination unless a specific form is mentioned. For example, SWNTs refer to ropes, tubes, or a combination of these while "SWNT tubes" refers only to separated nanotubes. Nanotubes as ropes or individual tube can be characterized by their aspect ratio (length/diameter). As shown in FIG 1A and B the SWNTs or ropes of them can have lengths of several tens of nanometers to several hundred nanometers. Nanotubes with length of several microns may be used. The diameters can be about 1 nanometer for SWNT tubes and larger for ropes of tubes. High aspect ratio materials can be used; in some embodiments the aspect greater than about 25, in other embodiments greater than about 100, and in still other embodiments greater than about 250. A higher aspect ratio is advantageous because less nanotube material needs to be used. Carbon nanotube or nanotubes according to the present invention can separately be single-wall carbon nanotubes (SWNTs), multi-wall carbon nanotubes (MWNTs), double-wall carbon nanotubes, buckytubes, carbon fibrils, and combinations thereof. Such carbon nanotubes can be made by any known technique, and they can be optionally purified, preferably without oxidation. Such carbon nanotubes can be metallic, semiconducting, semimetallic, and combinations thereof.

In some embodiments the amount of nanotubes extrusion dispersed in the polymer can be an amount that forms a network of the nanotubes in the continuous phase. The network can be a rheological network, for example as evidenced by a SWNT polymer composite material having a low frequency weakly dependent  $G'$  with a slope with  $z$  less than 1, a SWNT polymer composite material that has an improved axial force as illustrated in FIG. 6, an electrically dissipative material, or any combination of these.

Because of their small size, carbon nanotubes will tend to agglomerate when dispersed in a polymeric resin. To achieve good rheological and or electrical properties in a composite, uniform dispersion of the nanotubes or ropes of them within the polymer matrix is beneficial. The better the uniformity of the dispersion of nanotubes in the continuous phase, the lower the slope of the storage modulus. Further, the better the uniformity, the lower the mass or weight percent of nanotubes that can be used to achieve a given storage modulus or electrical conductivity. Lower loadings can be used to reduce material costs.

Agglomeration can occur in single walled carbon nanotubes because entanglement of the tubes can occur during nanotube growth. Embodiments of compositions and methods for making

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them are able to overcome such aggregation with these and other forms of nanotubes or single walled carbon nanotubes and achieve compositions above the rheological and or electrical percolation threshold at low nanotube loadings, about 7 wt% or less. Optionally deagglomeration of the nanotubes can be performed by sonication, coating, chemical treatment, or other known methods prior to extrusion compounding the components.

Some embodiments of the invention use nanotubes that consist, consist essentially of, or comprise SWNTs. SWNTs and methods for making them for various embodiment of the present invention include those disclosed in U.S. Patent Application Publication U.S. 2002/0046872 and U.S. Pat. No. 6,936,233, the teachings of each of these being incorporated herein by reference in their entirety. Suitable raw material nanotubes are known. The term "nanotube" has its conventional meaning as described; see R. Saito, G. Dresselhaus, M. S. Dresselhaus, "Physical Properties of Carbon Nanotubes," Imperial College Press, London U.K. 1998, or A. Zettl "Non-Carbon Nanotubes" *Advanced Materials*, 8, p. 443 (1996) the teachings of these incorporated herein by reference in their entirety. Nanotubes useful in this invention can include, e.g., straight and bent multi-wall nanotubes, straight and bent single wall nanotubes, and various compositions of these nanotube forms and common by-products contained in nanotube preparations. Nanotubes of different aspect ratios, i.e. length-to-diameter ratios, will also be useful in this invention, as well as nanotubes of various chemical compositions, including but not limited to dopants. Commercially available SWNTs can be obtained from CNI Houston, TX; embodiments of the invention can disperse various grades of nanotubes such as Bucky ESD34 or XD. Carbon nanotubes are also commercially available from CarboLex, Inc. (Lexington, Ky.) in various forms and purities, Hyperion Cambridge, MA, and from Dynamic Enterprises Limited (Berkshire, England) in various forms and purities.

Nanotubes in some embodiments may comprise tungsten disulfide, boron nitride, SiC, and other materials capable of forming nanotubes. Methods of making nanotubes of different compositions are known. (See "Large Scale Purification of Single Wall Carbon Nanotubes: Process, Product and Characterization," A. G. Rinzler, et. al., *Applied Physics A*, 67, p. 29 (1998); "Surface Diffusion Growth and Stability Mechanism of BN Nanotubes produced by Laser Beam Heating Under Superhigh Pressures," O. A. Louchev, *Applied Physics Letters*, 71, p. 3522 (1997); "Boron Nitride Nanotube Growth Defects and Their Annealing-Out Under Electron Irradiation," D. Goldberg, et. al, *Chemical Physics Letters*, 279, p. 191, (1997); Preparation of beta-SiC Nanorods with and Without Amorphous SiO<sub>2</sub> Wrapping Layers, G. W. Meng et. al., *Journal of*

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Materials Research, 13, p. 2533 (1998); U.S. Pat. Nos. 5,560,898, 5,695,734, 5,753,088, 5,773,834.

An improved method of producing single-wall nanotubes is described in U.S. Pat. No. 6,183,714, entitled "Method of Making Ropes of Single-Wall Carbon Nanotubes," incorporated herein by reference in its entirety. This method uses, inter alia, laser vaporization of a graphite substrate doped with transition metal atoms, preferably nickel, cobalt, or a mixture thereof, to produce single-wall carbon nanotubes in yields of at least 50% of the condensed carbon. The single-wall nanotubes produced by this method are much more pure than those produced by the arc-discharge method. Because of the absence of impurities in the product, the aggregation of the nanotubes is not inhibited by the presence of impurities and the nanotubes produced tend to be found in clusters, termed "ropes," of 10 to 5000 individual single-wall carbon nanotubes in parallel alignment, held together by van der Waals forces in a closely packed triangular lattice.

PCT/US/98/04513 entitled "Carbon Fibers Formed From Single-Wall Carbon Nanotubes" and which is incorporated by reference, in its entirety, discloses, inter alia, methods for cutting and separating nanotube ropes and manipulating them chemically by derivatization to form devices and articles of manufacture comprising nanotubes. Other methods of chemical derivatization of the side-walls of the carbon nanotubes are disclosed in PCT/US99/21366 entitled "Chemical Derivatization of Single Wall Carbon Nanotubes to Facilitate Solvation Thereof, and Use of Derivatized Nanotubes," the teachings of which are incorporated herein by reference their entirety.

Optionally the nanotubes can be purified. For contaminant sensitive fluid or substrate contacting applications in semiconductor or pharmaceutical applications, impurities such as but not limited to extractable metals or particulate can be removed from the nanotubes prior to extrusion compounding with a polymer. Examples of contaminants that can be removed include but are not limited to nanotube catalyst support, pyrolytic carbon, catalyst and others. Metals analysis of nanotube polymer composites in embodiments of the invention can be determined by acid digestion of the sample, for example by heating with nitric acid with subsequent analysis by ICP-MS. One embodiment is a composite with less than about 2,000 µg/g of total metals as exemplified by metals Table 2; in other embodiments the composite includes less than about 1,000 µg/g of total metals as exemplified by the metals Table 2; in other embodiments less than about 600 µg/g of total metals as exemplified by the metals in Table 2. Nanotubes and SWNTs in particular can be contaminated with metals and magnetic particles from the catalyst. Embodiments of the invention can include compositions of SWNT nanotubes that are extrusion compounded and dispersed in a polymer where the purity total metals of the composition is less

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than about 1,500  $\mu\text{g/g}$  of total metals as exemplified by metals in Table 2. Graphitic flakes, polyhedral particles amorphous carbon, or other undesirable particle forming material can be removed from the nanotubes especially where shear history becomes measurable.

In embodiments of the invention, the polymer used to form the continuous phase is a polymer that disperses nanotube with extrusion compounding. Preferably the polymer disperses or distributes SWNTs in the polymer with extrusion compounding. In some embodiments the polymer and dispersed nanotubes in the extrusion compounded composition forms an electrically dissipative article in a molding process, and preferably in a low shear flow molding process (extruding, compression molding, coining, etc).

Polymers that can be used as the continuous phase in extrusion compounded nanotube compositions of the present invention can include high temperature, high strength polymer. These polymers have high resistance to heat and chemicals. The polymer is preferably resistant to the chemical solvent N-methyl pyrrolidone, acetone, hexanone, and other aggressive polar solvents especially at room temperature, in some cases below about 50°C, or in some cases below about 100 °C. A high temperature, high strength polymer is one that has a glass transition temperature and/or melting point higher than about 150°C. Further, the high strength, high temperature polymer preferably has a stiffness of at least 2 GPa.

Examples of high temperature, high strength polymers for extrusion compounded compositions of the present invention are independently polyphenylene oxide, ionomer resin, nylon 6 resin, nylon 6,6 resin, aromatic polyamide resin, polycarbonate, polyacetal, polyphenylene sulfide (PPS), trimethylpentene resin (TMPPR), polyetheretherketone (PEEK), polyetherketone (PEK), polysulfone (PSF), tetrafluoroethylene/perfluoroalkoxyethylene copolymer (PFA), polyethersulfone (PES; also referred to as polyarylsulfone (PASF)), high-temperature amorphous resin (HTA), polyetherimide (PEI), liquid crystal polymer (LCP), polyvinylidene fluoride (PVDF), ethylene/tetrafluoroethylene copolymer (ETFE), tetrafluoroethylene/hexafluoropropylene copolymer (FEP), tetrafluoroethylene/hexafluoropropylene/perfluoroalkoxyethylene terpolymer (EPE), and the like. Mixtures, blends, and copolymers that include the polymers described herein may also be used. In some embodiments the high strength, high temperature polymers are PEK, PEEK, PES, PEI, PSF, PASF, PFA, FEP, HTA, LCP and the like. Examples of high temperature, high strength polymers are also given in, for example, U.S. Pat. Nos. 5,240,753; 4,757,126; 4,816,556; 5,767,198, and patent applications EP 1 178 082 and PCT/US99/24295 (WO 00/34381) which are hereby incorporated herein by reference. In some embodiments the blend may include about 60 to about 80% of PEEK. In some embodiments the blend may include PEI

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and PEEK, and in still further embodiments a blend of about 10 to about 20% PEI and about 70 to about 80% PEEK with the nanotubes making up the balance.

In some versions the polymers used to extrusion disperse the nanotubes are high temperature, high strength thermoplastic polymers; the polymers are not thermoset or solution cast polymers. Examples of high temperature, high strength thermoplastic polymers that can be used in versions of the invention are independently polyetheretherketone (PEEK®), Polyetherketoneketone (PEKK), polyetherketone (PEK), poly ether imide (PEI), polyimide (PI), perfluoro polymers like Teflon® FEP (copolymer of tetrafluoroethylene with. Hexafluoropropylene), PFA (a copolymer of tetrafluoroethylene and perfluoro-propylvinylether), MFA (a copolymer of TFE and perfluoro-methylvinylether), Polybutylene terephthalate (PBT), or co-polymers including these. In some embodiments the polymer can be a flame or fire retardant material including but not limited to polycarbonate, polyesters, polyphosphonates, polyphenylene sulfide (PPS), polysulfone (PSF), polyethersulfone (PES), UPE, or blends of these or copolymers including these. In other versions, polymers may include rigid rod polymers. Examples of useful rigid rod polymer can include but are not limited to PARMAX and blends of PARMAX with PEEK, PI, or PEI.

In some embodiments the polymer forming the continuous phase comprises PEEK, PI, or PEI. In other embodiments the continuous phase comprises PEEK or PEI. In still other embodiments the polymer comprises PEEK.

In some embodiments the polymer that is extrusion compounded with the nanotubes is not solution castable or soluble in a solvent. For example nanotubes are not suspended in a solvent with dissolved polymer and cast into a film that is subsequently extruded. In some embodiments the nanotubes are dispersed in a thermoplastic, for example a master batch with a high concentration of nanotubes in the polymer, where the polymer is characterized by not being solution castable. As used herein, "foam" refers to an article or composition that includes a polymer matrix in which the density of the article is less than the density of the polymer matrix alone. Embodiments of the invention include those whose density is about that of the polymer, the composition being free of a cellular structure that would reduce its density to that of a foam.

Embodiments of compositions and articles of the present invention can be characterized in that below the melting or glass transition temperature, the compositions and articles resist elongation or deformation under an externally applied force and that above a threshold force the elongation or deformation of the composition remains after the external force is released or

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removed. Embodiments of the invention include those materials which are not elastically compressible or elastically extensible.

In some embodiments, the molecular weight of the polymer in which the SWNTs are dispersed can be greater than about 50,000 g/mol. In some embodiments, the molecular weight of the polymer can range from 15,000 g/mol to 60,000 g/mol. In some embodiments the molecular weight or molecular weight range of the polymer can be chosen to provide a smaller low-frequency slope of  $G'$  vs  $\omega$  and a larger  $G'$  value at low frequency such as 0.1 to 1 rad/sec. This choice of molecular weight or range of molecular weights can be modified based on the polymer and aspect ratio of the nanotubes like SWNTs and can be used to constrain the motion of the polymer chains by the nanotube network in the polymer. The molecular weight distribution of the polymer in which the SWNTs are dispersed can vary. In some embodiments the storage modulus of the polymer can be characterized by a single distribution of molecular weights, in other embodiments the storage modulus can be characterized by a bimodal distribution, and still other embodiments a multimodal distribution of molecular weights. Blends of polymers having different compositions and different distributions of molecular weights can also be used.

In some embodiments, the molecular weight of the polymer can be chosen such that the radius of gyration of the polymer chain is less than the diameter of the nanotubes aggregates extrusion compounded into the polymer. Such a choice of polymer can give rise to low rheological percolation at low loading. For example, and without wishing to be bound by theory, the radius of gyration of the PEEK polymer chains in the extrusion compounded SWNT/PEEK composition in an embodiment of the present invention is about 18.7 nm. SWNTs aggregates that have a diameter less than about 18.7 nm may impede the movement of the PEEK molecular chains and provide the improved properties of these compositions.

The nanotubes, and preferably SWNTs dispersed in the polymer have a structure, distribution, orientation or form a network with the polymer. In some embodiments the SWNTs in the polymer have an isotropic orientation. The network resists deformation under an axial force, preferably a substantially constant axial force as illustrated in a squeeze flow test by the non-limiting composition (NT4) of FIG. 6. The networks of nanotubes, and preferably SWNTs, can solidify from the melt to an electrically dissipative solid in a low shear flow molding process.

The polymer melt with dispersed nanotubes in embodiments of the invention is free of solvent, especially when compared to solvent casting, coagulation, interfacial polymerization, monomer-SWNT compolymerization methods. Embodiments of the present invention do not outgas solvent vapor as would be expected from polymers dissolved solvents that have been used

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to cast disperse nanotube or SWNTs into a polymer. Outgassing may be determined by thermal gravimetric analysis, pressure decay, and or TG-MS under atmospheric pressure, reduced atmospheric pressure, or other predetermined application condition. Outgassing can be an important property of articles comprising or consisting of the polymer and dispersed nanotubes especially in applications where low levels of contamination are beneficial. Examples of articles prepared by molding nanotubes dispersed in polymers in embodiments of the present invention can include substrate carriers (reticle or wafer), tubing, valves, and other fluid contacting structures. Deleterious outgassing may include water vapor or organic solvents at levels of micrograms per gram or less, parts per million or less, parts per billion or less, or parts per trillion. Other vapors can include those detrimental to materials and processes used in semiconductor and pharmaceutical applications.

A method of making compositions and dispersions of nanotubes in polymers in embodiments of the invention include the steps or acts of dispersing nanotubes in a continuous polymer matrix. In some embodiments the method can comprise the steps or acts of extrusion compounding an amount of nanotubes with a polymer to form a composition. The extrusion compounding in embodiments of the present invention distributes the nanotubes in the polymer such that the composition has a storage modulus  $G'$  that is substantially invariant with further extrusion compounding of the composition. The method forms compositions with a dispersion of the nanotubes in the polymer that gives a network structure of the nanotubes with the polymer characterized by an approximate power law relationship of the storage modulus  $G'$  with frequency of the approximate form  $\omega^z$  where  $z$  is less than about 2, preferably less than about 1.7, and more preferably less than 0.5. A dispersion or distribution of nanotubes or aggregates of nanotubes gives a composite composition whose value of  $G'$  is greater than the value of  $G'$  for the neat continuous polymer phase; the nanotubes dispersed in the polymer in the composite composition can be characterized by an increase in the storage modulus  $G'$  at low frequency such as 0.1 (rad/s) of about 90x or more for SWNTs of 0.5% by weight; of about 400x or more for SWNTs of 1% by weight; of about 9,000x or more for SWNTs of 2% by weight; of about 90,000x or more for SWNTs of 5% by weight and about 150,000x or more for SWNTs of 7% by weight or more in the polymer. The method can further include the acts or steps of molding the composite composition into an article, and may optionally further include the acts or steps of heat treating the molded article to provide a predetermined or desired surface resistivity or volume resistivity. In other embodiments the method can comprise the steps or acts of extrusion compounding an amount of a composition comprising single walled carbon nanotubes with a polymer to form a composition.

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The extrusion compounding distributes the single walled carbon nanotubes in the polymer and the composition has a storage modulus  $G'$  that is substantially invariant, or decreases, with further extrusion compounding of the composition.

Another embodiment of the invention is a method of producing an article or stock pieces or pellets of a composite composition in embodiments of the invention. The method may comprise transferring the composite composition of polymer and network of nanotubes in embodiments of the present invention as a powder, pellets, or in stock billets to a location for selling molded articles of the composition. At this location for selling the composite composition, the composition may be molded into articles at the location for selling molded articles of the composition. The method may further comprise the act of heat treating molded articles. The method may further include the act or steps of assembling final products comprising articles molded from the composite composition of the present invention with other articles comprising materials that are not composite compositions of the present invention. In some embodiments the composite, articles made from the composite, stock pieces, pellets, or the like can have a surface resistivity uniformity within a factor of 100 and in some within a factor of 10 for two or more measurement test points on the sample, an article comprising the composition, a stock piece or the like. Molded articles may include but are not limited to portions or all of reticle carriers as illustrated in U.S. Pat. Nos. 6,513,654 and 6,216,873; disk shippers as illustrated in U.S. Pat. Nos. 4,557,382 and 5,253,755; chip trays as illustrated in U.S. Pat. No. 6,857,524; wafer carriers as illustrated in U.S. Pat. No. 6,848,578; fluid housings as illustrated in U.S. Pat. No. 6,533,933, wherein each of these references is incorporated herein by reference in its entirety into the present application. Articles comprising the composite composition in embodiments of the present invention may be used in processes for making semiconductor wafers; they may be used in delivering, transporting, or purifying liquid reagents for semiconductor or pharmaceutical manufacturing; the compositions of the present invention and articles made from them can be used in process tools that include but are limited to flow meters and flow controllers, valves, tubing, heat exchange devices, filter housings, and fluid fittings for connecting to tubing.

The dispersion of nanotubes, preferably SWNTs in a melted polymer made by extruding dry polymer and nanotubes together, in some embodiments occurs essentially simultaneously. For electrically conductive nanotubes, preferably SWNTs, this process can result in composite compositions whose electrical dissipative properties and storage modulus do not substantially change with repeated melt extrusion of the nanotube-polymer dispersion through an extruder as illustrated in FIG. 11A. These composite compositions in embodiments of the invention may be

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characterized by an axial force measured in a squeeze flow test of the composite composition that is greater than an axial force measured on a second extrusion compounded polymer composition. The second extrusion compounded composition comprises the nanotubes distributed into an extruded melt of the polymer, the nanotubes added into to the extruded melt of the polymer at a location equal to or greater than half the length of an extruder (extruder screws) used to make an electrically dissipative embodiment of the composite composition. For electrically conductive nanotubes, preferably SWNTs, this process can be used to prepare electrically dissipative materials whose resistivity can be varied depending upon the molding shear flow conditions. In particular these composite compositions can form electrically dissipative material when formed under low shear conditions (extrusion, compression molding, coining, gas pressure balanced injection molding) and can form insulating materials when formed under high shear conditions (injection molding). In some embodiments insulating materials formed under high shear flow can be thermally relaxed to an electrically dissipative state when heated.

When a polymer is mixed with immiscible nanotubes, the polymer is the continuous phase and the nanotubes are the dispersed phase. Where the nanotubes are considered single molecules, the nanotube may be referred to as being distributed in the polymer. A combination of dispersed and distributed nanotubes in the continuous phase can also exist. The nanotubes can form a discrete phase in the continuous matrix. In embodiments of the invention, the nanotubes can exist as individual tube or the tubes may be agglomerated together to form ropes of tubes. The extrusion compounding can distribute, disperse, or any combination of these, the nanotubes in the continuous polymer phase. The extrusion compounding can reduce the size of the agglomerated tubes in ropes of nanotubes and cause dispersive, distributive, or a combination of these types of mixing of the nanotubes in the continuous phase polymer matrix.

In some embodiments of the process, SWNTs or other nanotubes to be extrusion compounded with the polymer can optionally be deagglomerated by such acts such as sonication, ultrasonication, electrostatic treatment, ball milling, or electric field manipulation. In some embodiments of the process, the SWNTs or other nanotubes can also include optional dispersion additives or have surface functionalization.

Extrusion compounding of the polymer and composition comprising nanotube can occur in an approximately contemporaneous manner as illustrated in FIG. 10A and FIG. 10B. The polymer and composition comprising the nanotubes, preferably a composition comprising single walled carbon nanotubes, are compounded at about the same time in the with a sufficient amount of nanotubes and enough energy (torque applied to the screws), heat, and time (residence time) to

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form an extrusion compounded composition. The composition nanotubes distributed and or dispersed in the polymer has a storage modulus  $G'$  that is substantially invariant with further extrusion compounding of the composition. For compositions with a sufficient amount of conductive nanotubes dispersed, and that have nearly independent low frequency storage modulus behavior, an increase in molding shear flow rate of the composition increases the electrical resistivity of an article molded by the composition.

The amount of nanotubes by weight and polymer by weight can be varied to obtain compositions and molded articles having a desired set of properties and cost. For example higher amounts of electrically conductive nanotubes such as SWNTs can be used to obtain materials with lower electrical resistivity, lower amounts of nanotubes can be used to reduce material costs. Higher amounts of nanotubes can be used to obtain higher storage modulus for a given polymer or combination of polymers. In some embodiments of the present invention, the amount of nanotubes can be chosen to form a composition whose shear or storage modulus is at or above the rheological threshold. The rheological threshold or rheological percolation threshold occurs when the nanotubes impede the motion of the polymer chains and may be determined by sudden change in storage modulus versus nanotube loading in the composite composition. In other embodiments the amount of nanotubes can be chosen to form a composition whose electrical, magnetic, or other measurable property is at or above its percolation threshold. In some embodiments that amount of nanotubes in the thermoplastic polymer is about 10% or less by weight, in some embodiments the amount of nanotubes is less than 5% by weight, in some embodiments less than 4% by weight, in some embodiments less than 3% by weight, in some embodiments less than 2% by weight, in some embodiments less than 1% by weight, and in still other embodiments about 0.5% or less where a percolation threshold is achieved by the extrusion compounding. In some embodiments of the invention the amount of single walled carbon nanotubes in the polymer can range from 0.5% to 7% by weight or any amount in between these. In some embodiments the amount of single walled carbon nanotubes by weight in the polymer composite can be 0.5%, 1%, 2%, 3%, 4%, 5%, 6%, or 7% or amounts of SWNTs between any of these.

In embodiments of the invention, the density of the composite of polymer with the dispersed nanotubes can range from about  $1.2 \text{ g/cm}^3$  to about  $1.4 \text{ g/cm}^3$ , in other embodiments the density of the composites can range from  $1.3 \text{ g/cm}^3$  to about  $1.36 \text{ g/cm}^3$ .

In some embodiments, adding SWNTs or other nanotubes and polymer together at the same time in the extruder, melting together and extruding to compound the polymer and nanotubes, gives better dissipative properties through improved dispersion of the nanotubes. This

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can be better than adding SWNTs or other nanotubes to a melted polymer and then compounding. This is shown for example by side stuffing as illustrated in FIG. 11B which can result in clumps of SWNTs in the polymer rather than a dispersion. The inventors have discovered that once the SWNTs have been dispersed in the polymer, repeated extrusion (see for example FIG. 11A) does not improve the dispersion or dissipative properties of the composition or articles made from them, in some embodiments repeated extrusion decreases the storage modulus to a plateau or steady state value as shown in FIG. 20b.

In embodiments of the invention, SWNTs are mechanically dispersed with a thermoplastic; the thermoplastic can be in the form of a powder, pellet, film, fiber, or other form, to form an extruded composite.

Dispersion can occur using a twin screw extruder that includes kneading, shearing, and mixing sections. For example about 220 to about 320 newton-meters of torque can be the energy supplied to the screws which can have a length of about 95 cm and an L/D of about 38 to about 42; other values for these parameters can be used provided they result in the polymer composites of the present invention with a storage modulus that does not increase with further extrusion compounding. The extruder can have one or more temperature zones. The first temperature zone can be a temperature that results in melting of the polymer and dispersion of the nanotubes such as SWNTs in the polymer. Additional heating zones can be located downstream from the initial zone. Alternatively a temperature gradient can be formed along the extruder. The amount of energy and sections of the screw can be chosen to provide a dispersion of nanotubes and form a composition whose storage modulus does not increase with repeated extrusion of the material and whose value indicates that the nanotubes are dispersed. The essentially constant or non-increasing value of  $G'$  with further compounding as shown in FIG. 21 indicates that the polymer matrix is not degraded by the energy input to disperse and or distribute the nanotubes into the polymer matrix. Extrusion compounding of the nanotube with the continuous phase thermoplastic or polymer matrix in the melt overcomes attractive force between the ropes, tubes, or aggregates of nanotubes and disperses or distributes them in the matrix.

The method can further include the act of molding the extrusion compounded composition of polymer and nanotubes to form various articles. The articles can be solid, tape, tube, membrane, or other shaped form determined by the mold or die. The molded article can be flame resistant, electrically dissipative, electrically insulating, or any combination of these. Molding acts with the extrusion compounded compositions can include but are not limited to blow molding, rotational molding, compression molding, injection molding, extrusion, or other molding methods.

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Molding Shear flow ( $\text{sec}^{-1}$ ) can be used to modify or control the orientation of nanotubes in molded articles. Orienting flow can occur in low shear flow molding conditions and can be used to improve the cooperative interaction of the nanotubes in the molded article. The cooperative interaction include electrically dissipating or insulating properties of the polymer composite but may also include magnetic or optical properties of the nanotube. Orienting flows can be used to align conductive nanotubes during molding of an extrusion compounded composition to modify or reduce the electrical percolation threshold in a molded article. Low shear flow can be used to prepare electrically dissipative samples (conductive samples) from extrusion compounded polymer and SWNT resins while higher shear flow molding conditions for the same resin can be used to reduce electrical conductivity of the samples for a given nanotube or SWNT loading.

Low shear flow can be characterized by compression or transfer molding processes. Compression molding of extrusion compounded compositions with conductive nanotubes in embodiments of the present invention provide conductive articles at low nanotube loadings (7% wt or less), low flow and low shear. Compression or transfer molding produces material at shear flow rates of from about  $500 \text{ sec}^{-1}$  to about  $3000 \text{ (sec}^{-1})$ . In some embodiments of the present invention low shear flow can be less than about  $1300 \text{ sec}^{-1}$ .

Variable shear flow can be achieved by extrusion molding. The variable shear flow rate can be further modified by the take up rate of a reel (for tape, fiber, hollow tube, or other material). The extrusion molding shear flow rate can be used to modify the cooperative interaction of dispersed nanotubes in the polymer. Extrusion molding can be used for making high volume products and films or tapes. Extrusion shear flow rates can range from about  $500 \text{ sec}^{-1}$  to about  $11,000 \text{ (sec}^{-1})$ . In some embodiments of the invention the extrusion shear flow rate can be less than about  $1,000 \text{ (sec}^{-1})$ . For extrusion compounded polymer and SWNTs in embodiments of the invention, extrusion can be used to prepare an electrically dissipative material (see FIG. 3, FIG. 12, and Table 1).

High shear flow can be characterized by injection molding. Injection molding can be used for making high volume products from compositions of the present invention. Injection molding can be used to create fine features in an article. . Injection molding shear flow rates typically range from about  $8000 \text{ sec}^{-1}$  to about  $15000 \text{ (sec}^{-1})$

Injection molding nanotube and polymer compositions can be used to reduce the interaction between dispersed nanotubes in the molded articles compared to a compression molded article from the same composition. For example, where the nanotubes are electrically conductive like SWNTs, injection molding an extrusion compounded polymer and SWNT composition of the

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present invention results in an article with higher electrical resistivity compared to a similar article made by compression molding. The higher electrical resistivity is the result of the high flow and high shear rate of injection molding compared to compression molding.

Highly resistive and or insulating articles made by injection molding of compositions of the present invention can be subsequently heated and become more electrically dissipative or less resistive.

In some embodiment of the molding process, the injection molding may be modified to reduce shear flow and produce articles with improved cooperation between dispersed nanotubes in the molded article. For example the polymer and nanotube extrusion compounded composition can be injected into a open mold or a partially open mold to reduce shear flow and then perform a subsequent compression molding operation (this process can be referred to as coining) to form the article. For extrusion compounded polymer and SWNT composites, coining can lower electrical resistivity of molded articles compared to injection molding. In some embodiment of this coining process, shear flow conditions can be less than about 3,000 ( $\text{sec}^{-1}$ ). Alternatively a counter flow or pressure of heated gas can be introduced into a heated injection mold and can be used to reduce the shear flow of the polymer nanotube dispersion. While injection molding at high nanotube loading levels (5-7%) can produce electrically dissipative materials, the higher weight fraction of nanotubes may make these materials more expensive.

In some embodiments, the method can further include the act of modifying the electrical resistivity of the article by thermal relaxation treatment or by heating with extensional flow or stretching of the material. For example the composite composition may be stretched by but not limited to 1X, 2X or other non-integral values of its original dimension in the stretching direction. Relaxation treatment of high shear flow molded articles can include the acts of heating the article to a temperature that permits movement of the nanotubes dispersed in the polymer of the article. This temperature can be at or near the glass transition temperature, at or near the melting temperature, or any combination of these for polymers with amorphous and crystalline regions. The temperature and time for heating is sufficient to induce movement and relaxation of the chains to form an electrically dissipative material. Temperatures near the melting point or glass transition temperature or above can be used to hasten the relaxation process. Temperatures below the melting point or glass transition temperature can be used to preserve molding features and integrity. For example electrically insulating samples of extrusion compounded PEEK and SWNTs that were injection molded could be relaxation treated in a temperature range of from

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about 340-360 °C for 3-6 min to form electrically dissipative samples. Extensional flow with optional heating can be used to increase the resistivity of electrically dissipative molded articles.

Extrusion compounded polymer and nanotube composites in embodiments of the present invention have a structure that can be characterized by their rheological properties. The extrusion compounding distributes the nanotubes in the polymer and the composition has a storage modulus  $G'$  that is substantially invariant or resists an increase with further extrusion compounding of the composition. For example, as illustrated schematically in FIG. 11A, a sample of extruded material 1138A was taken after 5<sup>th</sup>, 10<sup>th</sup>, 15<sup>th</sup> and 20<sup>th</sup> cycles (depicted by 1110A as being fed back into the extruder 1150A) and the resistivity and shear modulus  $G'$  of the sample was measured. There was essentially no increase in storage modulus on the extruded sample. In other embodiments of the invention essentially or substantially invariant resistivity and or storage modulus  $G'$  includes changes of less than  $\pm 40\%$ . In other embodiments the storage modulus decreases to within a factor of 2 after 5 extrusion cycles, or decreases to a steady state value within a factor of about 5 or less of the original storage modulus.

Relaxation treatment of highly resistive or insulating articles molded from a conductive nanotube dispersion in a polymer under high shear flow process is shown by the graph of FIG. 7. Sample (A) and sample (B) were from the same molding process and resin. Sample (B) storage modulus has a low slope at frequency below about 1 rad/s when heated above the melting or glass transition temperature of the sample. Sample (A) storage modulus was determined at the same temperature but after a relaxation time of a several minutes. The sample (A) storage modulus showed an increase in the value of  $G'$  which indicates an improved dispersion of the nanotube in the sample after the relaxation treatment.

The Table of FIG. 2 illustrates that higher loading levels of dispersed SWNTs in the polymer in extrusion compounded compositions of the present invention results in lowering the crystallinity of the composites compared to the polymer; lowering the heat of fusion compared to the polymer, raising the onset of crystallization temperature, and lowering the heat of crystallization.

As illustrated for nanotubes dispersed by extrusion compounding, the storage modulus plot in FIG. 5 illustrates that  $G'$  is almost independent of  $\omega$  (rads/sec) at low frequency as shown by nanotube loadings of from 0.5% by wt. to about 5% by wt. This contrasts to the approximate  $\omega^2$  dependence for the polymer and without wishing to be bound by theory, may indicate a transition from liquid like behavior of the polymer to solid like viscoelastic behavior due to the nanotubes dispersed in the polymer. Further, this non-terminal behavior may be the result of a nanotube

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network in the polymer that restrains the long-range motion of the polymer chains. FIG. 14 illustrates this low frequency weakly dependent behavior,  $z$  less than 1.7 or preferably less than 1, for two compositions with 0.5wt. % and 2 wt. % SWNTs in PEEK taken from the data of FIG. 5. Curve fitting using Microsoft Excel of storage modulus and frequency illustrates that the storage modulus for the 0.5wt. % and 2 wt. % SWNTs in PEEK is proportional to frequency according to the relationship  $G' = K\omega^z$  where  $K$  is a proportionality constant (66.7 and 28630 respectively for the 0.5wt. % and 2 wt. % SWNTs in PEEK), and  $\omega$  is the frequency for  $z$  (0.46 and 0.16 respectively) for frequency between 0.01 and 1 rad/sec. The regression fit  $R^2$  is better than 0.95, in some embodiments better than 0.98, and in still other embodiments better than 0.99. For PEEK, a curve fit for the data in FIG. 5 provides  $K$  of 11.83,  $z$  of 1.79, and  $R^2$  of 0.99 for frequencies between 0.1 and 10 rad/s. Similar curve fits could be made for the other samples in FIG. 5.

FIG. 6 illustrates the axial load or squeeze flow behavior of compositions comprising nanotubes extrusion compounded in a polymer where the nanotubes were added to the polymer at two different locations in the extruder schematically illustrated by FIG. 10A and 11B. The samples each included 5 wt % SWNTs as nanotubes combined with PEEK pellets using a starve feed of dry materials. Sample NT4 was prepared by simultaneous or contemporaneously dry compounding of the SWNT and PEEK as illustrated in FIG. 10A. Sample NT1 was made with "side stuffing" or addition of SWNTs at 1130B to premelted polymer (1134B). The extrusion compounding to prepare the composition NT4 provided a material with a 4x or higher normal force (~800 g) in a squeeze flow test compared to the side stuffed material at the same gap (~1mm). It is reasonable to expect similar behavior with other materials made by the methods and materials disclosed herein. The difference in the force shows a structural difference in the network of nanotubes between the NT1 and NT4 samples as shown by the difference in gap force. As shown in FIG. 15b, the gap force of a PEI/SWNT composition with 5wt% SWNTs is about 1000 g or more for a gap of about 1.2 mm. As shown in FIG. 17a, the gap force of a PEEK/SWNT composition with 7wt% SWNTs is about 1000 g or more for a gap of about 1.2 mm. Embodiments of the invention include those compositions of SWNT and polymer where the gap force is greater than about 500 g at a gap of 1.2 mm or less; in some embodiments the amount of SWNTs by wt% in such compositions is about 5% or more.

The gap force behavior of NT4 in FIG. 6 also illustrates the formation of a denser network of dispersed nanotubes compared to NT1. Such a network of nanotube can provide improved rheological properties, improved electrical conductivity, improved magnetic susceptibility, or improved fire retardant properties (less material dripping and greater structural rigidity) compared

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to a material with a weaker network. By varying the location where the nanotubes are extrusion combined with the polymer, the density (as measured by the axial force) of the nanotube network can be modified.

In some embodiments of the invention, molding the composition comprising the nanotubes dispersed in the polymer provides an article that is flame retardant and can maintain its shape and prevents dripping or sagging of composite or articles comprising it when exposed to a flame. These composite materials in embodiments of the invention are useful for fire and flame retardant structural engineering plastics because they resist changes in shape and dripping of the molten plastic and provide an increase in melt strength (4x or more) as illustrated by the squeeze flow results of FIG. 6. Further, and without wishing to be bound by theory, the solid like behavior, for example the plateau in  $G'$  at low frequency (below about 1 rad/sec), indicates that the composites would resist dripping of the composite when exposed to a flame. The increase in melt strength translates directly in to prevention of the dripping during the burning process. In comparison, similarly prepared and tested PEEK or PEEK with carbon fibers showed the normal force decay to about zero- the sample squeezed out from test pads, under similar heating conditions and applied axial force illustrating loss of strength and no reduction in dripping. The extrusion compounding of nanotubes such as but not limited to SWNTs with a flame retardant polymer can be molded into a variety of articles that would benefit from improve flame retardancy or show improved structural properties at high temperature. Such articles can include wafer carrier, fluid tubing, wafer shippers, containers for chemicals, heat exchanger tubing, plastics used for computers and monitors, automotive applications.

The SWNTs in embodiments of the fire-retardant nanotube-polymer composite of the invention increases the melt strength of the polymer composite compared to the polymer thereby reducing the tendency of the composite, when heated to close to melting, to drip or sag. The nanotubes can be added in an amount effective to increase the melt strength as measured in a squeeze flow test or reduce drip. The nanotubes can be added in an amount for example in the range of from about 0.20 weight % or higher; in some embodiments about 0.5 wt% or higher; in some embodiments about 1 wt% or higher; in some embodiments about 3 wt% or higher; in some embodiments about 5 wt% or higher; in some embodiments from about 3 wt% to about 10% by weight; in some embodiment from about 0.5 to about 7% by weight; and in still other embodiments of from about 0.2 to about 10% by weight. Lower amounts of the SWNTs reduce the costs of these materials.

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Polymers that can be used to form flame retardant and fire resistant materials, which can optionally be electrically dissipative, can include PEEK, Poly imide (Aurum), PEI (Ultem) and mixture of these with PEEK since they are miscible with PEEK. In some embodiments the thermoplastic may comprise a branched polyphosphonate that is self-extinguishing in that they immediately stop burning when removed from a flame. Any drops produced by melting these branched polyphosphonates in a flame instantly stops burning and do not propagate fire to any surrounding materials. Moreover, these branched polyphosphonates do not evolve any noticeable smoke when a flame is applied. Accordingly, these branched polyphosphonates can be used as additives in commodity or engineering plastics to significantly improve fire resistance without severely degrading their other properties, such as toughness or processing characteristics. The thermoplastic may independently include polycarbonate, polyphosphonate, and other polyesters useful for flame retardant materials. These plastics may include but are not limited to those disclosed in U.S. Patent No. 6,861,499; U.S. Patent No. 5,216,113; U.S. Patent No. 4,350,793; and U.S. Patent No. 4,331,614.

The limiting oxygen index (LOI) of a material is indicative of its ability to burn once ignited. The test for LOI is performed according to a procedure set forth by the American Society for Test Methods (ASTM). The test, ASTM D2863, provides quantitative information about a material's ability to burn or "ease of burn". If a polymeric material has an LOI of at least 27, it will, generally, burn only under very high applied heat. It is expected that embodiments of the present invention can include molded articles having extrusion compounded nanotubes in a continuous phase of a polymer that have an LOI of at least 27 and an axial force in a squeeze flow test that is greater than the polymer without the nanotubes. In some embodiments the nanotubes are SWNTs, preferably from about 3% to about 10% by weight of the composite.

Optionally conventional additives which include, for example, thickening agents, pigments, dyes, stabilizers, impact modifiers, plasticizers, or antioxidants and the like can be added to the compositions of the present invention.

Table 1. Resistivity of molded extrusion compounded nanotube polymer compositions.

|                                                                   | 0.5 wt % SWNT<br>in PEEK<br>(ohm/sq) | 1 wt % SWNT<br>in PEEK<br>(ohm/sq) | 2 wt % SWNT<br>in PEEK<br>(ohm/sq) | 5 wt % SWNT<br>in PEEK<br>(ohm/sq) |
|-------------------------------------------------------------------|--------------------------------------|------------------------------------|------------------------------------|------------------------------------|
| Injection                                                         | $> 10^{12}$                          | $> 10^{12}$                        | $> 10^{12}$                        | $\sim 10^7$                        |
| Extruded                                                          | $> 10^{12}$                          | $> 10^{12}$                        | $\sim 10^5$                        | $\sim 10^6$                        |
| Compression                                                       | NA                                   | $\leq 10^4$                        | $< 10^4$                           | $< 10^4$                           |
| Injection-<br>relaxed (heat<br>treated @ 340<br>°C for ~5<br>min) | $\leq 10^9$                          | $\leq 10^4$                        | $< 10^4$                           | $< 10^4$                           |

## EXAMPLE 1

Single walled nanotubes (SWNTs) from supplier CNI were used without sonication, (separate sonication, inline sonication were used in other samples but were not necessary). The SWNTs exist mainly as ropes that were in the range of about 20 nm in diameter and lengths between about 0.05 and 5 microns. Their density was about 1.7-1.8 g/cm<sup>3</sup>. These SWNTs were used as received. Feed rates of SWNTs were shear mixed with a thermoplastic PEEK, see Table 3 for amounts that were used, at about 340 °C in a co-rotating, intermeshing twin screw extruder (length 95 cm, L/D 38 – 42) to obtain concentrations of 0.5, 1, 2, and 5 wt % of the SWNTs in PEEK. Compounding was carried out using a three zone heating with barrel temperatures of 340 °C, 360 °C, and 370 °C. Torque from about 220 to about 320 newton-meters was applied to the twin screw. The polymer and SWNTs were mixed by the screw of the extruder. No additives or dispersing agents were used. Bulk density of composites were about 1.33 g/cm<sup>3</sup>.

Samples were made with PEEK, PEI, PI, and mixtures of these which resulted in well dispersed SWNTs in the polymer as determined by the nearly independent frequency dependence of the storage modulus as shown for the SWNTs in PEEK in FIG. 5. Extruded samples were prepared using an orifice 3 mm, a feed rate 5 – 7 kg/hr. The electrical dissipative properties of the extruded samples could be modified by changing the take-up rate. This was illustrated by hand drawing a portion of an extruded sample (see for example FIG. 3) to simulate higher shear conditions and form less electrically dissipative samples.

Relaxation treatment of high shear electrically insulating samples (injection molded) were carried out at 340-360 °C for 3-6 min to form electrically dissipative samples. The storage

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modulus of samples with relaxation treatment (A) and without relaxation treatment (B) are shown in FIG. 7.

The resistivity of the injection molded, compression molded, extruded, and relaxation treated injection molded samples for various amounts of nanotubes extrusion compounded the polymer were determined on solid samples using a VOYAGER surface resistivity meter. These results are summarized in Table 1

Dynamic rheological measurements of injection molded, compression molded, extruded, and relaxation treated injection molded samples were determined on cut samples. The measurements were carried out in an oscillatory shear mode using a parallel plate geometry 25 mm diameter at 380 °C under a nitrogen atmosphere. Frequency sweeps between 0.1 and 100 rad/sec were carried out.

## EXAMPLE 2

Single walled nanotubes (SWNTs) from supplier CNI (Carbon Nanotechnologies Inc, Houston TX) were used without sonication.

The resistivity of an extruded sample prepared as in Example 1 was measured and was  $10^5$  to about  $10^6$  ohm/sq. The extruded sample output was fed back into the extruder for 5, 10, 15, 20 additional extrusion cycles as illustrated in FIG. 11A. A sample of extruded material was taken after 5<sup>th</sup>, 10<sup>th</sup>, 15<sup>th</sup> and 20<sup>th</sup> cycles and the resistivity and G' of the sample measured. There was essentially no increase in the measured storage modulus illustrating that the dispersion of the SWNTs in the polymer was stable and essentially invariant and that the properties did not change over time within the variation of the processing conditions. This result illustrates that the extrusion compounded composition is insensitive to shear history.

The properties of a molded article of this extrusion compounded nanotube and polymer composition could be modified by the shear flows used in the molding process and by subsequent thermal treatment. Thus articles produced by the different processes had different resistivity (FIG. 12 and Table 1), with low shear flow processes producing molded article with generally lower resistivity for the same amount of nanotube. An insulating article could be made from this composition in a high shear flow process. The graph of FIG. 7 shows that the SWNT storage modulus and nanotube dispersion of this insulating material could be modified by heat treatment.

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## EXAMPLE 3

Single walled nanotubes (SWNTs) from supplier CNI (Carbon Nanotechnologies Inc, Houston TX) were used without sonication and combined with PEEK thermoplastic as in Example 1 by injection molding. The extractables of the composite were determined by ICP-MS on acid digested samples as shown in the Table 2 below.

The extractables can be determined via Microwave Digestion and filtration. For example, weigh 1.0 gram polymer and SWNT composite sample pellets and place pellets in 125 - ml PFA sample digestion vessel. Add 10 ml 16.0 N HNO<sub>3</sub>, cap and seal vessel(s). Place vessel(s) in insulated sleeves and into sample vessel carousel. Place in microwave digestion oven which can be heated according to the Oven profile: (Stage 1) Heat at 50% power to 20 p.s.i. and hold 10 minutes. (Stage 2) Heat at 50% power to 50 p.s.i and hold 10 minutes. (Stage 3) Heat at 50% power to 90 p.s.i. and hold 10 minutes. (Stage 4) Heat at 50% power to 100 p.s.i. and hold 10 minutes. (Stage 5) Heat at 50% power to 110 p.s.i. and hold 10 minutes. Remove from microwave digestion oven and allow vessels to cool to room temperature in laboratory fume hood. The liquid can be analyzed by ICPMS, GFAA, or other suitable method. Where necessary, the liquid from the acid digestion may be filtered prior to analysis.

Table 2. Metal extractable from acid digestion of nanotube polymer compositions.

| Category<br>---<br>Parameter                      | Units                  | Test<br>Method                 | Virgin<br>150 of<br>PB3464 | 1.25%<br>NT | 2.5% NT | 5.0% NT |
|---------------------------------------------------|------------------------|--------------------------------|----------------------------|-------------|---------|---------|
| Acid<br>Digestion<br>Trace<br>Metals (ICP-<br>MS) | $\Sigma \mu\text{g/g}$ | FGTM<br>1343<br>Det.<br>Limits | 150                        | 560         | 1000    | 1760    |
| Al                                                | $\mu\text{g/g}$        | 0.22                           | 1.3                        | 0.86        | 1.0     | 1.2     |
| Ba                                                | $\mu\text{g/g}$        | 0.39                           | dl                         | dl          | dl      | 0.64    |
| <sup>40</sup> Ca                                  | $\mu\text{g/g}$        | 0.37                           | 7.3                        | 3.1         | 3.7     | 8.3     |
| Co                                                | $\mu\text{g/g}$        | 0.11                           | dl                         | 0.15        | 0.14    | 0.33    |
| <sup>52</sup> Cr                                  | $\mu\text{g/g}$        | 0.17                           | 1.0                        | 0.74        | 1.1     | 2.2     |
| Cu                                                | $\mu\text{g/g}$        | 0.13                           | 1.3                        | 4.1         | 7.8     | 27      |
| <sup>56</sup> Fe                                  | $\mu\text{g/g}$        | 0.36                           | 14                         | 360         | 670     | 1320    |
| K                                                 | $\mu\text{g/g}$        | 0.42                           | 1.4                        | 0.79        | 0.90    | 2.1     |
| Li                                                | $\mu\text{g/g}$        | 0.18                           | dl                         | dl          | dl      | dl      |
| Mg                                                | $\mu\text{g/g}$        | 0.33                           | 0.99                       | 2.0         | 3.6     | 5.7     |
| Mn                                                | $\mu\text{g/g}$        | 0.18                           | dl                         | 0.20        | 0.37    | 0.61    |
| Mo                                                | $\mu\text{g/g}$        | 0.30                           | dl                         | 84          | 190     | 260     |
| Na                                                | $\mu\text{g/g}$        | 0.57                           | 120                        | 99          | 130     | 120     |
| Nb                                                | $\mu\text{g/g}$        | 0.24                           | dl                         | dl          | dl      | dl      |
| Ni                                                | $\mu\text{g/g}$        | 0.15                           | 0.85                       | 0.34        | 0.33    | 0.55    |
| Pb                                                | $\mu\text{g/g}$        | 0.40                           | dl                         | 0.49        | 1.2     | 1.3     |
| Ti                                                | $\mu\text{g/g}$        | 0.42                           | dl                         | 0.75        | dl      | dl      |
| Zn                                                | $\mu\text{g/g}$        | 0.32                           | 5.2                        | dl          | dl      | 9.9     |

## EXAMPLE 4

Single walled nanotubes (SWNTs) from supplier CNI (Carbon Nanotechnologies Inc, Houston TX) were used without sonication and combined with PEEK thermoplastic as in Example 1.

Squeeze flow or Gap testing was performed on a melt of the sample using an Advance Rheometric Expansion System (ARES) Rheometer at 380 °C in a nitrogen atmosphere. FIG. 6 illustrates force gap test results on a melt of the samples heated to 380 °C. FIG. 6 illustrates the squeeze flow rheometry for SWNT dispersion on the properties of the materials prepared. NT4 is prepared by the dry melt method, NT1 is side stuff method. FIG. 6 illustrates the behavior of NT1 and NT4 under constant normal force and an initial gap of about 4mm. A sample of the material was placed between the plates and heated above the melting or glass transition temperature, for

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example to 380°C. The initial behavior (to about 75 sec) may be due to the sample filling the void between the plates, the void between the plates is essentially filled by about 150 sec. In order to maintain a constant normal force of about 100 [g] on the NT1 sample until the target test gap of 1 mm is reached, the vertical speed decreases exponentially up to about 500 seconds. To achieve a similar exponential decay for the NT 4 sample to a target gap of 1 mm, the constant normal force is about 400 to about 650 [g]. The nearly 4X increase in the constant normal force is a measure of the greater SWNT network density in NT4 compared to NT1. The two methods yield different materials with different nanotube network structure as evidenced by their squeeze flow and low shear flow process properties; NT4 forms high melt strength material, NT1 forms lower melt strength material. This example illustrates that the melt strength of articles molded from extrusion compounded nanotube polymer composites can be modified by the position where the nanotubes and polymer are compounded with the polymer in the extruder.

While the samples have different axial force, both samples show an essentially constant normal force with reduction in the gap over time. This illustrates the formation of a network of the SWNTs with the polymer; the network of NT4 is more dense than NT1. By retaining their structure, these materials are useful for fire and flame retardant structural engineering plastics that resist changes in shape and dripping of the molten plastic. In comparison, similarly prepared and tested PEEK or PEEK with carbon fibers showed the normal force decay in a squeeze flow test to about zero [0g] force, i.e., the sample squeezed out from test pads, under similar heating conditions illustrating loss of strength and no reduction in dripping.

#### EXAMPLE 5

This example illustrates the structure and properties of a melt dispersion of SWNTs in a polymer can be affected by high shear flow processing.

The frequency response of the storage modulus ( $G'$ ) for 2 wt % SWNTs in PEEK were determined in FIG. 7 at 380 °C. An injection molded sample that was initially insulating was cut into two pieces. (B) the sample was rotated with heating for 3 minutes and then a frequency sweep of the material was made. (A) the sample was rotated for 3 minutes with heating, allowed to relax with continued heating for 5 minutes, and then a frequency sweep of the material was made.

The results have shown that both samples have low frequency  $G'$  nearly independent behavior which suggests, and without wishing to be bound by theory, that large scale polymer relaxations are restrained by the nanotubes which form a network. Sample (A) has a higher  $G'$  at



## EXAMPLE 7

This example illustrates preparation and characterization of various polyether imide polymer combined with single walled carbon nanotube in an extruder by the methods and equipment of Example 1. Single walled carbon nanotubes, CNI, Houston, TX type (Bucky ESD34) were used, the molecular weight of the PEI polymer ranged from 15,000 to 60,000 g/mole.

FIG. 15a details rheological measurements, the shear dependent viscosity and storage modulus, as a function of frequency [rad/s] for polyether imide (PEI)/SWNT composites dispersed with 0.5 wt %, 1 wt%, and 2 wt% SWNTs in embodiments of the invention. The storage modulus curves for the (PEI)/SWNT composites for the 0.5 wt%, 1 wt%, and 2 wt% SWNTs are given by the curves 1510, 1520, and 1530 respectively; the viscosity curves for the (PEI)/SWNT composites for the 0.5 wt %, 1 wt%, and 2 wt% SWNTs are given by the curves 1540, 1550, and 1560 respectively. A curve fit of the data for frequency between 0.1 rad/sec and 1 rad/sec for 1510 to the function  $G' = K\omega^z$  gives  $K = 1219.6$  and  $z = 0.29$  with  $R^2 = 0.99$ ; a curve fit of the data for 1520 to the function  $G' = K\omega^z$  gives  $K = 1666.1$  and  $z = 0.25$  with  $R^2 = 0.99$ ; a curve fit of the data for 1530 to the function  $G' = K\omega^z$  gives  $K = 16396$  and  $z = 0.19$  with  $R^2 = 0.96$ . At low frequency of 0.1 rad/s the storage modulus for 1510 is about 640 [dynes/cm<sup>2</sup>]; the storage modulus for 1520 is about 963 [dynes/cm<sup>2</sup>]; the storage modulus for 1530 is about 11,000 [dynes/cm<sup>2</sup>]. The storage modulus curve of the PEI polymer alone, not shown, has a  $G'$  at 0.1 rad/sec of about 12; a plot of  $G'$  vs frequency for the polymer 0.1 to 100 rad/sec is characteristic of a polymer having a bimodal distribution of molecular weights. The results show that utilizing the methods and materials of the invention that for 0.5% SWNTs or more dispersed into a polymer, the  $G'$  value at 0.1 rad/sec is about 50 times greater, or more, than  $G'$  for the polymer alone; for 1% SWNTs or more dispersed into the polymer, the  $G'$  value at 0.1 rad/sec is about 70 times greater, or more, than  $G'$  for the polymer alone; for 2% SWNTs or more dispersed into the polymer, the  $G'$  value at 0.1 rad/sec is about 800 times greater, or more, than  $G'$  for the polymer alone. The composites can be characterized as having  $z$  of about 0.35 or less for the function  $G' = K\omega^z$ . The composite samples 1530 and 1520 had a surface resistivities in the range of  $10^5$  to  $10^9$  ohm/sq; the sample 1530 had a surface resistivity greater than about  $10^9$  ohm/sq.

FIG. 15b is a plot of force gap tests for (PEI)/SWNT composites for 0.5 wt % (1580), 1 wt% (1582), 2 wt% (1584), and 5 wt% (1586) SWNTs. The results show that for 0.5wt% (1580) and 1 wt% (1582) that the normal force is greater than 20-30 g for a gap of 1.2 mm or less, for 2 wt% (1584) the normal force is greater than about 100 g for a gap of 1.2mm or less, and for 5 wt%

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SWNTs (1586) the normal force is greater than about 1000 g for a gap of 1.2 mm or less. The gap for each of the samples forms the superimposed points in the trace 1572-1578. The high normal force for these materials is important for flame retardant materials.

### EXAMPLE 8

This example illustrates preparation and characterization of various polyether imide and PEEK blends of polymer with single walled carbon nanotube composites. Single walled carbon nanotubes, CNI, Houston, TX type (Bucky ESD34) were used in the method of Example 1 to prepare samples of composite materials.

FIG. 16a shows the normal force [g] as a function of time in a force gap or squeeze flow measurement on a non-solid sample of 2.5wt% SWNT in a polymer blend of 20 wt% PEI and 77.5 wt% PEEK; the normal force 1610 and gap 1620 are plotted as a function of time. In this embodiment the normal force is greater than about 150 g at a gap of less than 1.2 mm and preferably about 1 mm. FIG. 16b is a plot of storage modulus 1630 and viscosity 1640 as a function of Freq[rad/s] on a non-solid sample of 2.5wt% SWNT in a polymer blend of 20 wt% PEI and 77.5 wt% PEEK, a curve fit of this data for frequency between 0.1 rad/s and 1 rad/sec to a function  $G' = K\omega^z$  gives  $K = 22257$  and  $z = 0.26$  with  $R^2 = 0.99$ . At low frequency of 0.1 rad/s the storage modulus is about 12,000 [dynes/cm<sup>2</sup>]. Compared to the storage modulus for PEEK in FIG. 5 or the storage modulus for PEI in Example 7 at 0.1 rad/s, in this blend the increase in  $G'$  can for the composite with 2.5% or more SWNTs can range from about 1,000 or more to about 50,000 or more based on the neat polymers alone.

The results show that the composition is a polymer that is a continuous phase with an amount of single walled carbon nanotubes dispersed therein. The polymer is a blend of one or more polymers. The composition can be characterized as having a storage modulus proportional to frequency by the relationship  $G' = K\omega^z$  where the value of  $z$  is less than 0.35 and it has a high storage modulus of greater than 10,000 [dynes/cm<sup>2</sup>] for a loading of 2.5wt% or more of SWNTs. Consistent with the PEI/SWNT composition having 2% SWNTs, the normal force in a gap test for 2.5% SWNTs in the polymer blend was about 150 g illustrating that other compositions may be useful for fire retardant materials.

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## EXAMPLE 9

This example illustrates preparation and characterization of a composite of PEEK and 7 wt% single walled carbon nanotube composites. Single walled carbon nanotubes, CNI, Houston, TX type (Bucky ESD34) were used in the method of Example 1 to prepare samples of composite materials.

FIG. 17a illustrate gap for test results and FIG. 17b show the storage modulus as a function of frequency for 7% SWNTs in PEEK. In FIG. 17a the normal force 1710 and gap 1720 are plotted as a function of time. In this embodiment the normal force is greater than about 1500 g at a gap of less than 1.2 mm. FIG. 17b is a plot of storage modulus 1730 and viscosity 1740 as a function of Freq[rad/s] on a non-solid sample of 7wt% SWNT in PEEK, a curve fit of this data to a function  $G' = K\omega^z$  gives  $K = 42323$  and  $z = 0.12$  with  $R^2$  of 0.99. The surface resistivity of this material as measured by the methods described herein was less than  $10^4$  ohm/sq. At low frequency of 0.1 rad/sec,  $G'$  is about 33,000 [dynes/cm<sup>2</sup>].

The results show that electrically dissipative composite materials of SWNTs dispersed in a polymer can be made that have a high normal force, greater than about 500 g, and in this case greater than 1500 g. The dispersion of the SWNTs can be characterized by the high  $G'$  of greater than about 10,000 [dynes/cm<sup>2</sup>] at 0.1 rad/s and a low slope of  $z$  less than 0.2.

## EXAMPLE 10

This example illustrates dielectric spectroscopy (DES) of composites of the present invention. The measurements were made on substantially washer shaped samples having a 2 mm ring width and overall thickness, RMSV of 100 volts,  $f$  of 1 KHz, and 1 rad/sec. Measurements were made on 0.5wt% dispersed SWNTs in PEEK according to the method of Example 1.

Parallel-plate rheometry and dielectric spectroscopy can be combined, each of the parallel plates for the rheometer being used as an electrode in the dielectric spectroscopic setup. Percent strain and permittivity [pF/m] from a parallel-plate rheometer may be used to measure how the permittivity changes with changes in strain at a given temperature of a non-solid form of the composite material. The material can be placed on the rheometer parallel plates in a doughnut or washer shape with an open center and edge portions about 2mm wide; the sample between the parallel plates can be about 2 mm thick. The temperature of the composite can be kept stable or ramped, time sweeps can be performed. The root mean square voltage (RMSV) was 100 volts, electrical frequency was 1 kHz, and strain about 1 rad/sec.

For single point step strain measurements the rheometer plates undergo a single rotation.

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FIG. 18 shows plots of strain and permittivity as a function of time for 0.5wt% SWNTs in PEEK with pre-shear of 1/sec for various compositions. The graphs illustrate that the permittivity in embodiments of the invention can be increased with pre-shear, for example 1810 and 1820 and further increased at higher temperatures 1820 (380 °C) compared to 1810 at (360 °C). Scans 1830 (360 °C, no pre-shear), 1840 (380 °C, no pre-shear), and air 1850 are also shown. The permittivity of air is shown 1850.

FIG. 19a illustrates DES step strain measurement on a sample of 0.5%wt SWNT dispersed in PEEK by the methods of the present invention (Example 1). FIG. 19b illustrates DES single point step strain for SWNT loadings of 0.5%, 1%, and 2% by weight. FIG. 19a shows plots of strain and permittivity as a function of time at 380°C for 0.5wt% SWNTs in PEEK. Strain steps 1910 were 20, 40, 60, 80, 100, 150, 200%, and 1% and the measured permittivity 1920 as a function of time at 360 °C and the measured permittivity 1930 as a function of time at 380 °C were plotted. Embodiments of the invention show a decrease in permittivity with increasing strain and increase in permittivity with increasing temperature. FIG. 19b shows DES measurements of the permittivity as a function of time for single point strain data for 20% (s1), 60% (s2), 100% (s3), and 200% (s4). The permittivity for 2% SWNTs (a-d), 1% SWNTs (e-h), and 0.5% SWNTs (j-m) are given; air permittivity (i) is also shown. The permittivity of the sample decreases when the strain is increased at the point and then recovers when the strain is released. The recovery is substantially the starting permittivity value, especially for higher amounts of SWNTs such as 2wt% or greater.

These results illustrate that the resistivity of the material can be modified by changes in processing conditions such as shear flow conditions and temperature. The results also show that the resistivity can be manipulated by heat treatment.

### EXAMPLE 11

This example illustrates the Shear Modulus of a composite material of 2wt% SWNTs dispersed in PEEK subject to multiple shear cycles. This material was made by the method of Example 1. The material was subject to a residence time of about 1.8 min/cycle and the storage modulus was measured after 1, 5, 10, 15, and 20 cycles at 380°C.

FIG. 20a is an overlay plot of  $G'$  at 380 °C for the SWNT 2wt% in PEEK composition with different shear histories, passes or cycles through the extruder with 1.8 minute residence time in the extruder: 1 cycle (2010), 5 cycles (2020), 10 cycles (2030), 15 cycles (2040), and 20 cycles (2050). Between 1 and 5 extrusion cycles the storage modulus does not increase which would be expected for further SWNT dispersion. Rather the storage modulus decreases from about 35,000

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[dyne/cm<sup>2</sup>] to about 22,000 [dyne/cm<sup>2</sup>] after the fifth cycle. The decrease is less than a factor of 2. Continued extrusion cycles further reduce the value of G' and after about 15 cycles G' reaches a steady state value of about 15,000 [dyne/cm<sup>2</sup>]; this is about a 3x decrease, and less than a 5x decrease from the initial storage modulus value. FIG. 20b shows this trend for the storage modulus and illustrates the SWNT contribution to the plateau modulus as a function of the number of shear histories or residence time from FIG. 20a.. The relative modulus G'r was determined from data at 0.1 rad/s by the equation  $G'r = [(composition\ G'/PEEK\ G') - 1]$ .

FIG. 21 illustrates the change in storage modulus for PEEK only with different shear histories, passes or cycles through the extruder with 1.8 min residence time in the extruder for 1 cycle (2110), 5 cycles (2120), 10 cycles (2130), 15 cycles (2140), and 20 cycles (2150). The PEEK shear modulus appears to increase slightly with continued extrusion.

FIG. 20a illustrates that for compositions of the invention that the G' is invariant to further increase in G' with continued extrusion processing because there was no improvement in the dispersion as measured by G' with more extrusion time. Without wishing to be bound by theory, the results suggests that the reduction G' may be due to deterioration of the dispersion whereby the SWNTs are undergoing aggregation. The initially extruded composite material has the maximum dispersion as measured by the storage modulus and then after further induction of stress, the dispersion declines.

## EXAMPLE 12

This example illustrates the dispersion of the single walled carbon nanotubes in the polymer by the method of Example 1 can result in uniform resistance in samples or articles made, and in some cases made in a low shear process, from the composition. The samples contained 5 wt % SWNTs dispersed in PEEK.

Agilent 34401 Multimeter and Pro-Stat PRS-801 Resistance System Two-Point Probe were used. The resistance was measured to 2 significant figures at 9 positions. Multiple samples tested and each sample was tested multiple times. The uniformity of the surface resistivity of composite materials in embodiments of the invention and articles made therefrom can be determined using the standard ANSI/ESD STM11.13 the contents of which are incorporated herein by reference in their entirety. FIG. 22 (a) illustrates test points (1-9) on discs 2204 and a rectangular plaque 2208 used to measure the resistance.

FIG. 22(b) illustrates resistance of disc (circles) and rectangular plaques (triangles) molded from 5 wt% SWNTs in PEEK. The error bars represent  $\pm 1$  standard deviation based on 3 measurements. For both the disc and plaque, the resistance measurement results show that

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variation in resistance can be a factor of 100 or less and in some embodiments the variation in resistance can be a factor of 10 or less within a sample or for multiple samples.

FIG. 22(c) illustrates resistance test results for 5 wt% SWNTs in PEEK for molded discs 2204 of 5 wt% SWNTs in PEEK. Small error bars represent +/- 3 standard deviations of 15 measurements (5 samples x 3 measurements/sample using PRS-801). Large error bars (wide) represent measurement reproducibility (+/- 3 standard deviations) based on replicate measurements on one sample (9 positions x 10 measurements/position using PRS-801). The results show that variation in resistance can be a factor of 100 or less and in some embodiments the variation in resistance can be a factor of 10 or less within a sample or for multiple samples made with compositions in embodiments of the present invention.

The results show that the articles have a surface resistivity uniformity within a factor of 100 and in some cases within a factor of 10 for two or more resistance measurement test points on the test article. This illustrates the improved distribution of the single walled carbon nanotubes in the polymer in such compositions and is supported by the high storage modulus compared to the base polymer and low storage modulus slope  $z$ , in some embodiments  $z$  is less than about 0.5, in other embodiments  $z$  is less than 0.35, and in still others  $z$  is less than 0.2 for these materials. Embodiments of the present invention provide materials having substantially uniform surface resistivity across a sample, in some embodiments the substantial uniform surface resistivity of any point on the surface of a sample of the composite of single walled nanotube dispersed in the polymer. This is advantageous in electrostatic discharge applications of the composites in articles such as chip trays, reticle and wafer carriers, shippers, test sockets and the like.

### EXAMPLE 13

Thermal diffusivity of the sample in Example 12 was measured using ASTM Method E1461-01.

Representative material:  $1.95 \times 10^{-7} \text{ m}^2/\text{s}$ , the unfilled material:  $0.95 \times 10^{-7} \text{ m}^2/\text{s}$ .

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$$k = \alpha \rho C_p$$

$$\frac{k_{blend}}{k_{PEEK}} = \frac{\alpha_{blend} \rho_{blend} C_{p,blend}}{\alpha_{PEEK} \rho_{PEEK} C_{p,PEEK}}$$

$$\rho_{blend} C_{p,blend} \geq \rho_{PEEK} C_{p,PEEK}$$

$$k_{blend} \geq 2k_{PEEK}$$

Thermal conductivity was determined to be at least 2x neat PEEK. The higher thermal diffusivity improves thermal management.

#### EXAMPLE 14

This example illustrates a composite material of the present invention that used single walled carbon nanotubes, CNI, Houston, TX type (Bucky ESD34) in the method of Example 1 to prepare samples of composite materials. Test methods are incorporated herein by reference in their entirety.

The sample had a specific gravity of 1.33 g/cm<sup>3</sup> measured using ASTM test method D 792. The Izod impact strength (notched) measured utilizing ASTM test method D256 was found to be 43 J/m.

Surface resistivity was <10<sup>4</sup> ohms/sq as measured by test method FGTM-1207; surface resistance was measured to be 10<sup>5</sup> ohms by test method ESD S11.11 and the static decay of the sample was 0.22 sec as determined by test method FGTM-1208.

Aqueous leachable anions from the sample were determined to be about 510 ng/g by the method of FGTM-1344; aqueous leachable cations from the sample were determined to be about 59 ng/g by the method of FGTM-1344. Acid leachable metals from the sample were determined to be about 510 ng/g. Outgassing organics were determined to be less than 0.010 micrograms/g by test method FGTM-1350 (see also U.S. Pat. Appln. Publication No.: 2030066780, Zabka et al, filed October 4, 2001 the contents of which are incorporated herein by reference in their entirety).

Although the present invention has been described in considerable detail with reference to certain preferred embodiments thereof, other versions are possible. Therefore the spirit and scope of the appended claims should not be limited to the description and the preferred versions contain within this specification.

## CLAIMS

What is claimed is:

- Claim 1. A composition comprising:
- a polymer melt and an amount of single walled carbon nanotubes extrusion compounded together in the composition, the amount of said nanotubes dispersed in the polymer, said composition has a storage modulus  $G'$  that is substantially invariant with further extrusion compounding of the composition.
- Claim 2. The composition of claim 1 wherein said polymer is a high temperature, high strength thermoplastic polymer.
- Claim 3. The composition of claim 1 wherein a storage modulus at low frequency of the composition is at least about 90 times a storage modulus at low frequency of the polymer when the amount of single walled nanotubes distributed in the composition is 0.5% wt.
- Claim 4. The composition of claim 1 wherein an increase in molding shear flow rate or strain of the composition increases the electrical resistivity of an article molded by said composition.
- Claim 5. An article comprising a molded composition of claim 1 wherein said molded composition is electrically dissipative.
- Claim 6. An article comprising a molded composition of claim 1 wherein said molded composition is flame retardant.
- Claim 7. The composition of claim 1 wherein the polymer melt comprises PEEK, PI, or PEI.
- Claim 8. The composition of claim 1 wherein the polymer melt comprises PEEK or PEI.
- Claim 9. An article comprising a molded composition of claim 1 wherein said molded composition is electrically insulating and wherein said molded composition becomes electrically dissipative with heating.
- Claim 10. The composition of claim 1 wherein the amount of single walled carbon nanotubes is less than 10% by weight.

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- Claim 11. The composition of claim 1 wherein the amount of single walled carbon nanotubes is 7% by weight or less.
- Claim 12. The composition of claim 1 wherein an axial force measured in a squeeze flow test of said composition is greater than an axial force measured on a second extrusion compounded polymer composition comprising the nanotubes distributed into an extruded melt of the polymer, said nanotubes added into to the extruded melt of the polymer at a location equal to or greater than half the length of an extruder used to make the composition of claim 1 and the second composition.
- Claim 13. A composition comprising:  
a polymer melt and an amount of single walled carbon nanotubes extrusion compounded together in the composition, the amount of said nanotubes distributed and or dispersed in the polymer melt forms an electrically dissipative solid in a low shear flow molding process, the electrical resistivity of an article molded from said composition increases with increasing molding shear flow rate.
- Claim 14. The composition of claim 13 wherein said polymer is a high temperature, high strength thermoplastic polymer.
- Claim 15. The composition of claim 13 wherein a storage modulus at low frequency of a non-solid sample of the composition is at least about 90 times a storage modulus at low frequency of a non-solid sample of the polymer when the amount of single walled nanotubes distributed in the composition is 0.5% wt.
- Claim 16. An article comprising the composition of claim 13 molded in a low shear flow rate process.
- Claim 17. The article of claim 16 wherein the resistivity can be increased by extensional flow.
- Claim 18. An article comprising a molded composition of claim 13 wherein said molded composition is flame retardant.
- Claim 19. The composition of claim 13 wherein the polymer melt comprises PEEK, PI, or PEI.

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- Claim 20. The composition of claim 13 wherein the polymer melt comprises PEEK or PEI.
- Claim 21. An article comprising a molded composition of claim 13 wherein said molded composition is electrically insulating and wherein said molded composition becomes electrically dissipative with heating.
- Claim 22. The composition of claim 13 wherein the amount of single walled carbon nanotubes is less than about 10% by weight.
- Claim 23. The composition of claim 13 wherein the amount of single walled carbon nanotubes is about 7% by weight or less.
- Claim 24. An article comprising:  
a composition of a polymer that is a continuous phase and an amount of single walled carbon nanotubes dispersed in the polymer, wherein a storage modulus at low frequency on a non-solid sample of the article is at least about 90 times a storage modulus at low frequency of a non-solid sample of the polymer when the amount of single walled nanotubes dispersed in the composition is 0.5% wt.
- Claim 25. The article of claim 24 where the article is electrically dissipative.
- Claim 26. The article of claim 24 wherein an electrical resistivity of the article is reduced by extensional flow.
- Claim 27. The article of claim 24 where the article is flame retardant.
- Claim 28. The article of claim 24 where the article is flame retardant and electrically dissipative.
- Claim 29. The article of claim 24 wherein the polymer comprises PEEK, PI, or PEI
- Claim 30. The article of claim 24 wherein the polymer melt comprises PEEK or PEI.
- Claim 31. The article of claim 24 where the article is electrically insulating and wherein said the article becomes electrically dissipative with heating.

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- Claim 32. The article of claim 24 wherein the amount of single walled carbon nanotubes is less than about 10% by weight.
- Claim 33. The article of claim 24 wherein the amount of single walled carbon nanotubes is 7% by weight or less.
- Claim 34. The article of claim 24 that has an surface resistivity of less than about  $10^9$  ohms/sq.
- Claim 35. The composition of claim 24 that has an surface resistivity of less than about  $10^7$  ohms/sq.
- Claim 36. The composition of claim 24 that has an surface resistivity of less than about  $10^4$  ohms/sq.
- Claim 37. A composition comprising:  
a thermoplastic polymer; and  
a network of single walled carbon nanotubes dispersed in said thermoplastic polymer, a melt of said composition has a storage modulus proportional to frequency according to  $G' = K\omega^z$  where K is a proportionality constant,  $\omega$  is the frequency between 0.01 and 1 rad/sec, and z is less than 1.7; and  
wherein an amount of said single walled carbon nanotube in said composition is greater than 0.5 wt%, said storage modulus at a fixed frequency decreases with further extrusion compounding of the composition.
- Claim 38. The composition of claim 37 wherein the metal extractables of said composition is less than 200 microgram/gram of iron as determined by acid digestion of said composition.
- Claim 39. The composition of claim 37 wherein said single walled carbon nanotubes are single walled carbon nanotubes having an aspect ratio of 100 or more.
- Claim 40. The composition of claim 37 wherein said composition outgasses organics less than 0.01 microgram/gram.

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- Claim 41. The composition of claim 37 where said single walled carbon nanotubes are not polymer wrapped single walled carbon nanotubes.
- Claim 42. The composition of claim 37 having a surface resistivity less than  $10^9$  ohms/sq.
- Claim 43. The composition of claim 37 wherein the amount of single walled carbon nanotubes is between 0.5wt % and 10 wt%.
- Claim 44. The composition of claim 37 wherein the network is characterized by a storage modulus that is at least 90 times greater than the storage modulus of the polymer at a frequency of 1 rad/sec or less when the amount of single walled carbon nanotubes is between 2 and 7 wt %.
- Claim 45. The composition of claim 37 wherein the composition does not comprise added carbon powders.
- Claim 46. The composition of claim 37 wherein the volume resistivity or surface resistivity of said composition can be decreased with heat treatment.
- Claim 47. A fluid handling article comprising the composition of claim 37.
- Claim 48. A carrier comprising the composition of claim 37.
- Claim 49. A housing comprising the composition of claim 37.
- Claim 50. The composition of claim 37 wherein the network is characterized by a storage modulus that is at least 150 times greater than the storage modulus of the polymer at a frequency of 0.1 rad/sec when the amount of single walled carbon nanotubes is greater than 2 wt%.