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(54) **COMPOSITIONS COMPRISING CARBON NANOTUBES AND ARTICLES FORMED THEREFROM**

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(57) **ABSTRACT**

Improved compositions comprise a polymer and carbon fibers, such as nanotubes. In some embodiments, the carbon fibers, e.g., nanotubes, can be mechanically blended or incorporated into the polymer, while in some embodiments carbon nanotubes also may be covalently bonded to the polymer to form corresponding covalent materials. In particular, the polymer can be covalently bonded to the side walls of the carbon nanotubes to form a composite with particularly desirable mechanical properties. Specifically, the bonding of the polymer to the nanotube sidewall can provide desirable mechanical properties of the composite due to the orientation relative to other types of association between the nanotubes and the polymer. The processing of the nanotubes can be facilitated by the dispersion of the nanotubes in an aqueous solution comprising a hydrophilic polymer, such as ethyl vinyl acetate. A dispersion of nanotubes can be combined with a polymer in an extrusion process to blend the materials under high shear, such as in an extruder. In general, various articles can be formed that take advantage of the properties of the composite materials incorporating a polymer and carbon fibers, such as carbon nanotubes.

## COMPOSITIONS COMPRISING CARBON NANOTUBES AND ARTICLES FORMED THEREFROM

### FIELD OF THE INVENTION

[0001] The invention generally relates to compositions comprising polymers and carbon nanotubes or other carbon fibers. In particular, in some embodiments the invention relates to compositions having functionalized carbon nanotubes, which can be covalently attached to polymers. Additionally, the invention also relates to methods of making the compositions. Furthermore, the invention relates to articles, such as containers or functional articles, that are formed from the compositions.

### BACKGROUND OF THE INVENTION

[0002] Technological developments impose increasing demands on material properties to achieve desired objectives. On the other hand, improved material capabilities correspondingly can provide improved performance capabilities for corresponding products that incorporate the improved materials. Furthermore, composite materials have been found to be a way to combine desired properties of different compositions to obtain a material that benefits from the properties of the plurality of compositions.

[0003] Carbon fibers generally have been formed with a range of properties and morphologies. In particular, carbon nanotubes, which are generally cylindrical forms of graphitic carbon, exhibit useful mechanical and electrical properties including, for example, large tensile strength and large electrical conductivity. Carbon nanotubes can exist in single wall and multiple wall forms, both of which can be prepared by chemical vapor deposition (CVD) techniques. In general, process conditions such as, for example, deposition temperature and catalyst selection can influence the formation of the different structures. Additionally, carbon nanotubes can be electrically conducting or semiconducting, depending on structure.

[0004] Advanced products may require special handling approaches due to the sensitivity of the products to damage and degradation. In particular, some products, such as semiconductor devices, silicon wafers and the like, can be damaged during transportation, and/or processing, for example, as a result of the products contacting each other. Consequently, specialized containers have been developed to transport these products. These specialized containers can be formed, for example, from molded thermoplastic materials, which have structure suitable for holding a plurality of products in a desired orientation within the container. The interior structure of these containers typically prevents the products from contacting each other, and thus helps reduce product damage that can occur during transportation of the products.

[0005] Some articles have high electrical conductivities to appropriately function in their applications. Specifically, a range of components delivers high electrical conductivity within a corresponding device. For example, many electrical generation units incorporate electrically conductive elements. In particular, fuel cells can have bipolar plates that provide electrical conduction between neighboring cells connected in series while simultaneously providing for flow of fuels and oxidizing agents and preventing material flow between the neighboring cells. Similarly, many battery structures incorporate electrically conductive elements to facilitate electrical connection of the battery poles with the battery electrodes.

### SUMMARY OF THE INVENTION

[0006] In a first aspect, the invention pertains to a composition comprising a polymer covalently bonded to the side walls of carbon nanotubes. Additionally, the invention pertains to an article such as, for example, electrodes, containers and the like, comprising a polymer covalently bonded to the side walls of carbon nanotubes.

[0007] In a second aspect, the invention pertains to an aqueous dispersion of comprising ethyl vinyl acetate and carbon fibers. In these embodiments, the aqueous dispersion of the carbon fibers in the ethyl vinyl acetate can facilitate injection of the nanotubes into process equipment such as, for example, extruders.

[0008] In another aspect, the invention pertains to an article comprising a polymer and fluorinated carbon nanotubes, wherein the fluorinated carbon nanotubes provide increased resistance to chemical degradation.

[0009] In a further aspect, the invention pertains to a method of forming a composite comprising injecting a liquid dispersion of carbon fibers within an extruder having a polymer within the extruder and applying shear to the blend of carbon fibers and polymer.

[0010] In addition, the invention pertains to a wafer carrier comprising slots for the support of a wafer, wherein the slots comprise wafer contact points having a surface with a composite of polymer covalently bonded to the carbon nanotubes.

[0011] Furthermore, the invention pertains to a fuel cell comprising a bipolar plate comprising a composite of polymer covalently bonded to carbon nanotubes.

### DETAILED DESCRIPTION OF THE INVENTION

[0012] Improved compositions comprise a polymer and carbon fibers, such as nanotubes. In some embodiments, the carbon fibers, e.g., nanotubes, can be mechanically blended or incorporated into the polymer, while in some embodiments carbon nanotubes also may be covalently bonded to the polymer to form corresponding covalent materials. In particular, the polymer can be covalently bonded to the side walls of the carbon nanotubes to form a composite with particularly desirable mechanical properties. Specifically, the bonding of the polymer to the nanotube sidewall can provide desirable mechanical properties of the composite due to the orientation relative to other types of association between the nanotubes and the polymer. The processing of the nanotubes can be facilitated by the dispersion of the nanotubes in an aqueous solution comprising a hydrophilic polymer, such as ethyl vinyl acetate. A dispersion of nanotubes can be combined with a polymer in an extrusion process to blend the materials under high shear, such as in an extruder. In general, various articles can be formed that take advantage of the properties of the composite materials incorporating a polymer and carbon fibers, such as carbon nanotubes. Also, fluorinated nanotubes can be used to further improved the properties of the composites for certain applications. For example, fluorination of the nanotubes can impart greater chemical inertness, transparency and water resistance.

[0013] Due to the presence of the carbon nanotubes or carbon fibers generally, the compositions can exhibit improved physical properties such as, electrical conductivity, enhanced tensile strength, thermal stability, resistance to

chemical degradation, transparency and combinations thereof. The carbon nanotubes can be dispersed through the material, formed as a coating or incorporated into more elaborate structures. In some embodiments, the compositions can be used to form, for example, a container suitable for preventing electrostatic charge build up, which reduces the occurrence of electrostatic discharge (ESD) involving the products contained within the container. In other embodiments, the compositions can be used to form electrically conductive polymer structures such as bipolar plates, current collectors, battery pins, electrodes, gas diffusion electrodes and the like.

[0014] Carbon nanotubes are generally cylindrical forms of graphitic carbon that exhibit useful mechanical and electrical properties. In general, carbon nanotubes can exist as single wall and multiple wall structures. Single wall carbon nanotubes are tubular structures comprising a single graphene sheet, while multiple wall carbon nanotubes comprise multiple concentric graphene sheets. Single and multiple wall carbon nanotubes can be made, for example, by known catalytic chemical vapor deposition (CVD) techniques. For example, the synthesis of single wall carbon nanotubes by CVD is generally described in "Synthesis, Integration, and Electrical Properties of Individual Single-Walled Carbon Nanotubes," Kong et al., *Applied Physics A*, Volume 69, pp. 305-308 (1999), which is hereby incorporated by reference herein. Synthesis of multiple wall carbon nanotubes is generally described in "Rapid Synthesis of Carbon Nanotubes by Solid-State Metathesis Reactions," O'Loughlin et al., *J. Phys. Chem. B*, Volume 105, pp. 1921-1924 (2001), which is hereby incorporated by reference herein. Both forms of nanotubes are commercially available. For example, single wall nanotubes are available from CarboLex (Lexington, Ky.) and Carbon Nanotechnologies, Inc (Houston, Tex.), and multiple wall carbon nanotubes are available from Applied Sciences Inc. (Cedarville, Ohio). With respect to the materials described herein, in some embodiments, the nanotubes can be single wall carbon nanotubes, multiple wall carbon nanotubes or combinations thereof. The nanotubes can be agglomerated, for example into nanotube particles or nanotube wires, or they can be dispersed nanotubes or a combination thereof.

[0015] Additionally, carbon nanotubes can be functionalized to impart desired properties to the carbon nanotubes. For example, some functionalized nanotubes can be more easily dispersed into aqueous or nonaqueous dispersions, and some functionalized nanotubes can be covalently bonded to polymers. Furthermore, functionalized nanotubes can facilitate bonding with the polymer. Fluorine functionalized nanotubes can be incorporated into composites that can have increased resistance to chemical degradation and/or increased transparency.

[0016] Some functionalization of carbon nanotubes is thought to generally functionalize the nanotubes at their ends. In addition, carbon nanotubes can be functionalized along their side walls. Thus, these functionalizations provide for covalent bonding of the carbon nanotubes either at their ends and/or along the side walls. As described above, carbon nanotubes exhibit useful mechanical and electrical properties including electrical conductivity and tensile strength. For example, carbon nanotubes can conduct electricity better than copper or gold, and can have a tensile strength that is greater than the tensile strength of steel. It is believed that the increased tensile strength is a result of the three-dimensional carbon network that forms the structure of the nanotubes.

[0017] The composites of the present disclosure can comprise carbon fibers associated with a polymer, which can be formed into articles having improved properties. The improved properties of the articles can be attributed to both the properties of the nanotubes and the properties of the polymers. Generally, selection of a particular polymer or combinations of polymers can be made based on the desired properties of the final product. For example, the selection of a polymer can be based on desired structural properties such as, for example, tensile strength, elasticity, transparency, and the like. Suitable polymers for particular articles are described further below. As used herein, polymer refers to linear, branched and crosslinked covalent structures. While nanotubes are technically polymers, as used herein polymers do not include compounds with a rigid and unique tertiary structure, such as carbon nanotubes.

[0018] As discussed above, semi-conductor devices, as well as other products, may be susceptible to damage from electrostatic discharge (ESD). In theory, electrostatic potentials can exist whenever suitable electrical insulators or semi-conductors are present. Specifically, materials such as, for example, nylon, polyester, polyurethane, polyvinyl chloride and poly(tetrafluoroethylene), tend to build up static charges. The build up of electrostatic charges in containers made from these materials can result in electrical discharge to products, such as semi-conductor devices, located within the containers. While the amount of energy transferred through ESD is relatively small, significant damage can result to the products located in the containers. Furthermore, conventional conductive coatings, which can be applied to containers to reduce the occurrence of ESD, tend to be degraded by recycling processes, and therefore the recycled or refurbished containers have to be re-coated with the conductive coating or replaced. As described herein, one way of reducing ESD in containers and other products is to form the containers from an electrically conducting composite composition comprising a polymer associated with carbon nanotubes.

[0019] Polymer—Carbon Fiber Compositions

[0020] As described above carbon fibers can be incorporated into, for example, polymer composites to provide desired mechanical and electrical properties by covalently bonding the carbon fibers to the polymer and/or by dispersing the fibers in a polymer. In some embodiments, the carbon fibers can be nanotubes, such as single wall carbon nanotubes multiple wall carbon nanotubes, or combinations thereof. Carbon nanotubes, which are generally cylindrical forms of carbon, can be covalently bonded to polymer systems by functionalizing the ends and/or the side walls of the carbon nanotubes, and subsequently reacting the functionalized nanotube with an appropriate polymer. Additionally or alternatively, the carbon nanotubes can be incorporated into a polymer system by dispersing the carbon nanotubes in a suitable polymer. In some embodiments, the carbon nanotubes can also be functionalized to facilitate dispersion in desired polymer systems. Dispersing and/or covalently bonding the carbon nanotubes into polymer systems can provide good incorporation and uniformity of the nanotubes throughout the polymer, which can enhance the mechanical and/or electrical properties of the polymer.

[0021] Carbon fibers are chemically resistant, rigid structures that can be used to produce articles such as, for example, tennis rackets, bicycles and golf clubs. For industrial uses, the carbon fibers can be formed into structures, such as sheets or other shapes. Carbon fibers can be pro-

duced from organic polymers such as, for example, poly-(acrylonitrile) that are stretched and oxidized to produce precursor fibers. The precursor fibers can then be heated in a nitrogen environment, which facilitates the release of volatile compounds and yields fibers that are primarily composed of carbon. Carbon fibers are commercially available in varying grades, which can have varying tensile strengths and weights. As used herein, carbon fibers can be a range of carbon fiber materials including, for example, carbon nanotubes. Carbon nanotubes are rolled up graphene sheets of carbon which exhibit useful mechanical and electrical properties. Generally, carbon nanotubes are described as comprising tubular graphene walls which are parallel to the filament axis. Additionally, carbon nanotubes can be hollow and can have ends caps which seal the tubular structure.

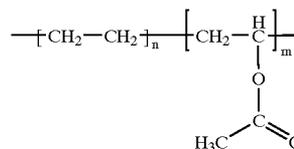
[0022] In some embodiments, the ends of single and multiple wall carbon nanotubes can be functionalized by treating the nanotubes with nitric acid (HNO<sub>3</sub>) or a sulfuric acid (H<sub>2</sub>SO<sub>4</sub>)-nitric acid mixture, both of which are known to remove the end caps of the carbon nanotubes and introduce oxygen-containing functional groups such as carboxyl groups. The carboxyl groups can be further reacted to form other functional groups, which can then be used to covalently bind the carbon nanotubes to polymers or other compounds. For example, primary amines (RNH<sub>2</sub>) can be reacted with carboxyl groups to form amide linkages using carbodimide chemistry, which can result CO—NH—R groups located on the ends of the nanotubes. Furthermore, nanotubes containing carboxyl groups can be refluxed in SOCl<sub>2</sub>, which can convert the carboxyl groups into acyl chlorides that can be further reacted into polymer systems having, for example, amine or alcohol functional groups. Generally, the functionalization reactions can be conducted in a suitable solvent such as, for example, 1,2-dichlorobenzene.

[0023] Purification and end functionalization of carbon nanotubes are generally discussed in, for example, "Covalently Functionalized Nanotubes as Nanometer-Sized Probes in Chemistry and Biology," Wong et al., *Nature*, Volume 392, July, (1998), "Large-Scale Purification of Single-Wall Carbon Nanotubes: Process, Product, and Characterization," Rinzler et al., *Applied Physics A*, Volume 67, pp. 29-37 (1998), "Strong Luminescence of Solubilized Carbon Nanotubes," Riggs et al., *J. Am. Chem. Soc.*, 122, 5879-5880 (2000), and "Oxygen-Containing Functional Groups on Single-Wall Carbon Nanotubes: NEXAFS and Vibrational Spectroscopic Studies," Kuznetsova et al., *J. Am. Chem. Soc.*, Volume 123, pp. 10699-10704 (2001), all of which are hereby incorporated by reference herein.

[0024] Additionally, the carbon nanotubes can be functionalized along their side walls, which can facilitate reacting the carbon nanotubes into desired polymer systems. Alternatively, the carbon nanotubes may be functionalized on both the ends and the side walls of the nanotubes. In some embodiments, the carbon nanotubes can be reacted with fluorine gas to fluorinate the side walls of the nanotubes. The fluorinated nanotubes can be further functionalized by reactions with nucleophiles such as amines, hydrazines and alkyl lithium compounds. These side wall derivatized carbon nanotubes are described further, for example, in Published U.S. patent application 2001/0031900A to Margrave et al., entitled "Chemical Derivatization Of Single-Wall Carbon Nanotubes To Facilitate Solvation Thereof: And Use Of

Derivatized Nanotubes To Form Catalyst-Containing Seed Materials For Use In Making Carbon Fibers," incorporated herein by reference. As described above, fluorinated carbon nanotubes can be incorporated into composites to provide increased resistance to chemical degradation and/or increased transparency.

[0025] The carbon nanotubes can also be incorporated into dispersions to facilitate processing of the nanotubes into desired articles and/or coating of the nanotubes onto articles. In some embodiments, the dispersion can comprise an aqueous dispersion of carbon nanotubes in ethyl vinyl acetate. Ethyl vinyl acetate is sold commercially under the trade name Bynel® by Dupont (Wilmington, Del.), under the trade name Plexar® by Equistar (Houston, Tex.), and under the trade name Evatane® by Atofina Chemicals (Philadelphia, Pa.). Generally, EVA is commercially available in various grades which can have varying vinyl acetate (VA) content (i.e., vinyl acetate monomer units in the polymer), density and melt indices. Suitable EVA formulations for use in the present disclosure include, for example, EVA formulations having a VA content from about 10 mole % to about 50 mole %, in further embodiments from about 15 mole percent to about 40 mole percent and in other embodiments from about 20 mole percent to about 35 mole percent. Additionally, suitable EVA formulations can have melt indices ranging from about 2.5 g/10 mn to about 800 g/10 mn at 190° C., using a 2.16 Kg load. The melt index is evaluated using the ASTM D1238 procedure, which is hereby incorporated by reference herein. In some embodiments, the EVA can have a density ranging from about 0.92 g/cm<sup>3</sup> to about 0.95 g/cm<sup>3</sup>. A person of ordinary skill in the art will recognize that additional ranges and subranges of VA content, melt indices and density within the explicit ranges are contemplated and are within the present disclosure. The structure of EVA is shown below wherein the relative amounts of the two monomer units is represented by the n and m subscripts:



[0026] Below are tables displaying data for several grades of commercially available EVA formulations.

TABLE 1

EVATANE® Grades	VA content (%)	Melt index (g/10 mn)	Melting point (° C.)
24-03	23-25	2.5-3.5	79
28-03	26-28	3-4.5	75
28-05	27-29	5-8	73
28-25	27-29	22-29	72

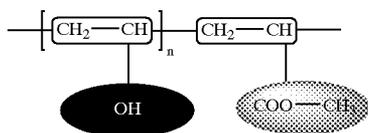
[0027]

TABLE 2

Property	ASTM Test Method	Unit	Bynel <sup>(®)</sup> Grades			
			1123	1124	1E554	11E573
Melt Index	D1238, 190/2.16	dg/min	6.4	25	8.0	6.9
Density	D1505	g/cm <sup>3</sup>	0.946	0.947	0.93	0.923
Melt Point	DSC, D3418	° C. (° F.)	74 (165)	70 (158)	94 (201)	95 (203)
Freeze Point	DSC, D3418	° C. (° F.)	51 (124)	51 (124)	76 (169)	80 (176)
Vicat Softening Point	D1525	° C. (° F.)	50 (122)	49 (120)	68 (154)	71 (160)

[0028] In other embodiments, the carbon nanotubes can be dispersed in poly(vinyl alcohol) (PVA). PVA is commercially sold under the trade name Elvanol<sup>®</sup> by Dupont (Wilmington, Del.), under the trade name Celvol<sup>™</sup> by Celanese Chemicals (Dallas, Tex.), and from Erkol (Spain). Generally, suitable PVA formulations can have a molecule weight average from about 10,000 to about 190,000. Below is a table which displays data for suitable formulations of PVA. The PVA generally can have a density from about 1.27 to about 1.31 g/cm<sup>3</sup>. The melting point of the PVA generally can range from about 85 to about 200° C. A person of ordinary skill in the art will recognize that additional ranges within the explicit ranges of molecular weight, density and melting point are contemplated and are within the present disclosure.

[0029] The PVA can be partially or fully hydrolyzed. The structure of PVA is shown below wherein the relative amounts of the two monomer units is represented by the n subscript:



[0030] In general, PVA is formed commercially by the hydrolysis/saponification of poly vinyl acetate or other poly vinyl small aliphatic ester. The degree of hydrolysis determines relative amounts of vinyl alcohol monomer units in the polymer.

TABLE 3

Grade Designations	Viscosity <sup>a</sup>	Percent Hydrolysis <sup>b</sup>	Solution pH	Volatiles, % max.	Ash, % max. <sup>c</sup>
Elvanol <sup>®</sup> 51-05	5-6	87-89	5.0-7.0	5	0.7
Elvanol <sup>®</sup> 52-22	21-26	87-89	5.0-7.0	5	0.7
Elvanol <sup>®</sup> 50-42	44-50	87-89	5.0-7.0	5	0.7

<sup>a</sup>Viscosity in mPa · s (cP) of a 4% solids aqueous solution at 20° C. (68° F.), determined by Hoesppler falling ball method

<sup>b</sup>Mole percent hydrolysis of acetate groups, dry basis

<sup>c</sup>Dry basis: calculated as % Na<sub>2</sub>O

[0031] For blends of nanotubes with polymers, the presence of EVA or PVA can stabilize the adhesion or dispersion of the blend, especially for additional structural polymers

such as polyolefins, polycarbonates, polystyrene, and acrylonitrile butadiene styrene copolymers. Similarly, other polyalcohols can be used. For example, soluble starches or other polysaccharides and derivatives thereof can be used. Also, other copolymers with varying degrees of vinyl monomers, vinylalcohol monomers, and/or vinyl ester monomers can be used if sufficiently soluble in aqueous solutions.

[0032] In other embodiments, the carbon nanotubes can be functionalized to increase the solubility of the nanotubes in desired polymers and/or solvents, which facilitates the formation of polymer/nanotube and/or solvent/nanotube dispersions. For example, as discussed above, carbon nanotubes can be treated with acid to form carboxyl groups on the ends of the nanotubes, which can be further reacted to form acyl chlorides. The acyl chlorides can be reacted with, for example, amines such as RNH<sub>2</sub>, where R=(CH<sub>2</sub>)<sub>n</sub>CH<sub>3</sub> and n=9-50, which can increase the solubility of the nanotubes in organic solvents such as, for example, chloroform, dichloromethane, benzene, toluene, tetrahydrofuran, chlorobenzene and combinations thereof. Additional description of solubilizing carbon nanotubes can be found in U.S. Pat. No. 6,331,262 to Haddon et al., entitled "Method Of Solubilizing Shortened Single-Walled Carbon Nanotubes In Organic Solutions," which is hereby incorporated by reference herein.

[0033] Suitable polymers for use in the compositions of the present invention include homopolymers, copolymers, block copolymers and blends and copolymers thereof. Suitable polymers include, for example, Polyetherimide (PEI), Polyimide (PI), Poly ether sulfone (PES), Poly phenyl sulfone (PPS), Poly sulfone, Polystyrene, Per fluoro alkoxy (PFA), Fluorinated Ethylene Propylene (FEP), ETFE, polybutylene terephthalate (PBT), polyolefins (PO), polyethylene terephthalate (PET), styrene block co-polymers (e.g. Kraton<sup>®</sup>), styrene-butadiene rubber, nylon in the form of polyether block polyamide (PEBA), polyetheretherketone (PEEK), poly(vinylidene fluoride), poly(tetrafluoroethylene) (PTFE), polyethylene, polypropylene, poly(vinylchloride) (PVC), ethyl vinyl acetate, and blends and copolymers thereof. In general, the selection of a particular polymer for use in the composition will be guided by the intended application of the composition. In some embodiments, the polymers can be functionalized to contain functional groups suitable for reacting with the functional groups on the derivatized nanotubes to form composites where the nanotubes are covalently bonded to the polymers. Suitable functional groups include, for example, amines, alcohols, alkyl lithium compounds, hydrazines, and combinations thereof. Alternatively, the selected polymer can contain suitable functional groups such that functionalization of the polymer

is not required. For example, polyamides such as nylon can contain un-reacted amine groups which can replace chloride groups on the functionalized nanotubes.

[0034] In general, the improved compositions comprise a polymer associated with carbon nanotubes. In some embodiments, the composition is not soluble in water and in particular, the polymer may not be soluble in water. Generally, the carbon nanotubes are present in a concentration less than about 50 percent by weight. In some embodiments, the carbon nanotubes are present in a concentration from about 0.1 percent by weight to about 40 percent by weight and in other embodiments the nanotubes can be present in a concentration from about 1 percent by weight to about 20 percent by weight. One of ordinary skill in the art will recognize that additional ranges within these explicit ranges are contemplated and are within the scope of the present disclosure.

[0035] In embodiments where preserving the transparency of the polymer is desired, the composition generally comprises carbon nanotubes at a concentration of less than about 0.5 percent by weight. Additionally, single wall carbon nanotubes tend to preserve transparency better than the multiple wall carbon nanotubes. In embodiments where it is desired to enhance the strength and/or thermal stability of the polymer, the carbon nanotubes can be incorporated into the polymer at a concentration from about 5 percent by weight to about 50 percent by weight.

[0036] Additionally, in some embodiments, the composition can further comprise additional components such as surfactants, fillers, processing aids, viscosity modifiers and the like. Generally, the additional components are each present at a concentration of no more than about 5 percent by weight. In particular, some embodiments of the present invention may comprise liquid dispersions of carbon nanotubes in a solvent. In these embodiments, the solvent can be removed during and/or after processing such that the final polymer/nanotube composite comprises less than 1 percent by weight of the solvent.

[0037] In some embodiments, the composition can comprise some or all of the carbon nanotubes covalently bonded to the polymer. Specifically, the composites can comprise at least about 25 weight percent of the carbon nanotubes being covalently bonded to the polymer, in further embodiments at least about 40 weight percent, in additional embodiments at least about 75 weight percent and in other embodiments at least about 95 weight percent of the carbon nanotubes are covalently bonded to the polymer. A person of ordinary skill in the art will recognize that additional ranges of covalent bonding amounts within the explicit ranges are contemplated and are within the present disclosure. Reacting the carbon nanotubes into a polymer can increase the dispersion of the nanotubes throughout the polymer and permits an atomic level order of the carbon nanotubes.

[0038] In general, the molecular weights of the polymers, the number of functional groups on the polymers, the relative amounts of the nanotubes and the polymer and the like influence the chemical structure of the composites. Similarly, these features can be adjusted to obtain a composite with desired properties. For example, the functionalized nanotubes can be used to cross link multifunctional polymers, such that the polymer chains are connected by the carbon nanotubes. In some embodiments, self-ordering

composites can be formed with properties reminiscent of block copolymers can be formed.

[0039] The composite structures can be formed under processing conditions that involve generally predictable bonding of the polymer with the nanotubes. For example, the polymers can have a single functional group for bonding with the functionalized nanotubes. The molecular weights of the polymers can be selected to yield appropriate structures in view of the sizes of the nanotubes. The processing conditions and the functionalization can be controlled to generally form structures with a single polymer chain bonded with a single nanotube. By analogy with polymer block copolymers, this polymer-block-nanotube structure can exhibit standard block copolymer behavior with the nanotubes having the properties of one block and the polymer having the properties of a second block. Similar, multiple block structures can be formed. These blocked structures can exhibit self-ordering.

#### [0040] Composite Processing

[0041] The compositions of the present disclosure, which generally comprise carbon nanotubes associated with a polymer, can be processed directly into desired articles by processes such as extrusion, injection molding and the like and/or can be incorporated into a process to provide a coating or layer on a preformed article. In some embodiments, the carbon nanotube can be associated with the polymer by mechanically blending or mixing the nanotubes into a polymer. In other embodiments, the carbon nanotubes can be functionalized and reacted with a polymer to form a polymer/carbon nanotube composite structure. As described above, functionalizing the nanotubes can make the nanotubes more dispersible in a polymer, which can increase the uniformity of the nanotubes throughout the polymer. In some embodiments, the composites can be produced and the articles formed in one continuous process, while in other embodiments the production of the composite and the formation of an article from the composite can be done separately.

[0042] In general, the bonding between a functionalized carbon nanotube and a suitable polymer can be performed in solution, in a polymer melt or some combination thereof, such as the blending of a carbon nanotube dispersion and polymer melt. In general, the nanotubes are mixed through the polymer composition to form a roughly uniform composition. A significant amount of shear may be applied to combine the materials.

[0043] In some embodiments, to form a polymer/nanotube composite, a liquid nanotube dispersions can be formed and injected into an extruder having a polymer within the extruder, wherein the extruder can provide shear to blend the carbon nanotubes within the polymer to obtain a composite having suitable mixing of the nanotubes throughout the polymer. As described further below, it may be desirable to include a hydrophilic polymer, in particular ethyl vinyl acetate, to facilitate dispersion of the carbon nanotubes. In other embodiments, the nanotubes can be introduced into an extruder in an agglomerated particle form by using a solid feeder or the like, and combined with a polymer located within the extruder to form a nanotube/polymer composite. In general, suitable extruders are available commercially. The extruder can be a single screw or multiple screw extruder, such as a two screw extruder. Suitable commercial

extruders include, for example, Berstorff model ZE or KE extruders (Hannover, Germany), Leistritz model ZSE or ESE extruders (Somerville, N.J.) and Davis-Standard mark series extruders (Pawcatuck, Conn.).

[0044] In general, dispersions can be formed with the carbon nanotubes in aqueous or non-aqueous dispersants. Processing aids can be used, such as surfacants and the like. In particular, the dispersion can comprise an aqueous dispersion of carbon nanotubes and ethyl vinyl acetate. It has been discovered that ethyl vinyl acetate (EVA) can stabilize an aqueous dispersion of carbon nanotubes. In other embodiments, the dispersion can comprise an aqueous dispersion of carbon nanotubes and a poly alcohol. Generally, any poly alcohol that is soluble or partially soluble in water can be used to form the dispersions. In one embodiment, the dispersion can comprise an aqueous dispersion of carbon nanotubes in poly(vinyl alcohol) (PVA). In some embodiments, the polymer/nanotubes dispersion can comprise a weight ratio of polymer to nanotubes from about 0.005 to about 1, while in other embodiments from about 0.01 to about 0.67. One of ordinary skill in the art will recognize that additional ranges of concentration ratios of polymer to nanotubes within these explicit ranges are contemplated and are within the scope of the present disclosure. In some embodiments, to form the liquid nanotube dispersions, desired amounts of nanotubes and liquid along with an optional polymer such as EVA and/or PVA, can be combined and mixed by any suitable processing apparatus such as a blender, mixer or the like. The liquid nanotube dispersion can then be injected into an extruder or a high shear mixer and mixed with a polymer material that is present in the extruder/mixer. Generally, any liquids used to form the polymer/nanotube dispersion can be evaporated during the extrusion process such that the final composite is substantially free of solvents, processing aids and other liquids. Vapors from the liquid can be vented from the extruder as appropriate. In general, the polymer in the extruder can be introduced into the extruder by, for example, a hopper or other feeding apparatus, and the feeding apparatus can be heated to facilitate the process by softening the polymer.

[0045] Generally, the extruder can apply shear forces to the nanotube polymer mixture such that the nanotubes are mixed throughout the polymer to form a nanotube/polymer composite. In embodiments employing functionalized nanotubes, the shear forces applied by the extruder can promote reaction of the nanotubes with a suitable polymer(s) to form a composite structure in which the nanotubes are covalently attached to the polymer. Additionally, the nanotube/polymer composite can be directly processed into articles having desired size and shape by processes such as, for example, calendering, injection molding, compression molding and the like. For example, the composite can be feed from the extruder to a injection molding or compression molding apparatus such that the production of the nanotube/polymer composite and the formation of an article from the composite is a single process. In other embodiments, the extruder can be used to form an article by injecting the composite through a die and calendering the composite to form an article having a desired shape. One of ordinary skill in the art will recognize that the selection of a particular shaping process can be guided by the intended application of a particular article. Alternatively, the composite formed in the extruder or other mixing apparatus can be collected in

pellets or other desirable form and stored for subsequent processing into a final article.

[0046] In one embodiment, the nanotube/polymer composite can be feed from the extruder to an injection molding apparatus where the composite can be formed into a bipolar plate suitable for use in electrochemical cell applications. In these embodiments, the mold can be designed such that the bipolar plate has reactant flow channels formed into each side of the plate suitable for providing flow path for gasses. In other embodiments, the polymer/nanotube composite can be feed from the extruder to a mold where the composite can be molded into a container suitable for transporting semi-conductor wafers. In these embodiments, the mold can be designed such that the container has structural elements suitable for supporting the semi-conductor wafers.

[0047] In further embodiments, the carbon nanotubes/polymer composite can be coated onto an article by coating the article with a solvent/composite mixture or by forming the composite into a thin film that is laminated or calendered onto the surface of the structure. For solution based approaches, once the solvent evaporates, the carbon nanotubes/polymer composite can be deposited onto a surface of the article. In these embodiments, any appropriate means for coating can be used to apply the solvent/composite mixture to the article including, for example spraying, dip coating or the like. Additionally, in these embodiments, the solvent/dispersant can be, for example, a suitable commercially available solvent that can disperse or suspend the carbon nanotubes/polymer composite. In some embodiments, the solvent may be a non-polar solvent such as, for example, 1,2-dichlorobenzene. The solubility of single wall carbon nanotubes is generally discussed in, for example, "Dissolution of Small Diameter Single-Wall Carbon Nanotubes In Organic Solvents?," Bahr et al., Chem. Commun., pp. 193-194 (2001), which is hereby incorporated by reference herein. The polymer coated carbon nanotubes can then be used to coat an article such as, for example, a wafer carrier to provide an electrically conductive coating on the carrier.

[0048] Articles Formed From Composites

[0049] Articles, such as containers, carriers, fluid handling equipment, electrodes, electrically conductive elements for electrochemical cells and the like, can be formed from the polymer/carbon nanotube compositions described herein. Additionally or alternatively, an article can be coated with a polymer/carbon nanotube composition to form a layer on the surface of the article. In further embodiments, a coating comprising carbon nanotubes dissolved or suspended in a solvent can be applied to an article to form a coating on the surface of the article. Articles formed by polymer/nanotube composites and/or articles having a nanotube coating can have enhanced electrical and mechanical properties. Due to improved wear properties, some articles such as, containers, made from coating of polymer/nanotube composites can be refurbished and/or reused without a significant reduction of the mechanical and electrical properties of the container over reasonable periods of time.

[0050] In some embodiments, the polymer/carbon nanotube composition can be formed into a container by injection molding, compression molding or the like. In some embodiments, the containers can have structure on the interior of the container suitable for holding a plurality of products in a desired orientation within the container. For example, the

container can be designed to hold a plurality of semiconductor devices, while in other embodiments the container may be design to hold silicon wafers. A container designed to hold silicon wafers is described in, for example, U.S. Pat. No. 6,428,729 to Bhatt et al., entitled "Composite Substrate Carrier," which is hereby incorporated by reference herein. Additionally, a tray for semiconductor devices is described in application Ser. No. 10/194,948, filed on Jul. 12, 2002, entitled "Tray for Semiconductors," which is hereby incorporated by reference herein. Due to the carbon nanotubes, the containers or appropriate surfaces thereof can be electrically conductive and can reduce the build up of electrostatic charges, which may reduce the occurrence of ESD damage to the products contained within the container. In some embodiments, the wafer carrier or trays can comprise slots for supporting semi-conductor wafers, and the slots can comprise wafer contacts points having a surface with a composite of polymer associated with carbon nanotubes. The carbon nanotubes can be covalently attached to the polymer, blended into the polymer to form a physical composite, or a combination thereof. Since low levels of carbon nanotubes may be effective to generate desired levels of electrical conductivity especially if applied as a coating, the containers made out of the compositions of the present disclosure can have the ability to reduce ESD without the transparency of the container being compromised.

[0051] In other embodiments, a product such as a container can be formed from a thermoplastic material, and subsequently coated with a coating layer comprising a polymer associated with carbon nanotubes. In some embodiments, the product can be composed of the same polymer used to form the coating layer, while in other embodiments the polymer used to form the product can be a different polymer than the polymer used to form the coating layer. In these embodiments, the product can be coated with the coating layer by any suitable means including, for example, dip coating, spray coating, brushing, calendering, knife coating and/or the like. In some embodiments, the coating layer can be from about 0.0005 inches to about 0.005 inches thick, although a person of ordinary skill in the art will recognize that additional ranges within the explicit range are contemplated and are within the present disclosure. In further embodiments, the polymer/carbon nanotube compositions can be used to form electrically conductive structures such as bipolar plates, electrodes, gas diffusion electrodes for fuel cells, current collectors, components thereof and the like. In general, bipolar plates of a fuel cell are electrically conductive structures that electrically connect the anode of one electrochemical cell with the cathode of an adjacent electrochemical cell. Additionally, in a hydrogen/oxygen fuel cell, the bipolar plates generally have channels that provide flow pathways for oxygen to reach the cathode and hydrogen to reach the anode. For example, a bipolar plate can have horizontal channels on one side of the plate and vertical channels on the other side of the plate. The plates can be formed, for example, by injection molding or compression molding. In addition to providing electrical conductivity, the bipolar plates formed from compositions comprising carbon nanotubes can have greater mechanical strength, resistance to chemical degradation and thermal stability compared with bipolar plates formed from other materials. Bipolar plates suitable for use in electrochemical cell applications are disclosed, for example, in U.S. Pat. No. 6,677,071 to Yang, entitled "Bipolar Plate For A Fuel Cell,"

and U.S. Pat. No. 6,503,653 to Rock, entitled "Stamped Bipolar Plate For PEM Fuel Cell Stack," which are hereby incorporated by reference herein.

[0052] The polymer/nanotube compositions of the present disclosure can also be used to form electrode structures suitable for use in electrochemical cell applications. Generally, electrodes can comprise an active layer associated with a backing layer. The backing layer can be impervious to electrolyte but permeable to gas, while the active layer can be a porous structure comprising catalyst particles suitable for catalyzing the electrochemical reactions, conductive particles and a porous particle binder. In some embodiments, the polymer/nanotube composite can be processed, along with suitable catalytic particles, to form a porous active layer, which can be attached to a backing layer by adhesives or lamination to form an electrode structure. Suitable catalyst particles include, for example, platinum powders.

[0053] Generally, products, such as containers, made from a polymer/carbon nanotube composition, or products coated with a polymer/carbon nanotube composition, can be reused repeatedly, i.e., recycled without losing the electrically conductive properties. Thus, products made from the compositions of the present disclosure can be recycled and formed into recycled products, which retain the electrical products of the original product through many uses. Thus, the products may be less expensive to use relative to products that can only be used one or a few times without reapplying the electrically conductive coating.

[0054] The embodiments above are intended to be illustrative and not limiting. Additional embodiments are within the claims. Although the present invention has been described with reference to particular embodiments, workers skilled in the art will recognize that changes may be made in form and detail without departing from the spirit and scope of the invention.

We claim:

1. A composition comprising a polymer covalently bonded to the side walls of carbon nanotubes.
2. The composition of claim 1 wherein the nanotubes comprise single wall carbon nanotubes, multiple wall carbon nanotubes, or a combination thereof.
3. The composition of claim 1 wherein the carbon nanotubes are present in a concentration of less than about 50 percent by weight.
4. The composition of claim 1 wherein the carbon nanotubes are present in a concentration from about 0.1 percent by weight to about 40 percent by weight.
5. The composition of claim 1 wherein the polymer is selected from the group consisting of PEI, Polyimide, Poly ether sulfone (PES), Poly phenyl sulfone (PPS), Per fluoro alkoxy (PFA), Fluorinated ethylene propylene (FEP), Ethylene tri fluoro ethylene (ETFE) Poly sulfone, Polystyrene, Poly ether Ketone (PEK), Poly ether ketone ketone (PEKK), polybutylene terephthalate (PBT), polyolefins (PO), polyethylene terephthalate (PET), styrene block co-polymers, styrene-butadiene rubber, nylon in the form of polyether block polyamide (PEBA), polyetheretherketone (PEEK), poly(vinylidene fluoride), poly(tetrafluoroethylene) (PTFE), polyethylene, polypropylene, poly(vinylchloride) (PVC), ethyl vinyl acetate and blends and copolymers thereof.

6. The composition of claim 1 wherein the carbon nanotubes have functional groups attached to the side walls that bridge between the walls of the nanotubes and the polymer.

7. The composition of claim 6 wherein the polymer is a multifunctional polymer having two or more functional groups that are covalently bonded with carbon nanotubes.

8. The composition of claim 7 wherein the polymer is covalently bonded to the nanotubes to form polymer-nanotube structures that can self order.

9. The composition of claim 7 wherein the polymer is covalently bonded to the nanotubes such that polymer chains are crosslinked by the nanotubes.

10. An article comprising the composition of claim 1.

11. The article of claim 10 wherein the article comprises a wafer carrier suitable for transporting semi-conductor wafers.

12. The article of claim 10 wherein the article comprises a bipolar plate.

13. The article of claim 10 wherein the article comprises an electrode.

14. A liquid dispersion comprising ethyl vinyl acetate and carbon fibers.

15. The liquid dispersion of claim 14 wherein the carbon fibers comprise single wall carbon nanotubes, multiple wall carbon nanotubes or a combination thereof.

16. The liquid dispersion of claim 14 wherein the carbon fibers are present in a concentration of less than about 50 percent by weight.

17. The liquid dispersion of claim 14 wherein the carbon fibers are presenting a concentration from about 0.1 percent by weight to about 40 percent by weight.

18. The liquid dispersion of claim 14 wherein the carbon fibers comprise functional groups located on the ends of the nanotubes, along the side walls of the nanotubes, or both.

19. The liquid dispersion of claim 18 wherein the functional groups comprise fluorine.

20. The liquid dispersion of claim 14 wherein the dispersion comprises an aqueous dispersion.

21. The liquid dispersion of claim 14 wherein the EVA has a melt index from about 2 g/10 mn to about 800 g/10 mn as determined by ASTM D1238 procedure with a temperature of 190° C. and a load of 2.16 Kg.

22. The liquid dispersion of claim 14 wherein the EVA has a density from about 0.92 g/cm<sup>3</sup> to about 0.95 g/cm<sup>3</sup>.

23. The liquid dispersion of claim 14 wherein the EVA has a VA content from about 20 percent to about 30 percent.

24. The liquid dispersion of claim 14 wherein the weight ratio of EVA to nanotubes is from about 0.005 to about 1.

25. A liquid dispersion comprising poly(vinyl alcohol) and carbon fibers.

26. An article comprising a polymer and fluorinated carbon nanotubes.

27. The article of claim 25 wherein the carbon nanotubes comprise single wall carbon nanotubes, multiple wall carbon nanotubes or a combination thereof.

28. The article of claim 26 wherein the fluorinated carbon nanotubes are covalently bonded to the polymer.

29. The article of claim 26 wherein the fluorinated carbon nanotubes are mixed throughout the polymer.

30. The article of claim 26 wherein the polymer and fluorinated carbon nanotubes are coated onto the surface of the article.

31. The article of claim 26 wherein the fluorinated carbon nanotubes are present in a concentration of less than about 50 percent by weight.

32. The article of claim 26 wherein the fluorinated carbon nanotubes are present in a concentration from about 0.1 percent by weight to about 40 percent by weight.

33. The article of claim 26 wherein the polymer is selected from the group consisting of polybutylene terephthalate (PBT), polyolefins (PO), polyethylene terephthalate (PET), styrene block co-polymers, styrene-butadiene rubber, nylon in the form of polyether block polyamide (PEBA), polyetheretherketone (PEEK), poly(vinylidene fluoride), poly(tetrafluoroethylene) (PTFE), polyethylene, polypropylene, poly(vinylchloride) (PVC), ethyl vinyl acetate and blends and copolymers thereof.

34. The article of claim 26 wherein the article comprises a wafer carrier having structural elements suitable for transporting a plurality of semi-conductor wafers.

35. The article of claim 26 wherein the article comprises a bipolar plate suitable for use in electrochemical cells.

36. A method of forming a composite, the method comprising injecting a liquid dispersion of carbon fibers within an extruder having a polymer within the extruder and applying shear to blend the carbon fibers and the polymer.

37. The method of claim 36 wherein the liquid dispersion of carbon fibers comprises an aqueous dispersion of carbon fibers and ethyl vinyl acetate.

38. The method of claim 37 wherein the carbon fibers comprise single wall carbon nanotubes, multiple wall carbon nanotubes, or a combination thereof.

39. The method of claim 37 wherein the carbon fibers are present at a concentration of less than about 50 percent by weight.

40. The method of claim 37 wherein the carbon fibers are present at a concentration from about 0.1 percent by weight to about 40 percent by weight.

41. The method of claim 36 wherein the carbon fibers comprise functional groups that can covalently bond with the polymer, wherein covalent bonding between the carbon fibers and the polymer occurs in the extruder.

42. The method of claim 36 wherein the composite is fed from the extruder to a shaping apparatus where the composite is formed into an article having a desired shape and size.

43. The method of claim 42 wherein the shaping apparatus is selected from the group consisting of rollers, injection molds, compression molds, and combinations thereof.

44. The method of claim 36 wherein the composite is fed from the extruder and coated onto an article to provide a layer of the composite on a surface of the article.

45. The method of claim 36 wherein the extruder comprises a twin-screw extruder.

46. A wafer carrier comprising a slot for the support of a wafer, wherein the slot comprises wafer contact points having a surface with a composite of polymer associated with carbon nanotubes.

47. The wafer carrier of claim 46 wherein carbon nanotubes are mixed throughout the polymer.

48. The wafer carrier of claim 46 wherein the carbon nanotubes are covalently bonded to the polymer.

49. The wafer carrier of claim 46 wherein the carbon nanotubes comprise single wall carbon nanotubes.

**50.** The wafer carrier of claim 46 wherein the carbon nanotubes are present in a concentration of less than about 1 percent by weight.

**51.** The wafer carrier of claim 46 wherein the carbon nanotubes are present in a concentration less than about 0.5 percent by weight.

**52.** The wafer carrier of claim 46 wherein the transparency of the polymer not affected by the carbon nanotubes.

**53.** The wafer carrier of claim 46 wherein the composite reduces electrostatic discharge relative to carriers made of plastic.

**54.** The wafer carrier of claim 46 wherein the polymer is selected from the group consisting of polybutylene terephthalate (PBT), polyolefins (PO), polyethylene terephthalate (PET), styrene block co-polymers, styrene-butadiene rubber, nylon in the form of polyether block polyamide (PEBA), polyetheretherketone (PEEK), poly(vinylidene fluoride), poly(tetrafluoroethylene) (PTFE), polyethylene, polypropylene, poly(vinylchloride) (PVC), ethyl vinyl acetate and blends and copolymers thereof.

**55.** A fuel cell comprising a bipolar plate, the bipolar plate comprising a composite of polymer associated with carbon nanotubes.

**56.** The bipolar plate of claim 55 wherein the carbon nanotubes are mixed within the polymer.

**57.** The bipolar plate of claim 55 wherein the carbon nanotubes are covalently bonded to the polymer.

**58.** The bipolar plate of claim 55 wherein the carbon nanotubes comprise single wall carbon nanotubes, multiple wall carbon nanotubes, or a combination thereof.

**59.** The bipolar plate of claim 55 wherein the carbon nanotubes are present in a concentration from about 1 percent by weight to about 50 percent by weight.

**60.** The bipolar plate of claim 55 wherein the polymer is selected from the group consisting of polybutylene terephthalate (PBT), polyolefins (PO), polyethylene terephthalate (PET), styrene block co-polymers, styrene-butadiene rubber, nylon in the form of polyether block polyamide (PEBA), polyetheretherketone (PEEK), poly(vinylidene fluoride), poly(tetrafluoroethylene) (PTFE), polyethylene, polypropylene, poly(vinylchloride) (PVC), ethyl vinyl acetate and blends and copolymers thereof.

**61.** The bipolar plate of claim 55 further comprising a first side and a second side wherein the first side comprises reactant flow channels formed into the surface of the plate.

**62.** The bipolar plate of claim 61 wherein the second side comprises reactant flow channels formed into the surface of the plate.

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