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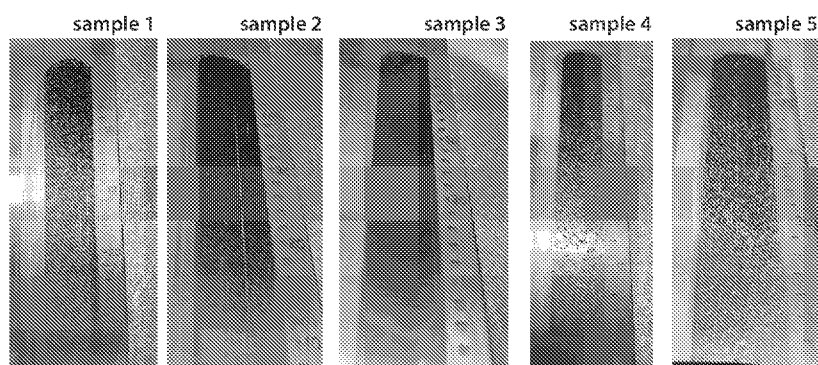


Figure 4

(57) Abstract: A composition contains 5-15 wt% CNS-derived species, which are polymeric, highly branched and crosslinked network of CNTs, and a polymer resin having a hydroxyl content of at least 1.5 wt% and a melt viscosity of at least 8 Pa.s at a shear rate of 0.1 s⁻¹ at a temperature 60 °C greater than the highest temperature at which the resin undergoes a thermal transition. The polymer resin further has either a solubility in a 1:1 (w/w) mixture of butyl acetate and propylene glycol methyl ether acetate of at least 5 wt%, an acid number of at least 100, or both.



DISPERSION OF CARBON NANOSTRUCTURES

BACKGROUND OF THE INVENTION

1. Field of the Invention.

[0001] This invention relates to the use of soluble polymers to aid dispersion of carbon nanostructures in liquid carriers.

2. Description of the Related Art.

[0002] One of the most notable features of carbon nanotubes is high conductivity resulting from their graphemic structures and large aspect ratios. Due to their branched, tree-like structure, carbon nanostructures (CNS) can form networks more efficiently than carbon nanotubes having much higher aspect ratios. That is, carbon nanostructures can provide higher conductivity at a given loading than typical multiwalled carbon nanotubes. However, these branched structures also render carbon nanostructures difficult to disperse, especially in organic solvent-borne coatings. Up to now, adequate dispersion in many coating formulations has required long grinding times and low concentrations. Inadequate grinding times may not fully exfoliate the carbon nanostructures, while complete exfoliation may also fracture the CNS to such an extent that its conductive efficiency is impaired. Thus, it is desirable to have a method to disperse CNS in liquids, especially organic solvents, that optimizes dispersion and conductive efficiency.

SUMMARY OF THE INVENTION

[0003] In one embodiment, a composition comprises 5-15 wt% CNS-derived species and a polymer resin having a) a hydroxyl content of at least 1.5 wt%, b) a melt viscosity of at least 8 Pa.s at a shear rate of 0.1 s^{-1} at a temperature $60 \text{ }^{\circ}\text{C}$ greater than the highest temperature at which the resin undergoes a thermal transition and c) at least one of i) a solubility in a 1:1 (w/w) mixture of butyl acetate and propylene glycol methyl ether acetate of at least 5 wt%, and ii) an acid number of at least 100. The thermal transition may be glass transition temperature, melting temperature, or softening point. The polymer resin may have a hydroxyl content of from 1.5 wt% to 5 wt%. The melt viscosity may be

from 8 Pa.s to 1000 Pa.s. The polymer resin may have a solubility of 5 wt% to 10 wt% in a 1:1 (w/w) mixture of butyl acetate and propylene glycol methyl ether acetate and/or a molecular weight Mn of 15000 to 80000. The polymer resin may have an acid number of 100 to 300. The polymer resin may have a solubility in water of at least 5 wt% when at least 50% of the acid groups on the polymer resin are non-ionized and/or a molecular weight (Mn) of 8000 to 40000. The composition may further include a dispersant, which may be present in an amount of 20 to 60 wt% with respect to the amount of dispersant and CNS-derived species.

[0004] A coating composition may comprise the composition and a coating resin, e.g., acrylic, polyurethane, polyester, and/or epoxy, for example, acrylic or polyester resin. The coating composition may comprise 0.05 to 1 wt% (dry basis) CNS-derived species, e.g., 0.1 to 0.5 wt% or 0.05 to 0.2 wt%. The coating composition may have a Hegman grind of 10-30 microns, e.g., 15-20 microns.

[0005] In another embodiment, a method for preparing a composition comprises combining carbon nanostructures with a polymer resin having a hydroxyl content of at least 1.5 wt%, a melt viscosity of at least 8 Pa.s at a shear rate of 0.1 s^{-1} at a temperature 60°C greater than the highest temperature at which the resin undergoes a thermal transition and at least one of a) a solubility in a 1:1 (w/w) mixture of butyl acetate and propylene glycol methyl ether acetate of at least 5 wt%, and b) an acid number of at least 100 to form a composition having 5-15 wt% CNS-derived species. The carbon nanostructures may be coated with a dispersant, which may be present in an amount of 20 to 60 wt% relative to the amount of coated carbon nanostructures.

[0006] The dispersant may be selected from poly(vinyl pyrrolidone), poly(vinylpyrrolidone-co-vinyl acetate), poly(vinyl butyral), poly(vinyl alcohol), polyalkylene oxides, polyalkylene oxides or acrylic polymers comprising amine functional groups, poly(propylene carbonate), cellulosic dispersants, poly(carboxylic acid), polyacrylates, poly(methylacrylate), poly(acrylamide), amide wax, styrene maleic anhydride resins, amine-functionalized or amine-terminated compounds, alkylphenol ethoxylates, or alkyl ethoxylates, AMP™ dispersants, dispersants containing 2-amino-2-methyl-1-propanol, polyesters, polyamides block copolymers having both a hydrophobic and a hydrophilic group, sodium dodecyl sulfate (SDS), sodium dodecyl benzyl sulfonate,

amine-functionalized derivatives of any of these, acid functionalized derivatives of any of these, or a mixture of two or more of any of these.

[0007] In another embodiment, the composition may be used to form a coating composition by combining it with a solvent and optional dispersant, allowing the polymer resin to dissolve in the solvent to produce a dispersion of CNS-derived species in the solvent, and combining the dispersion with a coating resin and optional additive. The coating resin may comprise an acrylic, polyurethane, polyester, or epoxy resin. The coating resin may be an acrylic or polyester resin. The optional additive may be at least one of a co-solvent, surfactant, filler, adhesion promoter, flow modifier, leveling aide, biocide, and colorant. The coating composition may comprise 0.05 to 1 wt% (dry basis) CNS-derived species, e.g. 0.1 to 0.5 wt% or 0.05 to 0.2 wt%. The coating composition may have a Hegman grind of 10-30 microns, e.g., 15-20 microns.

[0008] It is to be understood that both the foregoing general description and the following detailed description are exemplary and explanatory only and are intended to provide further explanation of the present invention, as claimed.

BRIEF DESCRIPTION OF THE DRAWING

[0009] The invention is described with reference to the several figures of the drawing, in which,

[0010] FIGS. 1A and 1B are diagrams illustrating differences between a Y-shaped MWCNT, not in or derived from a carbon nanostructure (FIG. 1A), and a branched MWCNT (FIG. 1B) in a carbon nanostructure.

[0011] FIGS. 2A and 2B are TEM images showing features characterizing multiwall carbon nanotubes found in carbon nanostructures.

[0012] FIG. 3A is an illustrative depiction of a carbon nanostructure flake material after isolation of the carbon nanostructure from a growth substrate;

[0013] FIG. 3B is a SEM image of an illustrative carbon nanostructure obtained as a flake material;

[0014] FIG. 4 is a photograph of several solubilized CNS-CAB compositions according to embodiments of the invention after application to a Hegman gauge.

DETAILED DESCRIPTION OF THE INVENTION

[0015] In one embodiment, a composition contains 5-15 wt% CNS-derived species and a polymer resin having a hydroxyl content of at least 1.5 wt% and a melt viscosity of at least 8 Pa.s at a shear rate of 0.1 s^{-1} at a temperature $60 \text{ }^{\circ}\text{C}$ greater than the highest temperature at which the resin undergoes a thermal transition. The polymer resin further has either a solubility in a 1:1 (w/w) mixture of butyl acetate and propylene glycol methyl ether acetate of at least 5 wt%, an acid number of at least 100, or both.

[0016] The compositions provided herein may be prepared with water soluble polymer resins or with organic solvent soluble polymer resins. In either case, the polymer resin has a hydroxyl content of at least 1.5 wt%, for example, at least 1.6 wt%, at least 1.7 wt%, at least 1.8 wt%, or from 1.5 wt% to 2 wt%. Furthermore, the polymer resin has a melt viscosity of at least 8 Pa.s at a shear rate of 0.1 s^{-1} at a temperature $60 \text{ }^{\circ}\text{C}$ greater than the highest temperature at which the resin undergoes a thermal transition. For example, the melt viscosity may be at least 10 Pa.s at a shear rate of 0.1 s^{-1} , or, e.g., from 8 Pa.s to 1000 Pa.s, from 10 Pa.s to 800 Pa.s, from 12 Pa.s to 500 Pa.s, or from 14 Pa.s to 200 Pa.s. The relevant thermal transition is preferably the highest temperature transition of the glass transition temperature (T_g), softening point, or melting point (T_m). However, one of skill in the art will recognize that not every polymer resin will exhibit all three of these transitions. For example, not every polymer resin has a melting point. Rather, the melt viscosity is measured at a temperature $60 \text{ }^{\circ}\text{C}$ higher than the highest temperature thermal transition, e.g., T_g , T_m , or softening point, actually exhibited by the polymer resin. Differential scanning calorimetry is preferably used to measure T_g and T_m . The softening point is preferably measured using a ring and ball method, e.g., according to DIN 53180. Where the softening point measurement yields a range of temperatures, the highest temperature in the range is used. The melt viscosity may be measured using any commercial rheometer. In the instant examples, viscosity was measured in a Discovery HR-2 Hybrid Rheometer – 2 using a 25 mm parallel disposable aluminum plate. The test sample was equilibrated at the testing temperature for two minutes, presheared at 0.5 1/s for 30 s, and equilibrated for an additional 5 min. A flow sweep was performed from 0.1 1/s to 1000 1/s at the testing temperature.

[0017] The composition may be prepared with a polymer resin having a solubility in a 1:1 (w/w) mixture of butyl acetate and propylene glycol methyl ether acetate of at least 5

wt%, for example, at least 5.5 wt%, at least 6 wt%, at least 6.5 wt%, at least 7 wt%, at least 7.5 wt%, at least 8 wt%, at least 8.5 wt%, or up to 10 wt%. Such a solvent-soluble polymer resin may also have a glass transition temperature of at least 80 °C, for example, at least 85 °C, at least 90 °C, at least 95 °C, at least 100 °C, or from 80 °C to 140 °C. Alternatively or in addition, a solvent-soluble polymer resin may have molecular weight (Mn) from 15000 to 80000.

[0018] Alternatively or in addition, the polymer resin may have an acid number of at least 100, for example, from 100 to 300 or from 150 to 250. A high acid number promotes solubility of the polymer resin, especially in aqueous solvents. For example, the polymer resin may have a solubility in water of at least 5 wt% when at least 50% of the acid groups on the polymer resin are non-ionized, for example, at least 10%, from 5% to 80%, from 15% to 65%, or from 20% to 50%. Solubility is evaluated when at least 50% of the acid groups on the polymer resin are in the -OH form, rather than having an ionic group requiring a counterion to maintain neutrality. Alternatively or in addition, a water soluble polymer resin may have a molecular weight (Mn) of at least 8000, for example, from 8000 to 40000.

[0019] The compositions are used as a carrier to predisperse CNS prior to being fully formulated. The use of polymer resins to provide increased viscosity enables improved exfoliation of the CNS bundles. To formulate the compositions into coating compositions, the polymer resin used for predispersion should be compatible with the polymer binder systems used in the coatings, e.g., acrylic, polyester, polyurethane, and epoxy systems. Preferred polymer systems for primer coating systems are acrylics and polyesters. Hydroxyl groups on the polymer resins used to predisperse CNS can be cross-linked with these common binders for coatings. The molecular weight, determined directly or using the glass transition temperature as a proxy, of the polymer resin should be high enough to generate friction during mixing with the CNS but low enough that the polymer resin remains soluble in the liquid carrier for the coating composition. Suitable polymer resins to predisperse CNS for organic solvent borne systems include but are not limited to cellulose acetate butyrate, cellulose acetate propionate, polyester based solid resins such as Tego AddBond LP1600 and LP1611 (1.85 % hydroxyl groups) from Evonik, and acrylic or polyester resins that are available as liquids but that can be stripped of solvent and used in solid form, e.g., Setalux XCS 1518 from Allnex and Paraloid AU-

830 (3.45 % hydroxyl). Suitable water soluble polymer resins include Ottopol 25-30 from Gellner Industrial LLC and resins available under the Joncryl name from BASF, under the ISOBAM name from Kururay, under the SMA name from Cray Valley, and under the XiRan name from Polyscope Polymers.

[0020] As known in the art, carbon nanotubes (CNT or CNTs plural) are carbonaceous materials that include at least one sheet of sp^2 -hybridized carbon atoms bonded to each other to form a honey-comb lattice that forms a cylindrical or tubular structure. The carbon nanotubes can be single-walled carbon nanotubes (SWCNTs) or multi-walled carbon nanotubes (MWCNTs). SWCNTs can be thought of as an allotrope of sp^2 -hybridized carbon similar to fullerenes. The structure is a cylindrical tube including six-membered carbon rings. Analogous MWCNTs, on the other hand, have several tubes in concentric cylinders. The number of these concentric walls may vary, e.g., from 2 to 25 or more. Typically, the diameter of MWNTs may be 10 nm or more, in comparison to 0.7 to 2.0 nm for typical SWNTs.

[0021] In many of the CNSs used in various embodiments, the CNTs are MWCNTs, having, for instance, at least two coaxial carbon nanotubes. The number of walls present, as determined, for example, by transmission electron microscopy (TEM), at a magnification sufficient for analyzing the number of wall in a particular case, can be within the range of from 2 to 30 or so, for example: 4 to 30; 6 to 30; 8 to 30; 10 to 30; 12 to 30; 14 to 30; 16 to 30; 18 to 30; 20 to 30; 22 to 30; 24 to 30; 26 to 30; 28 to 30; or 2 to 28; 4 to 28; 6 to 28; 8 to 28; 10 to 28; 12 to 28; 14 to 28; 16 to 28; 18 to 28; 20 to 28; 22 to 28; 24 to 28; 26 to 28; or 2 to 26; 4 to 26; 6 to 26; 8 to 26; 10 to 26; 12 to 26; 14 to 26; 16 to 26; 18 to 26; 20 to 26; 22 to 26; 24 to 26; or 2 to 24; 4 to 24; 6 to 24; 8 to 24; 10 to 24; 12 to 24; 14 to 24; 16 to 24; 18 to 24; 20 to 24; 22 to 24; or 2 to 22; 4 to 22; 6 to 22; 8 to 22; 10 to 22; 12 to 22; 14 to 22; 16 to 22; 18 to 22; 20 to 22; or 2 to 20; 4 to 20; 6 to 20; 8 to 20; 10 to 20; 12 to 20; 14 to 20; 16 to 20; 18 to 20; or 2 to 18; 4 to 18; 6 to 18; 8 to 18; 10 to 18; 12 to 18; 14 to 18; 16 to 18; or 2 to 16; 4 to 16; 6 to 16; 8 to 16; 10 to 16; 12 to 16; 14 to 16; or 2 to 14; 4 to 14; 6 to 14; 8 to 14; 10 to 14; 12 to 14; or 2 to 12; 4 to 12; 6 to 12; 8 to 12; 10 to 12; or 2 to 10; 4 to 10; 6 to 10; 8 to 10; or 2 to 8; 4 to 8; 6 to 8; or 2 to 6; 4 to 6; or 2 to 4.

[0022] Since a CNS is a polymeric, highly branched and crosslinked network of CNTs, at least some of the chemistry observed with individualized CNTs may also be

carried out on the CNS. In addition, some of the attractive properties often associated with using CNTs also are displayed in materials that incorporate CNSs. These include, for example, electrical conductivity, attractive physical properties including maintaining or enabling good tensile strength when integrated into a silicone-based composition, thermal stability (sometimes comparable to that of diamond crystals or in-plane graphite sheets) and/or chemical stability, to name a few.

[0023] However, as used herein, the term “CNS” is not a synonym for individualized, un-entangled structures such as “monomeric” fullerenes (the term “fullerene” broadly referring to an allotrope of carbon in the form of a hollow sphere, ellipsoid, tube, e.g., a carbon nanotube, and other shapes). In fact, many embodiments of the invention highlight differences and advantages observed or anticipated with the use of CNSs as opposed to the use of their CNTs building blocks. Without wishing to be held to a particular interpretation, it is believed that the combination of branching, crosslinking, and wall sharing among the carbon nanotubes in a CNS reduces or minimizes the van der Waals forces that are often problematic when using individual carbon nanotubes in a similar manner, especially when it is desirable to prevent agglomeration.

[0024] In addition, or alternatively to performance attributes, CNTs that are part of or are derived from a CNS can be characterized by a number of features, at least some of which can be relied upon to distinguish them from other nanomaterials, such as, for instance, ordinary CNTs (namely CNTs that are not derived from CNSs and can be provided as individualized, pristine or fresh CNTs).

[0025] In many cases, a CNT present in or derived from a CNS has a typical diameter of 100 nanometers (nm) or less, such as, for example, within the range of from about 5 to about 100 nm, e.g., within the range of from about 10 to about 75, from about 10 to about 50, from about 10 to about 30, from about 10 to about 20 nm.

[0026] In specific embodiments, at least one of the CNTs has a length that is equal to or greater than 2 microns, as determined by SEM. For example, at least one of the CNTs will have a length within a range of from 2 to 2.25 microns; from 2 to 2.5 microns; from 2 to 2.75 microns; from 2 to 3.0 microns; from 2 to 3.5 microns; from 2 to 4.0 microns; or from 2.25 to 2.5 microns; from 2.25 to 2.75 microns; from 2.25 to 3 microns; from 2.25 to 3.5 microns; from 2.25 to 4 microns; or from 2.5 to 2.75 microns; from 2.5 to 3 microns; from 2.5 to 3.5 microns; from 2.5 to 4 microns; or from 3 to 3.5 microns; from 3

to 4 microns; of from 3.5 to 4 microns or higher. In some embodiments, more than one, e.g., a portion such as a fraction of at least about 0.1%, at least about 1%, at least about 10%, at least about 15%, at least about 20%, at least about 25%, at least about 30%, at least about 35%, at least about 40, at least about 45%, at least about 50% or even more than one half, of the CNTs, as determined by SEM, can have a length greater than 2 microns, e.g., within the ranges specified above.

[0027] For many CNTs in a CNS, at least a portion of a CNT sidewall is shared with another CNT. While it is generally understood that every carbon nanotube in the CNS need not necessarily be branched, crosslinked, or share common walls with other CNTs, at least a portion of the CNTs in the carbon nanostructure can be interdigitated with one another and/or with branched, crosslinked, or common-wall carbon nanotubes in the remainder of the carbon nanostructure.

[0028] The morphology of CNTs present in a CNS, in a fragment of a CNS or in a fractured CNT derived from a CNS will often be characterized by a high aspect ratio, with lengths typically more than 100 times the diameter, and in certain cases much higher. For instance, in a CNS (or CNS fragment), the length to diameter aspect ratio of CNTs can be within a range of from about 200 to about 1000, such as, for instance, from 200 to 300; from 200 to 400; from 200 to 500; from 200 to 600; from 200 to 700; from 200 to 800; from 200 to 900; or from 300 to 400; from 300 to 500; from 300 to 600; from 300 to 700; from 300 to 800; from 300 to 900; from 300 to 1000; or from 400 to 500; from 400 to 600; from 400 to 700; from 400 to 800; from 400 to 900; from 400 to 1000; or from 500 to 600; from 500 to 700; from 500 to 800; from 500 to 900; from 500 to 1000; or from 600 to 700; from 600 to 800; from 600 to 900; from 600 to 1000; from 700 to 800; from 700 to 900; from 700 to 1000; or from 800 to 900; from 800 to 1000; or from 900 to 1000.

[0029] It has been found that in CNSs, as well as in structures derived from CNSs (CNS-derived species, e.g., fragments of CNSs or in fractured CNTs) at least one of the CNTs is characterized by a certain “branch density”. As used herein, the term “branch” refers to a feature in which a single carbon nanotube diverges into multiple (two or more), connected multiwall carbon nanotubes. One embodiment has a branch density according to which, along a two-micrometer length of the carbon nanostructure, there are at least two branches, as determined by SEM. Three or more branches also can occur.

[0030] In addition, or in the alternative, the number of walls observed at the area (point) of branching in a CNS, fragment of CNSs or fractured CNTs differ from one side of the branching (e.g., before the branching point) to the other side of this area (e.g., after or past the branching point). Such a change in the number of walls, also referred to herein as an “asymmetry” in the number of walls, is not observed with ordinary Y-shaped CNTs (where the same number of walls is observed in both the area before and the area past the branching point).

[0031] Diagrams illustrating these features are provided in FIGS. 1A and 1B. Shown in FIG. 1A, is an exemplary Y-shaped CNT 11 that is not derived from a CNS. Y-shaped CNT 11 includes catalyst particle 13 at or near branching point 15. Areas 17 and 19 are located, respectively, before and after the branching point 15. In the case of a Y-shaped CNT such as Y-shaped CNT 11, both areas 17 and 19 are characterized by the same number of walls, i.e., two walls in the drawing.

[0032] In contrast, in a CNS (FIG. 1B), a CNT building block 111, that branches at branching point 115, does not include a catalyst particle at or near this point, as seen at catalyst devoid region 113. Furthermore, the number of walls present in region 117, located before, prior (or on a first side of) branching point 115 is different from the number of walls in region 119 (which is located past, after or on the other side relative to branching point 115. In more detail, the three-walled feature found in region 117 is not carried through to region 119 (which in the diagram of FIG. 1B has only two walls), giving rise to the asymmetry mentioned above.

[0033] These features are highlighted in the TEM images of FIGS. 2A and 2B.

[0034] In more detail, the CNS branching in TEM region 40 of FIG. 2A shows the absence of any catalyst particle. In the TEM of FIG. 2B, first channel 50 and second channel 52 point to the asymmetry in the number of walls featured in branched CNSs, while arrow 54 points to a region displaying wall sharing.

[0035] One, more, or all these attributes can be encountered in the coating compositions described herein.

[0036] In some embodiments, the CNS is present as part of an entangled and/or interlinked network of CNSs. Such an interlinked network can contain bridges between CNSs.

[0037] Suitable techniques for preparing CNSs are described, for example, in U.S. Patent Application Publication No. 2014/0093728 A1, published on April 3, 2014, U.S. Patent Nos. 8,784,937B2; 9,005,755B2; 9,107,292B2; and 9,447,259B2. The entire contents of these documents are incorporated herein by this reference.

[0038] As described in these documents, a CNS can be grown on a suitable substrate, for example on a catalyst-treated fiber material. The product can be a fiber-containing CNS material. In some cases, the CNSs is separated from the substrate to form flakes.

[0039] As seen in US 2014/0093728A1 a carbon nanostructure obtained as a flake material (i.e., a discrete particle having finite dimensions) exists as a three-dimensional microstructure due to the entanglement and crosslinking of its highly aligned carbon nanotubes. The aligned morphology is reflective of the formation of the carbon nanotubes on a growth substrate under rapid carbon nanotube growth conditions (e.g., several microns per second, such as about 2 microns per second to about 10 microns per second), thereby inducing substantially perpendicular carbon nanotube growth from the growth substrate. Without being bound by any theory or mechanism, it is believed that the rapid rate of carbon nanotube growth on the growth substrate can contribute, at least in part, to the complex structural morphology of the carbon nanostructure. In addition, the bulk density of the CNS can be modulated to some degree by adjusting the carbon nanostructure growth conditions, including, for example, by changing the concentration of transition metal nanoparticle catalyst particles that are disposed on the growth substrate to initiate carbon nanotube growth.

[0040] The flakes can be further processed, e.g., by cutting or fluffing (operations that can involve mechanical ball milling, grinding, blending, etc.), chemical processes, or any combination thereof.

[0041] In some embodiments, the CNSs employed are “coated”, also referred to herein as “encapsulated” CNSs. In a typical coating process, the coating is applied onto the CNTs that form the CNS. The coating process can form a partial or a complete coating that is non-covalently bonded to the CNTs and, in some cases, can act as a binder. In addition, or in the alternative, the coating can be applied to already formed CNSs in a post-coating (or encapsulation) process. With coatings that have binding properties, CNSs can be formed into larger structures, granules or pellets, for example. In other

embodiments the granules or pellets are formed independently of the function of the coating.

[0042] For example, the flake material can be captured and sprayed with an aqueous solution containing a binder (e.g., polyethylene glycol or polyurethane) to form wet flakes. The weight ratio of aqueous binder solution to the flake material can range from 8:1 to 15:1, e.g., from 10:1 to 15:1, from 10:1 to 13:1, or from 10:1 to 12:1. The wet flakes can then be extruded to form wet extrudates. Drying the wet extrudates (e.g., by air drying, drying in an oven) results in formation of the CNS pellets. Alternatively, drying the wet flakes results in formation of CNS granules.

[0043] Various types of coatings can be selected. In many cases, sizing solutions commonly used in coating carbon fibers or glass fibers could also be utilized as coating materials for CNSs. In these embodiments, relative to the overall weight of the coated CNS material, the coating can be within the range of from about 0.1 weight % to about 10 weight % (e.g., within the range, by weight, of from about 0.1% to about 0.5%; from about 0.5 % to about 1%; from about 1% to about 1.5%; from about 1.5% to about 2%; from about 2% to about 2.5%; from about 2.5% to about 3%; from about 3% to about 3.5%; from about 3.5% to about 4%; from about 4% to about 4.5%; from about 4.5% to about 5%; from about 5% to about 5.5%; from about 5.5% to about 6%; from about 6% to about 6.5%; from about 6.5% to about 7%; from about 7% to about 7.5%; from about 7.5% to about 8%; from about 8% to about 8.5%; from about 8.5% to about 9%; from about 9% to about 9.5%; or from about 9.5% to about 10%). Specific examples of sizing materials include but are not limited to fluorinated polymers such as poly(vinylidene difluoroethylene) (PVDF), poly(vinylidene difluoroethylene-co-hexafluoropropylene) (PVDF-HFP), poly(tetrafluoroethylene) (PTFE), polyimides, and water-soluble binders, such as poly(ethylene) oxide, polyvinyl-alcohol (PVA), cellulose, carboxymethylcellulose (CMC), starch, hydroxypropylcellulose, regenerated cellulose, polyvinyl pyrrolidone (PVP), and copolymers and mixtures thereof. In many implementations, the CNSs used are treated with a polyurethane (PU), a thermoplastic polyurethane (TPU), or with polyethylene glycol (PEG). Polymers such as, for instance, epoxy, polyester, vinylester, polyetherimide, polyetherketoneketone, polyphthalamide, polyetherketone, polyetheretherketone, polyimide, phenol-formaldehyde, bismaleimide, acrylonitrile-butadiene styrene (ABS), polycarbonate, polyethyleneimine, polyurethane,

polyvinyl chloride, polystyrene, polyolefins, polypropylenes, polyethylenes, polytetrafluoroethylene, elastomers such as, for example, polyisoprene, polybutadiene, butyl rubber, nitrile rubber, ethylene-vinyl acetate polymers, silicone polymers, and fluorosilicone polymers, combinations thereof, or other polymers or polymeric blends can also be used as sizing materials in some cases. In order to enhance electrical conductivity, conductive polymers such as, for instance, polyanilines, polypyrroles and polythiophenes can also be used.

[0044] Alternative implementations may utilize coating materials that can assist in stabilizing a CNS dispersion in an aqueous or organic solvent. In one example, the coating is selected to facilitate and/or stabilize dispersing CNSs in a vehicle produced by combining the desired resin for the coating with a desired solvent together with optional dispersant. Any suitable combination of the resins and solvents provided above may be employed. In another example, the coating material is the same as, similar to, or compatible with a dispersant or thickener employed when processing CNSs. For example, CNS flake material may be coated with a suitable dispersant for use with the solvent (e.g., organic or aqueous) system in which the CNS – polymer resin composition is dissolved/dispersed. To provide an appropriate amount of dispersant for the liquid dispersion or other formulation, it may be desirable to increase the amount of the dispersant, as a coating material, in comparison to the coating amounts for CNS pellets or granules listed for the sizing materials described above. For example, relative to the mass of coated CNS material, the amount of dispersant may be at least 20% by weight, e.g., 25% – 60%, 30% - 55%, 40 % - 50%, or 45% - 60%.

[0045] Exemplary dispersants include but are not limited to poly(vinyl pyrrolidone), poly(vinylpyrrolidone-co-vinyl acetate), poly(vinyl butyral), poly(vinyl alcohol), polyalkylene oxides (such as polyethylene oxide or polypropylene oxide), polyalkylene oxides or acrylic polymers comprising amine functional groups, poly(propylene carbonate), cellulosic dispersants such as methyl cellulose, carboxymethyl cellulose, ethyl cellulose, hydroxymethyl cellulose and hydroxypropyl cellulose; poly(carboxylic acid) such as poly (acrylic acid), polyacrylates, poly(methylacrylate), poly(acrylamide), amide wax, styrene maleic anhydride resins, amine-functionalized or amine-terminated compounds such as polyamine, tertiary amine, or quaternary ammonium functionalized compounds, e.g., tetraoctylammonium bromide, ethoxylates such as alkylphenol

ethoxylates, e.g., octylphenol ethoxylate, or alkyl ethoxylates, multifunctional co-dispersants such as AMP™ dispersants, dispersants containing 2-amino-2-methyl-1-propanol, polyesters (such as polycaprolactone, polyvalerolactone, poly(hydroxy stearic acid), or poly(hydroxyoleic acid), polyamides such as polycaprolactam, and block copolymers having both a hydrophobic and a hydrophilic group. Other possible candidates include sodium dodecyl sulfate (SDS), sodium dodecyl benzyl sulfonate, derivatives of polyacrylic acid and so forth. Additional examples include amine-functionalized derivatives (such as polyamine, tertiary amine, or quaternary ammonium functionalized derivatives), acid functionalized derivatives (such as carboxylic acid or phosphonic acid functionalized derivatives) of these, such as amine-functionalized or amine-terminated polyalkylene oxides or acrylic polymers comprising amine or acid functional groups. Other suitable dispersants include those that are known to those of skill in the art for use with carbon black, graphene, or carbon nanotubes. The compositions can include one dispersant or mixtures of two or more dispersants.

[0046] In one illustration, the dispersant belongs to a class that includes a styrene maleic anhydride resin and/or its derivatives, the latter being polymers made via a chemical reaction of styrene maleic anhydride resin or prehydrolyzed styrene maleic anhydride resin with small or large organic molecules having at least one reactive end group, for example an amine or epoxide group. In general, this class of polymeric dispersants (also referred to herein as styrene maleic anhydride-based) have a styrene maleic anhydride copolymer backbone modified with various polymeric brushes and/or small molecules.

[0047] In another illustration, the dispersant includes PVP (in various molecular weights) or its derivatives, the latter generally referring to dispersants that have a PVP backbone modified with small or large molecules via chemical reactions, for example. Examples of PVP-based dispersants include Ashland PVP K-12, K-15, K-30, K-60, K-90 and K-120 products, polyvinyl pyrrolidone copolymers such as polyvinyl pyrrolidone-co-vinyl acetate, butylated polyvinyl pyrrolidone such as Ganex™ P-904LC polymer.

[0048] In a further illustration, the dispersant is a cellulose-based dispersant, including, for instance, cellulose or cellulose derivatives, the latter having a cellulose backbone optionally modified by small or large organic molecules having at least one reactive end group. In one specific example, the cellulose-based dispersant is CMC (e.g., at various

viscosities), a compound typically prepared by the reaction of cellulose with chloroacetic acid. In another example, the dispersant is hydroxyethyl cellulose.

[0049] Many embodiments described herein use CNS-materials that have a 97% or higher CNT purity. Often, the CNSs used herein require no further additives to counteract Van der Waals forces.

[0050] CNSs can be provided in the form of a loose particulate material (as CNS flakes, granules, pellets, etc., for example) or in formulations that also include a liquid medium, e.g., dispersions, slurries, pastes, or in other forms. In many implementations, the CNSs employed are separated from their growth substrate.

[0051] In some embodiments, the CNSs are provided in the form of a flake material after being removed from the growth substrate upon which the carbon nanostructures are initially formed. As used herein, the term “flake material” refers to a discrete particle having finite dimensions. Shown in FIG. 3A, for instance, is an illustrative depiction of a CNS flake material after isolation of the CNS from a growth substrate. Flake structure 100 can have first dimension 110 that is in a range from about 1 nm to about 35 microns thick, particularly about 1 nm to about 500 nm thick, including any value in between and any fraction thereof. Flake structure 100 can have second dimension 120 that is in a range from about 1 micron to about 750 microns tall, including any value in between and any fraction thereof. Flake structure 100 can have third dimension 130 that can be in a range from about 1 micron to about 750 microns, including any value in between and any fraction thereof. Two or all of dimensions 110, 120 and 130 can be the same or different.

[0052] For example, in some embodiments, second dimension 120 and third dimension 130 can be, independently, on the order of about 1 micron to about 10 microns, or about 10 microns to about 100 microns, or about 100 microns to about 250 microns, from about 250 to about 500 microns, or from about 500 microns to about 750 microns.

[0053] CNTs within the CNS can vary in length from about 10 nanometers (nm) to about 750 microns (μm), or higher. Thus, the CNTs can be from 10 nm to 100 nm, from 10 nm to 500 nm; from 10 nm to 750 nm; from 10 nm to 1 micron; from 10 nm to 1.25 micron; from 10 nm to 1.5 micron; from 10 nm to 1.75 micron; from 10 nm to 2 micron; or from 100 nm to 500 nm, from 100 nm to 750 nm; from 100 nm to 1 micron; from 100 to 1.25 micron; from 100 to 1.5 micron; from 100 to 1.75 micron from 100 to 2 microns; from 500 nm to 750 nm; from 500 nm to 1 micron; from 500 nm to 1 micron; from 500

nm to 1.25 micron; from 500 nm to 1.5 micron; from 500 nm to 1.75 micron; from 500 nm to 2 micron; from 750 nm to 1 micron; from 750 nm to 1.25 micron; from 750 nm to 1.5 micron; from 750 nm to 1.75 microns; from 750 nm to 2 microns; from 1 micron to 1.25 micron; from 1.0 micron to 1.5 micron; from 1 micron to 1.75 micron; from 1 micron to 2 microns; or from 1.25 micron to 1.5 micron; from 1.25 micron to 1.75 micron; from 1 micron to 2 microns; or from 1.5 to 1.75 micron; from 1.5 to 2 micron; or from 1.75 to 2 microns. In some embodiments, at least one of the CNTs has a length that is equal to or greater than 2 microns, as determined by SEM, for example, up to 4 microns or greater.

[0054] Shown in FIG. 3B is a SEM image of an illustrative carbon nanostructure obtained as a flake material. The carbon nanostructure shown in FIG. 3B exists as a three-dimensional microstructure due to the entanglement and crosslinking of its highly aligned carbon nanotubes. The aligned morphology is reflective of the formation of the carbon nanotubes on a growth substrate under rapid carbon nanotube growth conditions (e.g., several microns per second, such as about 2 microns per second to about 10 microns per second), thereby inducing substantially perpendicular carbon nanotube growth from the growth substrate. Without being bound by any theory or mechanism, it is believed that the rapid rate of carbon nanotube growth on the growth substrate can contribute, at least in part, to the complex structural morphology of the carbon nanostructure. In addition, the bulk density of the carbon nanostructure can be modulated to some degree by adjusting the carbon nanostructure growth conditions, including, for example, by changing the concentration of transition metal nanoparticle catalyst particles that are disposed on the growth substrate to initiate carbon nanotube growth.

[0055] A flake structure can include a webbed network of carbon nanotubes in the form of a carbon nanotube polymer (i.e., a “carbon nanopolymer”) having a molecular weight in a range from about 15,000 g/mol to about 150,000 g/mol, including all values in between and any fraction thereof. In some cases, the upper end of the molecular weight range can be even higher, including about 200,000 g/mol, about 500,000 g/mol, or about 1,000,000 g/mol. The higher molecular weights can be associated with carbon nanostructures that are dimensionally long. The molecular weight can also be a function of the predominant carbon nanotube diameter and number of carbon nanotube walls present within the carbon nanostructure. The crosslinking density of the carbon

nanostructure can range between about 2 mol/cm³ to about 80 mol/cm³. Typically, the crosslinking density is a function of the carbon nanostructure growth density on the surface of the growth substrate, the carbon nanostructure growth conditions and so forth. It should be noted that the typical CNS structure, containing many, many CNTs held in an open web-like arrangement, removes Van der Waals forces or diminishes their effect. This structure can be exfoliated more easily, which makes many additional steps of separating them or breaking them into branched structures unique and different from ordinary CNTs.

[0056] With a web-like morphology, carbon nanostructures can have relatively low bulk densities, for example, from about 0.005 g/cm³ to about 0.1 g/cm³ or from about 0.01 g/cm³ to about 0.05 g/cm³. As-produced carbon nanostructures can have an initial bulk density ranging from about 0.003 g/cm³ to about 0.015 g/cm³. Further consolidation and/or coating to produce a carbon nanostructure flake material or like morphology can raise the bulk density to a range from about 0.1 g/cm³ to about 0.15 g/cm³. In some embodiments, optional further modification of the carbon nanostructure can be conducted to further alter the bulk density and/or another property of the carbon nanostructure. In some embodiments, the bulk density of the carbon nanostructure can be further modified by forming a coating on the carbon nanotubes of the carbon nanostructure and/or infiltrating the interior of the carbon nanostructure with various materials. Coating the carbon nanotubes and/or infiltrating the interior of the carbon nanostructure can further tailor the properties of the carbon nanostructure for use in various applications. Moreover, forming a coating on the carbon nanotubes can desirably facilitate the handling of the carbon nanostructure. In some embodiments, further compaction can raise the bulk density to an upper limit of about 1 g/cm³, with chemical modifications to the carbon nanostructure raising the bulk density to an upper limit of about 1.2 g/cm³.

[0057] In addition to the flakes described above, the CNS material can be provided as granules, pellets, or in other forms of loose particulate material, having a typical particle size within the range of from about 1 mm to about 1 cm, for example, from about 0.5 mm to about 1 mm, from about 1 mm to about 2 mm, from about 2 mm to about 3 mm, from about 3 mm to about 4 mm, from about 4 mm to about 5 mm, from about 5 mm to about 6 mm, from about 6 mm to about 7 mm, from about 7 mm to about 8 mm, from about 8 mm to about 9 mm or from about 9 mm to about 10 mm.

[0058] Commercially, examples of CNS materials that can be utilized are those developed by Applied Nanostructured Solutions, LLC (ANS) (Massachusetts, United States).

[0059] Techniques used to combine CNS with the polymer resin can generate CNS-derived species as “CNS fragments” and/or “fractured CNTs” that become distributed (e.g., homogeneously) in individualized form throughout the masterbatch. Except for their reduced sizes, CNS fragments (a term that also includes partially fragmented CNSs) generally share the properties of intact CNS and can be identified by electron microscopy and other techniques, as described above. Fractured CNTs can be formed when crosslinks between CNTs within the CNS are broken, under applied shear, for example. Derived (generated or prepared) from CNSs, fractured CNTs are branched and share common walls with one another.

[0060] In some situations, an initial CNS is broken into smaller CNS units or fragments. Except for their reduced sizes, these fragments generally share the properties of intact CNS and can be identified by electron microscopy and other techniques, as described above.

[0061] Also possible are changes in the initial nanostructure morphology of the CNS. For example, applied shear can break crosslinks between CNTs within a CNS to form CNTs that typically will be dispersed as individual CNTs in the polymer resin. It is found that structural features of branching and shared walls are retained for many of these CNTs, even after the crosslinks are removed. CNTs that are derived (prepared) from CNSs and retain structural features of CNT branching and shared walls are referred to herein as “fractured” CNTs. These species are capable of imparting improved interconnectivity (between CNT units), resulting in better conductivity at lower concentrations.

[0062] Thus, in comparison to coating compositions that employ ordinary, individualized CNTs, e.g., in pristine form, coating compositions described herein will often include fractured CNTs. These fractured CNTs can readily be differentiated from ordinary carbon nanotubes through standard carbon nanotube analytical techniques, such as SEM, for example. It is further noted that not every CNT encountered needs to be branched and share common walls; rather it is a plurality of fractured CNTs, that, as a whole, will possess these features.

[0063] The CNSs used herein can be identified and/or characterized by various techniques. Electron microscopy, including techniques such as transmission electron microscopy (TEM) and scanning electron microscopy (SEM), for example, can provide information about features such as the frequency of specific number of walls present, branching, the absence of catalyst particles, etc. See, e.g., FIGS. 2A-2B.

[0064] Raman spectroscopy can point to bands associated with impurities. For example, a D-band (around 1350 cm^{-1}) is associated with amorphous carbon; a G band (around 1580 cm^{-1}) is associated with crystalline graphite or CNTs). A G' band (around 2700 cm^{-1}) is expected to occur at about 2X the frequency of the D band. In some cases, it may be possible to discriminate between CNS and CNT structures by thermogravimetric analysis (TGA).

[0065] Carbon nanostructures are preferably combined with the polymer resin to form highly dispersed mixtures of the polymer resin and CNS-derived species. Any method known to those of skill in the art for combining particulate fillers with the polymer resin may be used. For example, devices such as planetary mixers, roll mills, Brabender mixers, Banbury mixers, and others known to those of skill in the art for use with the polymer resins described herein may be employed. In preferred embodiments, the mixture of the polymer resin and CNS-derived species contains 5-15 wt% CNS-derived species. For example, the composition may contain 5-7 wt%, 7-9 wt%, 9-11 wt%, 11-13 wt%, or 13-15 wt% CNS-derived species.

[0066] The resulting composition may be cut or ground into chips, pellets, or powders using any suitable apparatus known to those of skill in the art, such as a cutting mill. Such powders may any particle size useful for the desired end use application but will typically be on the order of a few millimeters, e.g. 0.5-5 mm. The resulting particles contain the polymer resin and CNS-derived species and are referred to herein as CNS-resin powder regardless of the shape of the particles. This CNS-resin powder may be incorporated into coating formulations without the need for a milling step. For example, the CNS-resin powder may be incorporated into solvent (either organic or aqueous) by incubating the CNS-resin powder in the solvent for a suitable period of time and then processing the mixture in a high speed mixer to dissolve the polymer resin and disperse the CNS-derived species.

[0067] Suitable liquid vehicles include any liquid vehicle suitable for the desired end-use application. For coatings, typical organic solvents include but are not limited to ester solvents such as butyl acetate, glycol ether esters such as propylene glycol methyl ether acetate, ketone solvents such as acetone, and mixtures of these with aromatic solvents such as xylene, toluene, and Aromatic 100 (sometimes termed A-100 or Solvent 100). Alternatively, the CNS-resin powder may be dispersed in aqueous solvents, e.g., water, for use with waterborne coatings. For waterborne coatings, sufficient base is preferably added to the aqueous solvent with the CNS-resin powder to neutralize at least 50% (mole basis) of any acid groups in the polymer resin, e.g. to convert ionized species in the acid groups (that may have an ionic counterion) to the -OH form of the acid. For example, sufficient base may be added to neutralize at least 60%, at least 70%, at least 80%, at least 90 %, or at least 100% of any acid groups in the polymer resin, for example 50-100% of the acid groups in the polymer resin. Regardless of the liquid vehicle composition, a dispersant is typically employed to facilitate dispersion of the CNS fragments. Suitable dispersants include any dispersants suitable for coating formulations known to those of skill in the art and may be cationic, anionic, or non-ionic.

[0068] Once dissolved in either organic or aqueous solvent, the resulting liquid solution containing CNS-derived species may be combined with the other components of the desired coating to form a coating composition. These components typically include a coating resin, for example, an acrylic, polyurethane, polyester, or epoxy resin, e.g., acrylic or polyester resins. Additional additives may impact other properties of the coating composition such as viscosity, leveling, and dry time. Exemplary additives include but are not limited to co-solvents (e.g., water soluble organic solvents for waterborne coating compositions), surfactants, and fillers such as clays, talcs, hydrophilic and hydrophobic fumed and precipitated silicas, and carbonates. Additionally, adhesion promoters, flow modifiers, leveling aides, and biocides may be used. Exemplary adhesion promoters include but are not limited to modified polyolefins (with or without chlorine). The coating resin itself may also be modified with a modified polyolefin adhesion promoter. Additional colorants such as titania or colored pigments or dyes may also be employed. Because the CNS-derived species are already pre-dispersed by the polymer resin, it is not necessary to mill the coating composition to disperse the CNS.

Thus, coating compositions containing CNS-derived species may have a Hegman grind of 10-20 microns, for example, 15-20 microns.

[0069] The resulting coating compositions may be used to impart surface conductivity to coated substrates. The desired loading of CNS-derived species in the coating (dry basis) will vary depending on the intended application and may range, for example, from 0.05-1 wt%, for example 0.1 to 0.5 wt%. Because of the elongated structure of the CNS-derived species, suitable conductivity may be achieved at low loadings, e.g., up to 0.2 wt%. For example, the coating compositions may be employed as primer coatings to facilitate electrostatic painting of otherwise non-conductive materials such as plastics. Electrostatic painting is used to coat a grounded surface with charged paint particles from a specialized gun. A CNS-loaded primer coating can provide a conductive surface that can be grounded to even non-conductive substrates.

[0070] Alternatively or in addition, a conductive CNS-loaded primer coating can facilitate electroplating of non-conductive substrates. For example, a plastic workpiece can be coated with an CNS-loaded primer and immersed in an appropriate plating bath. Application of a current causes a thin layer of metal to be deposited on the workpiece. The metal can be patterned by controlling where the CNS-loaded primer is applied. For example, standard photolithography techniques may be employed to deposit the CNS-loaded primer in desired locations on a non-conductive substrate. In one embodiment, a workpiece is coated with a photoresist and patterned with appropriate radiation. The CNS-loaded primer is coated onto the workpiece. Washing the workpiece with an appropriate fluid will remove those sections of the photoresist that were not exposed to radiation, washing those sections of the primer coating away as well. Since the substrate is not conductive, only those sections of the surface coated with the CNS-loaded primer can be electroplated. Other methods of patterning coatings known to those of skill in the art may also be employed.

[0071] Alternatively or in addition, a CNS-loaded coating can contribute to electromagnetic shielding. Many automobile components are formulated to provide EMI shielding for electronic components from external radio signals. While older automobiles with metal bodies performed this function automatically, lightweighting trends in automobile manufacturing have let many of these metal parts to be replaced by plastic. Moreover, the increased use of electronics and powered components in vehicles, such as

keyless ignitions, remote starters, automatic sliding doors, and powered seat controls and windows generates increasing amounts of electromagnetic emissions. Meanwhile, vehicles continue to have incorporate more electronic systems such as GPS navigation systems, entertainment systems, Bluetooth compatible devices, hands-free control of cabin features ranging from navigation to entertainment systems, and touchscreen controlled systems that both generate and are susceptible to electromagnetic interference (“EMI”). CNS-loaded coatings provide an additional tool to automobile and component designers that can augment the EMI shielding capabilities of the coated parts. The coating containing CNS-derived fragments may be used as a primer coating or may include color pigments and be employed as a decorative coating.

[0072] The dispersion of CNS-derived species into coating compositions provides an additional, electrically conductive functionality to the final coating. For example, coatings are often used to provide primers for concrete for flooring and other applications, anti-corrosion primers for metals, and linings for tanks, containers, and pipes. Well dispersed CNS-derived species in these coatings can help dissipate static charge in all these and additional applications.

[0073] The present invention will be further clarified by the following examples which are intended to be only exemplary in nature

EXAMPLES

Viscosity measurements

[0074] The melt viscosity of several polymer resins in a Discovery HR-2 Hybrid Rheometer – 2 using a 25 mm parallel disposable aluminum plate. The test sample was equilibrated at the testing temperature for two minutes, presheared at 0.5 1/s for 30 s, and equilibrated for an additional 5 min. A flow sweep was performed from 0.1 1/s to 1000 1/s at the testing temperature. Results are shown Table 1 below. The CAB 551-0.2 and 551-0.01 resins (Eastman Chemical Company) have a melting range of 127-142 °C per the manufacturer and were measured at 200 °C. The Laropal A81 resin (BASF) has a softening range of 80-95 °C per the manufacturer, and the melt viscosity was measured at 155 °C. Addbond LP1611 resin has a Tg of -40 °C, and the melt viscosity was measured at 20 °C.

		Viscosity (Pas.s)			
Resin:		CAB 551-0.2	CAB 551-0.01	Addbond LP 1611	Laropal A81
Shear Rate (1/s)	0.1	121.0	13.9	15.6	5.2
	1	119.2	12.4	15.9	3.4
	10	115.0	11.4	15.9	1.3

Table 1

Example 1

[0075] CNS-resin mixture: Polymer resin (53.3 g) as designated in Table 2 below (CAB551-0.01 and CAB551-0.2, both from Eastman Chemical Company, and Laropal A81 resin from BASF) was loaded into a 60 mL mixing chamber in a Brabender mixer and mixed at 60 rpm at 180 °C until a homogeneous melt was obtained. Polyethylene glycol-coated CNS pellets (4.7 g, Applied Nanostructured Solutions, LLC) were then incorporated into the liquid melt at 60 rpm, after which the mixing speed was increased to 100 rpm and allowed to continue for the time indicated in Table 2. The mixture was taken out of the mixing chamber, cooled to ambient temperature, and ground into a dry powder having 8.1 wt% CNS-derived particles with a Retsch Cutting Mill SM300 (bottom sieve aperture size 4 mm).

Sample ID	Resin type	Mixing time (min.)	Appearance rating after dissolving in propylene glycol methyl ether acetate and EFKA 4310 dispersant(1-5; 5 is best)
Sample 1	CAB551-0.01	8	3
Sample 2	CAB551-0.2	5	4
Sample 3	CAB551-0.2	8	5
Sample 4	Laropal A81	8	1
Sample 5	Laropal A81	11	1

Table 2

[0076] Coating formulation: The dry powder containing CNS-derived species (2 g) was soaked in a mixture of propylene glycol methyl ether acetate (PGMEA, 27 g) and Efka® PX 4310 dispersant (0.486 g, 50% solids) overnight. The solid/liquid mixture was then dispersed using a Dispermat CV (blade diameter, 4 cm, volume 100 mL) at 1000 rpm for 1 hour to obtain a liquid mixture with a total solids concentration of 6.78 wt% and a concentration of CNS-derived species of 0.55 wt%. This mixture was evaluated using a Hegman gauge; the results are shown in Figure 4 and described in Table 2 and show that

the Sample 3 was the best dispersed of the five samples. The liquid mixtures with CAB resin of Samples 1-3 were used directly with the other components in the formulation for part A of the coating formulations of Examples 2 and 4 below.

Example 2

[0077] To prepare Part A, 18g of Setalux 1753 SS-70 resin (70% solids, Allnex GmbH), 41 g of a 50/50 w/w mixture of butyl acetate and PGMEA, 0.5 g of EFKA 4310 dispersant, and 26 g of Ti-Pure R-960 titania (Chemours) were mixed at 2000 rpm for 1 hr using the Dispermat CV high-speed disperser as described above. 17.5 g of the liquid mixture with CNS-derived species was then added, and the entire mixture ground with 150 g (1.5X the total weight of part A formulation) of 1 mm ZrO₂ beads in a LAU DAS 200 disperser for half an hour. The Part B components (11 g of the butyl acetate/PGMEA solution and 8.5 g Desmodur N3390 hardener from Covestro, 90% solids) were mixed with Part A under gentle mixing with a Speedmixer DAC600 FVZ mixer at 1000 rpm for 1 minute. The resulting coating composition was evaluated with a Hegman grindometer and also cast with a wire wound coating rod to make a 100 µm (wet) film on a Leneta Form 2C chart. The wet film was allowed to cure at 140 °C for 30 minutes to form a dry coating having 0.2 wt% CNS-derived species, along with 2.27 wt% CAB. The tinting strength (L* and b*) was measured using an X-Rite SP64, hand-held spectrophotometer in the CIE L*a*b* colorimetric system while excluding the specular reflectance mode. The surface resistivity was measured with a Keithley model 6517B electrometer fitted with Keithley 8009 test fixtures. The film appearance was evaluated qualitatively. All results are shown in Table 3. While the lower MW CAB551-0.01 provided inferior film appearance, the difference in results between Samples 2 and 3 demonstrate that increased grinding time can improve coating appearance (Table 3). It is expected that increased grinding time for the CAB-CNS mixture of Sample 1 would also result in improved coating appearance.

Sample ID	Fineness of wet coat (µm)	Tinting strength		Surface Resistivity (ohm/sq)	Coating appearance (1 poor, 8 best)
		L*	b*		
Sample 1	15	69.57	-4.22	2.30E+06	5
Sample 2	15	67.78	-4.15	1.20E+06	6
Sample 3	15	66.88	-4.09	1.10E+07	8

Table 3

Example 3 (Comparative)

[0078] In a comparative example, PEG-coated CNS (Advanced Nanostructure Materials, LLC, Boston MA) was milled in a LAU DAS 200 disperser for eight hours with resin, solvent, dispersant (BYK 163 dispersant from BYK Chemie), pigment, and 140 g of 1 mm zirconia beads to prepare Part A of a two part coating composition as shown in Table 4. After the zirconia beads were filtered out, Part A was combined with the Part B components in the same manner as in Example 2 to form a coating composition which was cast, cured to form a coating having 0.2 wt% CNS-derived species, and evaluated in the same manner as in Example 2. The results are shown in Table 5. While the resistivity of the coating is less than all three of the Example 2 coatings, the Hegman grind of the wet coating composition and appearance of the dry coating are far worse.

Part A Ingredients	Wt/g	Solids
Setalux 1753 SS-70 resin	18.00	70%
Butyl Acetate/PGMEA (50/50)	40.00	0
BYK163 dispersant	1.00	100%
Ti-Pure R-960 titania	20.62	100%
CNS pellets (with PEG binder)	0.083	100%
Part B		
Butyl Acetate/PGMEA (50/50)	20.30	0
N3390 hardener	8.50	90%

Table 4

Fineness of wet coat (μm)	Tinting strength		Resistivity (ohm/sq)	Appearance (1 poor, 8 best)
	L*	b*		
100	65.33	-4.31	5.50E+05	3

Table 5

Example 4

[0079] The liquid mixture of CNS-derived species and CAB resin of Sample 3 (Example 1) was used to prepare a polyester coating in the same manner as in Example 2, except with the formulation as set forth in Table 6 below (Setal 189xx-65 polyester resin and Cymel 325 cross-linker from Allnex). The performance of the wet coating composition

and dry coating (0.2% CNS-derived species along with 2.27% CAB on a dry basis) was evaluated as in Example 2 and is set out in Table 7.

Part A Ingredients	Wt/g	Solids
Setal 189xx-65 resin	23	65%
Butyl Acetate/PGMEA (50/50)	41	0
BYK163 dispersant	0.5	50%
Ti-Pure R-960 titania	22.3	100%
Solvent based solution of Sample 3	15	6.78%
Part B		
Butyl Acetate/PGMEA (50/50)	3	0
Cymel 325 cross-linker	2.6	80%

Table 6

Fineness of wet coat (μm)	Tinting strength		Resistivity (ohm/sq)	Appearance (1 poor, 8 best)
	L*	b*		
15	69.50	-3.54	2.00E+07	8

Table 7

[0080] The results show that the coating had comparable appearance to the acrylic coatings of Example 2 and excellent resistivity.

Example 5 (Comparative)

[0081] A millbase was prepared with 0.4 wt% CNS derived species using 0.4 g PEG-coated CNS, 88.4 g of a 1:1 (w/w) mixture of butyl acetate and PGMEA, 1.2 g EFKA 4310 dispersant, and 10g Setal 189xx-65 resin according to the method described in Example 3, but with 150 g zirconia beads (150% of the mass of the millbase formulation).

[0082] A white millbase were prepared with following process and recipe. 17.0 g propylene glycol methyl ether acetate (PGMEA), 17.0 g butyl acetate and 6.0 g DISPERBYK®-161 dispersant (BYK Chemie) were charged into a tin can and stirred at 1500 rpm for 15 min with a Dispermat CV-SIP mixer. While maintaining stirring, 60.0g Ti-Pure® R960 titania was added, following which the stir rate was increased to 2000 rpm and the mixture stirred an additional 15 min. The titania dispersion was loaded into a paint can with 150 g of 1 mm zirconium beads. The paint can was allowed to grind for

one hour in a Lau Model DAS 200 Disperser and the contents passed through a 200-mesh filter to separate the beads and millbase dispersion (60 wt% TiO₂).

[0083] The millbase with CNS-derived species was combined with the other components of a coating formulation (Table 8) in a Speedmixer DAC600 FVZ mixer at 1000 rpm for 3 minutes. A coating having 0.2 wt% CNS-derived fragments was cast and evaluated as described in Example 3 (Table 9). The resulting coating composition and coating have inferior Hegman grind, conductivity and appearance to coatings prepared in Example 2.

Component	Amount (g)
Setal 189XX-65 resin	30.00
Cymel 325 (80% solids) cross-linker	3.00
Butyl Acetate	4.65
PGMEA	4.65
BYK 346 leveling agent	0.20
TiO ₂ Dispersion (60 wt%)	35.00
CNS-Millbase	22.50

Table 8

Fineness of wet coat (μ m)	Tinting strength		Resistivity (ohm/sq)	Appearance (1 poor, 8 best)
	L*	b*		
55	69.28	-1.11	1.10E+09	5.5

Table 9

Example 6 (Comparative)

[0084] A millbase with 0.4 wt% CNS-derived species was prepared in an acrylic system using 0.4 g PEG-coated CNS, 88.4 g of a 1:1 (w/w) mixture of butyl acetate and PGMEA, 1.2 g EFKA 4310 dispersant, and 10 g Setalux 1753 SS70 resin (70% active) according to the method described in Example 5. A titania dispersion was also prepared as described in Example 5. A coating having 0.2% CNS-derived fragments was prepared using the method described in Example 5 and the formulation in Table 10. The properties of the wet coating composition and dry coating are shown in Table 11 and are inferior to those of the coating formulation and coating in Example 4.

Component	wt/g
Setalux 1753SS70 resin	28.00
Cymel 325 (80%) crosslinking agent	3.00
Butyl acetate	5.65

PGMEA	5.65
BYK 346 leveling agent	0.20
TiO ₂ Dispersion (60%)	35.00
CNS Millbase	22.50

Table 10

Fineness of wet coat (μm)	Tinting strength		Resistivity (ohm/sq)	Appearance (1 poor, 8 best)
	L*	b*		
60	63.14	-3.34	1.10E+11	6.5

Table 11

Example 7 (Comparative)

[0085] A millbase with 0.4 wt% CNS-derived species was prepared using 0.4 g PEG-coated CNS, 79 g of a 1:1 (w/w) mixture of butyl acetate and PGMEA, 0.6 g EFKA 4310 dispersant, and 20 g CAB 551-0.2 resin (30% active) according to the method described in Example 5, as was a 60 wt% titania dispersion. The CAB 551-0.2 solution was prepared by adding the resin powder slowly to a 1:1 mixture of butyl acetate and PGMEA with overhead mixing until the resin dissolved. A coating having 0.2 wt% CNS-derived fragments was prepared using the method described in Example 5 and the formulation in Table 12. The properties of the wet coating composition and dry coating are shown in Table 13. The coating composition has inferior Hegman grind to the coating compositions of Samples 2 and 3. While the coating resistivity was comparable, the appearance of the coating was inferior to those of Samples 2 and 3.

Components	wt/%
Setal 189XX65 resin	30.00
Cymel 325 (80%) cross-linker	3.00
Butyl Acetate	4.65
PGMEA	4.65
BYK 346 leveling agent	0.20
TiO ₂ Dispersion (60%)	35.00
CNS-Millbase	22.50

Table 12

Fineness of wet coat (μm)	Tinting strength		Resistivity (ohm/sq)	Appearance (1 poor, 8 best)
	L*	b*		
60	70.35	-2.38	1.30E+07	4.5

Table 13

[0086] The foregoing description of preferred embodiments of the present invention has been presented for the purposes of illustration and description. It is not intended to be exhaustive or to limit the invention to the precise form disclosed. Modifications and variations are possible in light of the above teachings, or may be acquired from practice of the invention. The embodiments were chosen and described in order to explain the principles of the invention and its practical application to enable one skilled in the art to utilize the invention in various embodiments and with various modifications as are suited to the particular use contemplated. It is intended that the scope of the invention be defined by the claims appended hereto, and their equivalents.

[0087] What is claimed is:

CLAIMS

1. A composition, comprising:
 - 5-15 wt% CNS-derived species; and
 - a polymer resin having a hydroxyl content of at least 1.5 wt%, a melt viscosity of at least 8 Pa.s at a shear rate of 0.1 s^{-1} at a temperature $60 \text{ }^{\circ}\text{C}$ greater than the highest temperature at which the resin undergoes a thermal transition and at least one of a) a solubility in a 1:1 (w/w) mixture of butyl acetate and propylene glycol methyl ether acetate of at least 5 wt%, and b) an acid number of at least 100.
2. The composition of claim 1, wherein the thermal transition is glass transition temperature, melting temperature, or softening point.
3. The composition of claim 1 or 2, wherein the polymer resin has a hydroxyl content of from 1.5 wt% to 5 wt%.
4. The composition of any of claims 1-3, wherein the melt viscosity is from 8 Pa.s to 1000 Pa.s.
5. The composition of any of claims 1-4, wherein the polymer resin has a solubility of 5 wt% to 10 wt% in a 1:1 (w/w) mixture of butyl acetate and propylene glycol methyl ether acetate.
6. The composition of any of claims 1-5, wherein the polymer resin has a molecular weight M_n of 15000 to 80000.
7. The composition of any of claims 1-6, wherein the polymer resin has an acid number of 100 to 300.
8. The composition of any of claims 1-7, wherein the polymer resin has a solubility in water of at least 5 wt% when at least 50% of the acid groups on the polymer resin are non-ionized.
9. The composition of any of claims 1-8, wherein the polymer resin has a molecular weight (M_n) of 8000 to 40000.
10. The composition of any of claims 1-9, further comprising a dispersant.

11. The composition of claim 10, wherein the dispersant is present in an amount of 20 to 60 wt% with respect to the amount of dispersant and CNS-derived species.
12. A method for preparing a composition, comprising:

combining carbon nanostructures with a polymer resin having a hydroxyl content of at least 1.5 wt%, a melt viscosity of at least 8 Pa.s at a shear rate of 0.1 s⁻¹ at a temperature 60 °C greater than the highest temperature at which the resin undergoes a thermal transition and at least one of a) a solubility in a 1:1 (w/w) mixture of butyl acetate and propylene glycol methyl ether acetate of at least 5 wt%, and b) an acid number of at least 100 to form a composition having 5-15 wt% CNS-derived species.
13. The method of claim 12, wherein the carbon nanostructures are coated with a dispersant.
14. The method of claim 13, wherein the dispersant is present in an amount of 20 to 60 wt% relative to the amount of coated carbon nanostructures.
15. The method of claim 13 or 14, wherein the dispersant is selected from poly(vinyl pyrrolidone), poly(vinylpyrrolidone-co-vinyl acetate), poly(vinyl butyral), poly(vinyl alcohol), polyalkylene oxides, polyalkylene oxides or acrylic polymers comprising amine functional groups, poly(propylene carbonate), cellulosic dispersants, poly(carboxylic acid), polyacrylates, poly(methylacrylate), poly(acrylamide), amide wax, styrene maleic anhydride resins, amine-functionalized or amine-terminated compounds, alkylphenol ethoxylates, or alkyl ethoxylates, AMP™ dispersants, dispersants containing 2-amino-2-methyl-1-propanol, polyesters, polyamides block copolymers having both a hydrophobic and a hydrophilic group, sodium dodecyl sulfate (SDS), sodium dodecyl benzyl sulfonate, amine-functionalized derivatives of any of these, acid functionalized derivatives of any of these, or a mixture of two or more of any of these.
16. A method of preparing a coating composition, comprising:

combining the composition of any of claims 1-11 with a solvent and optional dispersant;

allowing the polymer resin to dissolve in the solvent to produce a dispersion of CNS-derived species in the solvent; and
combining the dispersion with a coating resin and optional additive.

17. The method of claim 16, wherein the coating resin comprises an acrylic, polyurethane, polyester, or epoxy resin.
18. The method of claim 17, wherein the coating resin is an acrylic or polyester resin.
19. The method of any of claims 16-18, wherein the coating composition comprises 0.05 to 1 wt% (dry basis) CNS-derived species.
20. The method of any of claims 16-19, wherein the coating composition contains 0.1 to 0.5 wt% or 0.05 to 0.2 wt% CNS-derived species.
21. The method of any of claims 16-20, wherein the coating composition has a Hegman grind of 10-20 microns, for example, 15-20 microns.
22. The method of any of claims 16-21, wherein the optional additive is at least one of a co-solvent, surfactant, filler, adhesion promoter, flow modifier, leveling aide, biocide, and colorant.
23. A coating composition comprising the composition of any of claims 1-11 and a coating resin.
24. The coating composition of claim 23, wherein the coating composition comprises 0.05 to 1 wt% (dry basis) CNS-derived species.
25. The coating composition of claim 23 or 24, wherein the coating composition contains 0.1 to 0.5 wt% or 0.05 to 0.2 wt% CNS-derived species.
26. The coating composition of any of claims 23-25, wherein the coating composition has a Hegman grind of 10-20 microns, for example, 15-20 microns.
27. The coating composition of any of claims 23-26, wherein the coating resin comprises an acrylic, polyurethane, polyester, or epoxy resin.
28. The coating composition of any of claims 23-27, wherein the coating resin is an acrylic or polyester resin.

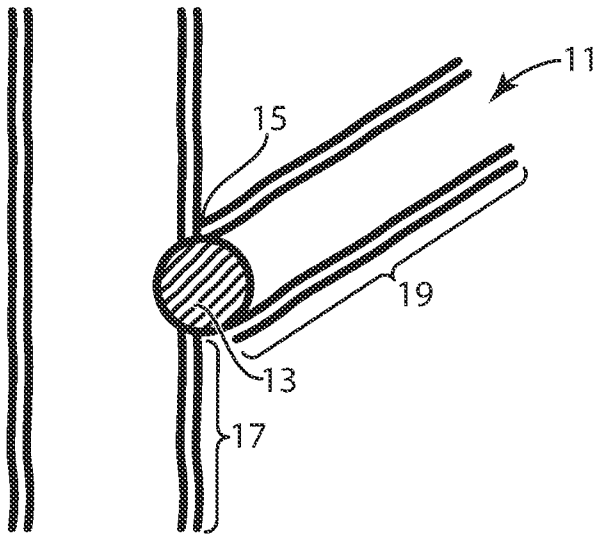


FIG. 1A

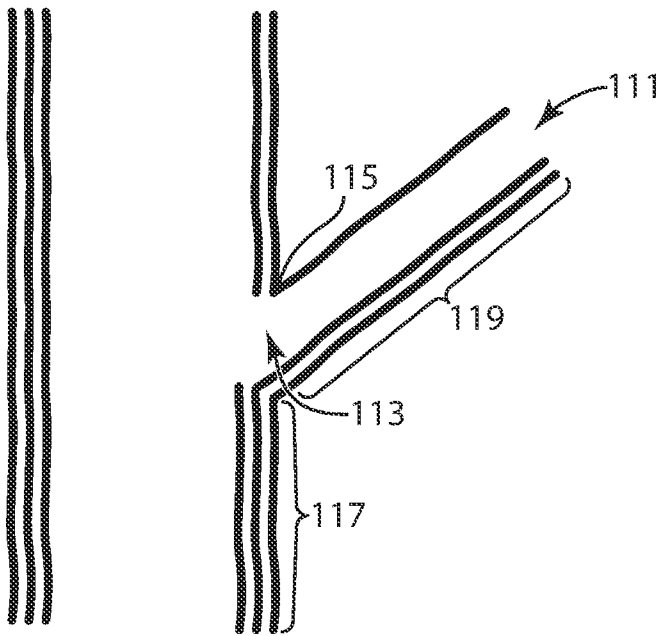


FIG. 1B

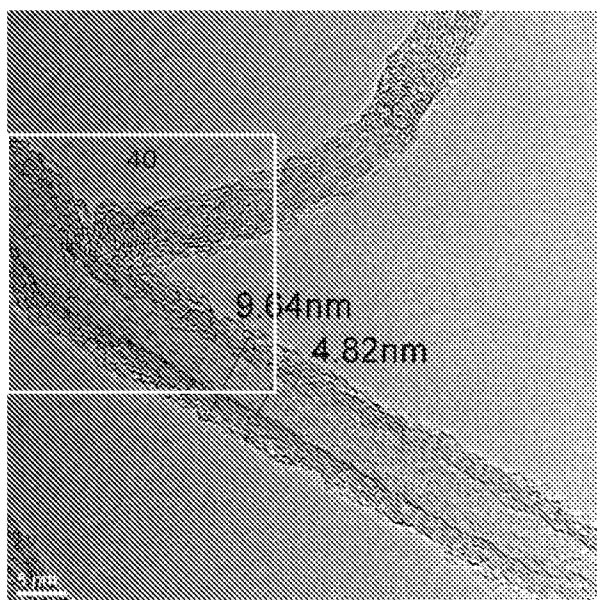
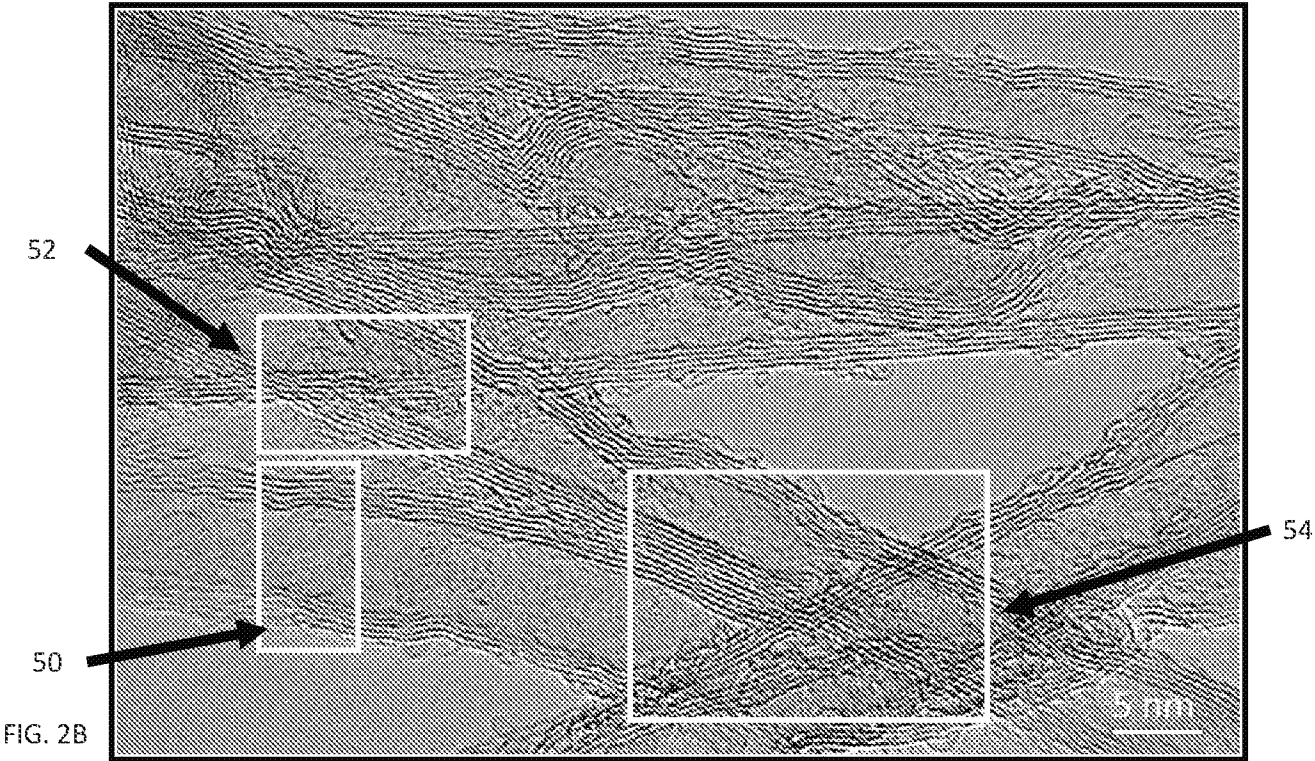


FIG. 2A



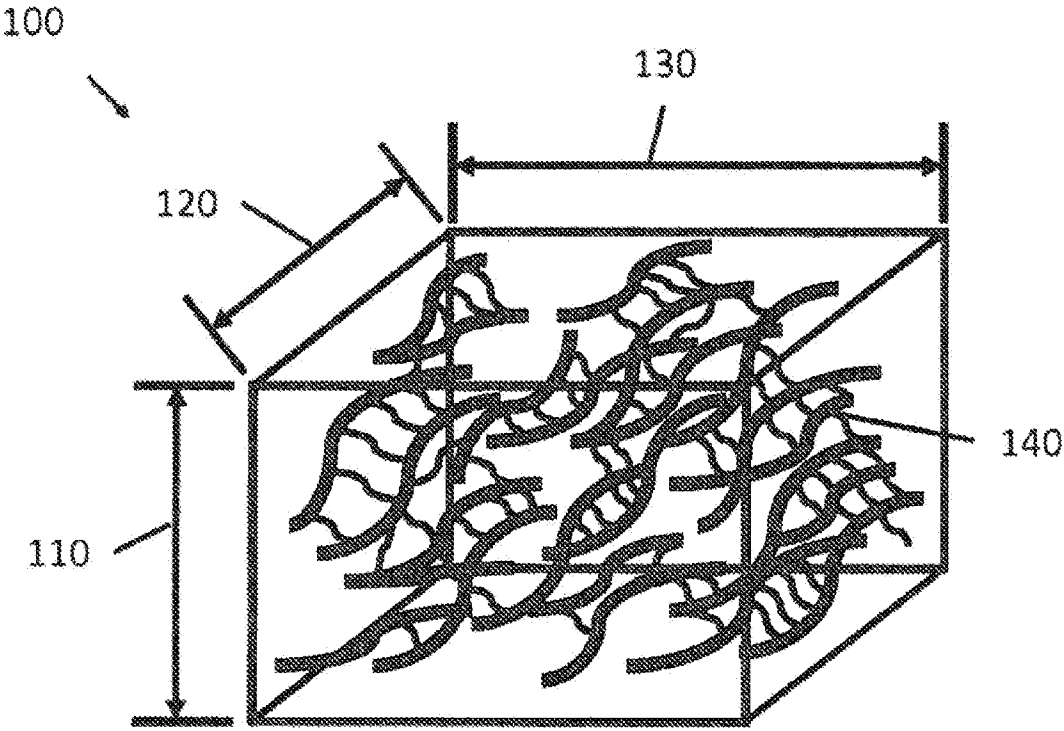


FIG. 3A

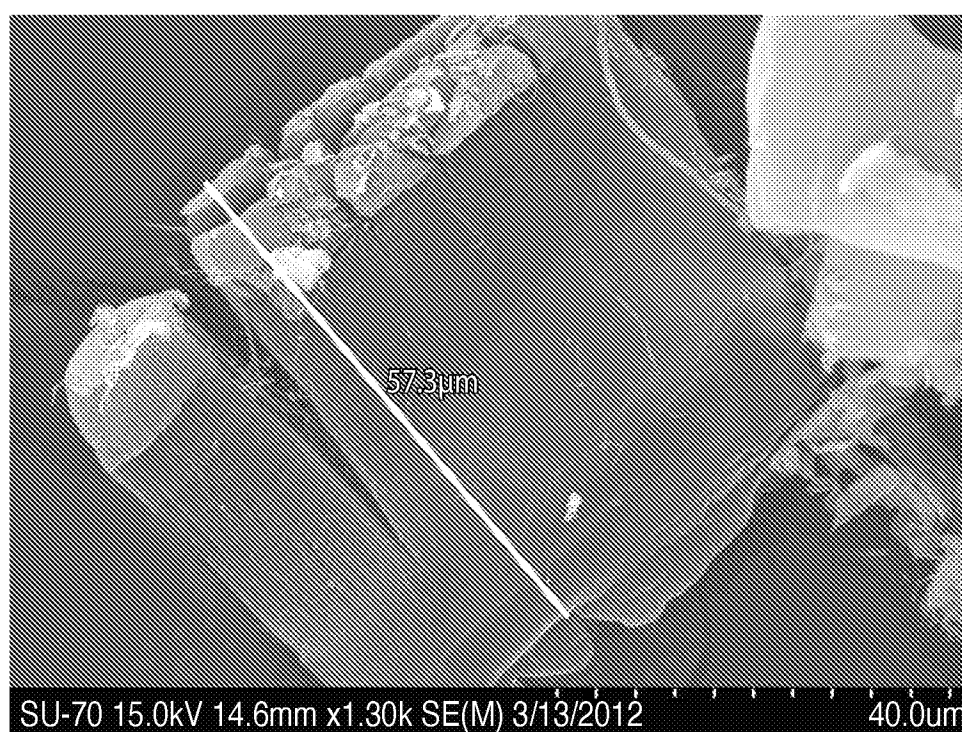


FIG. 3B

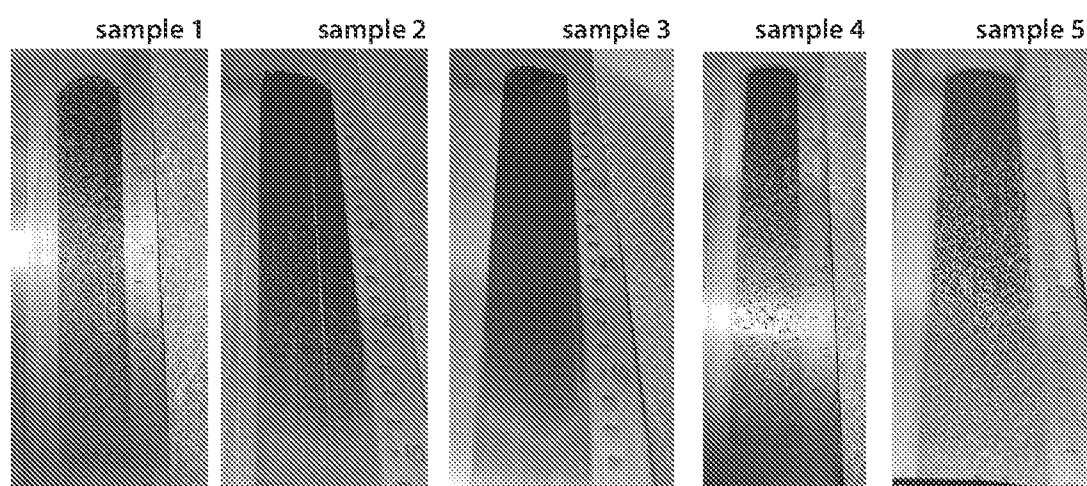


Figure 4

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2022/048022

A. CLASSIFICATION OF SUBJECT MATTER INV. C01B32/15 C08K3/04 C09D7/40 C09D175/00 C01B32/174 ADD.		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) C01B C09G C08K C09D		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) EPO-Internal		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2021/180158 A1 (CABOT CORP [US]; GUI ZHANGLIANG [CN]) 16 September 2021 (2021-09-16) abstract claim 1 examples 1-9 tables 2,3	1-28
A	US 2014/094541 A1 (SHAH TUSHAR K [US] ET AL) 3 April 2014 (2014-04-03) abstract paragraphs [0057], [0058]	1-28
	----- -/-	
☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.		
* Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance;; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance;; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search		Date of mailing of the international search report
10 February 2023		20/02/2023
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer Mertins, Frédéric

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2022/048022

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☒ Claims Nos.: **1-28 (partially)**
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
see FURTHER INFORMATION sheet PCT/ISA/210

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims;; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box II.2

Claims Nos.: 1-28 (partially)

Present claim 1 relates to an extremely large number of possible products. Support and disclosure in the sense of Article 6 and 5 PCT is to be found however for only a very small proportion of the products claimed, see the whole application as filed, especially the examples and comparative examples and paragraphs [0002], [0022] and [0023] of the description, which clearly state that the "CNS-derived species" of said claim 1 are in fact a polymeric, highly branched and crosslinked network of carbon nanotubes (CNTs). The application explains that due to this specific structure networks can be formed more efficiently than with regular CNTs but at the same time that the dispersion of the said specific structure is difficult, especially in organic solvent (see the description in paragraph [0002]), and that the goal of the present application is to solve this specific problem.

A similar reasoning applies to claims 2-28 due to their direct or indirect dependence on claim 1.

The non-compliance with the substantive provisions is to such an extent, that the search was performed taking into consideration the non-compliance in determining the extent of the search of claims 1-28 (PCT Guidelines 9.19 and 9.23).

The search of claims 1-28 was thus restricted to those claimed products and methods which appear to be supported and a generalisation of their structural formulae, namely products and methods as defined in said claims 1-28 but where the term "CNS-derived species" is replaced or completed by the term "polymeric, highly branched and crosslinked network of carbon nanotubes (CNTs)".

The applicant's attention is drawn to the fact that claims relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure. If the application proceeds into the regional phase before the EPO, the applicant is reminded that a search may be carried out during examination before the EPO (see EPO Guidelines C-IV, 7.2), should the problems which led to the Article 17(2) PCT declaration be overcome.

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2022/048022

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	CHAO-XUAN LIU ET AL: "Improved Dispersion of Carbon Nanotubes in Polymers at High Concentrations", NANOMATERIALS, vol. 2, no. 4, 26 October 2012 (2012-10-26), pages 329-347, XP055284571, DOI: 10.3390/nano2040329 the whole document -----	1-28
A	KRAUSE BEATE ET AL: "Comparative study of singlewalled, multiwalled, and branched carbon nanotubes melt mixed in different thermoplastic matrices", POLYMER, vol. 159, 10 November 2018 (2018-11-10), pages 75-85, XP085546501, ISSN: 0032-3861, DOI: 10.1016/J.POLYMER.2018.11.010 the whole document -----	1-28

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2022/048022

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2021180158 A1	16-09-2021	CN 115279826 A	01-11-2022
		EP 4118138 A1	18-01-2023
		KR 20220165249 A	14-12-2022
		TW 202204251 A	01-02-2022
		TW 202218982 A	16-05-2022
		WO 2021180158 A1	16-09-2021

US 2014094541 A1	03-04-2014	AU 2013323175 A1	02-04-2015
		CA 2885330 A1	03-04-2014
		EP 2900473 A2	05-08-2015
		ES 2820556 T3	21-04-2021
		JP 2015533187 A	19-11-2015
		KR 20150065742 A	15-06-2015
		US 2014094541 A1	03-04-2014
		US 2016362542 A1	15-12-2016
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