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(54) Title: CARBON NANOTUBE REINFORCED POLYMER COMPOSITE AND METHOD FOR MAKING SAME

(57) Abstract: The present invention is directed to methods of dispersal of CNTs into one or more solvents with one or more carrier compounds. The CNT-dispersion mixture is then added to a polymer to produce a CNT -polymer composite material. Integration of CNTs in the matrix is augmented with greater dispersal of CNTs. The methods comprise the steps of: (a) dispersing CNTs in a solvent containing a carrier compound; (b) adding a polymer matrix to the dispersion, forming a mixture; (c) removing the solvent and carrier compound from the mixture to form a largely solvent- free mixture, which forms a CNT -polymer antifouling coating. Additional steps can include; (d) adding a curing agent to the solvent-free mixture; and (d) curing the solvent- free mixture, forming a CNT -polymer composite, wherein the CNTs are dispersed and integrated into the polymer mixture. Alternatives in the methods include replacing a single solvent with a plurality of solvents.



CARBON NANOTUBE REINFORCED POLYMER COMPOSITE AND METHOD FOR MAKING SAME

This application claims priority under 35 U.S.C. §119 to U.S. Provisional Patent Application Ser. No. 61/643959, filed May 8, 2012, the entire contents of which are incorporated herein by reference.

FIELD OF THE INVENTION

The present invention relates generally to reinforced polymer composites, and specifically to methods of dispersal and addition of carbon nanotubes into one or more polymer matrices.

BACKGROUND

Carbon nanotubes (CNTs) came to light in the early 1990's. The first reported CNTs comprised tubular structures of carbon atom sheets, basically a graphite structure, with multiple tubes nested in a concentric fashion, termed multi-wall carbon nanotubes (MWCNTs) [Iijima, S. *Nature* 1991, 354, 56]. Soon after the discovery of MWCNTs, single-wall carbon nanotubes (SWCNTs) were found. SWCNTs comprised a single graphene rolled up as a tubular structure [Iijima et al., *Nature*, 1993, 363, 603]. Synthesis of the SWCNTs was accomplished using an arc-discharge process having carbon electrodes doped with transition metals [Iijima, S. and Ichihashi, T. *Nature* 1993, 363, 603; Bethune, D. S., et al. *Nature* 1993, 363, 605]. Because of their unique properties, CNTs have the potential to be useful in multiple areas of technology. CNTs are the strongest materials

known at this time in terms of tensile strength and elastic modulus, suggesting a role in mechanical reinforcements for lightweight composite materials. SWCNTs have a tensile strength 50-100 GPa and a modulus of 1-2 TPa, five and ten times greater than steel, respectively, while one-sixth of the weight. *See* Baughman, R. H et al. *Science* 2002, 297, 787. They can withstand pressure up to 24 GPa, surpassing even diamonds. Popov, et al. *Phys. Rev. B*, 2002, 65, 033408. Additionally, CNTs possess certain kinetic, optical, thermal and electrical properties that suggest an important role in such areas as materials, nanomachines, semiconductors, conductive polymer composites, sensor devices and radar-absorbing coatings.

Dispersion of CNTs within a matrix and CNT interaction with the matrix determine whether the properties of CNTs are integrated well into the polymeric matrix. Difficulties in uniformly dispersing CNTs within a matrix are caused by the strong van der Waals interactions amongst the tubes. Aggregation of CNTs within a matrix causes defects in the composite material. Enough aggregation can cause the composite material to fail. Other problems associated with incorporating CNTs into other materials occur because of the lack of interfacial interactions between the matrix and the CNTs. Failure of CNTs to interact with the matrix leads to low or no material reinforcement from lack of load transfer efficiency from the matrix to the CNTs. *See* Huang, Y.Y. and E. M. Terentjev, *Polymers*, 2012, 4, 275; Jogi, B. F. et al., *J Encapsulation and Adsorption Sciences*, 2012, 2, 69. Providing further complications, the behavior of a CNT-polymer composite is dependent on the processing of the CNT, where the processing chosen can lead to increases in some aspects of the composite while not influencing or reducing other aspects of the composite. Thus, the theoretical potential of CNTs has yet to be realized.

Resolution of the problems associated with CNTs opens numerous new avenues in engineering and materials science technologies. CNT- epoxy composites, including CNT-epoxy coatings and paint, are highly important polymer composites. CNT-epoxy composites promise new composite materials that are stronger, more flexible yet less dense, thus less heavy, than current materials. CNT-polymer paints and coatings open the possibility of replacing many paints and coatings, especially those found to be environmentally toxic, such as marine antifouling paints and coatings containing copper compounds or biocides. These CNT-polymer composites will apply to numerous areas, including aerospace, aeronautics, electromagnetics, antifouling coatings, high-strength low-density corrosion-resistant components, and many others.

Mechanical dispersion of CNTs, such as mechanical stirring and sonication, generally results in poor dispersion. The CNTs precipitate from the suspension quickly. Use of mechanical dispersion for CNT-polymer composites has been utilized with little success.

Chemical modification (functionalization) of CNTs forms functional groups on the sidewalls or the ends of the CNTs ("functionalized CNTs"). The functional groups of the functionalized CNTs provide bonding sites providing an interface for CNTs to connect to each other and to the surrounding matrix, increasing cross-linking in composites. Functionalization of CNTs generally involves exposing the CNTs to one or more strong oxidizing acids, such as nitric or sulfuric acid, to form functional groups, such as carboxylic acid groups. Treatment of CNTs to functionalization disrupts the internal bonds within the CNT, leading to diminished mechanical strength and degradation of the very properties unique to CNTs.

Thus, a need remains for a method for dispersion of non-functionalized CNTs or non-covalently functionalized CNTs in aqueous or non-aqueous solutions, where the desired properties of the CNTs remain intact, little to no aggregation of the CNTs occurs in solution and interfacing between the CNTs and a matrix occurs at a level to transfer the unique properties of the CNTs to the matrix. Furthermore, a need remains for a method to create a stable non-functionalized CNT or non-covalently functionalized CNT dispersion where the dispersion remains stable for significant lengths of time, such as weeks or months.

SUMMARY OF THE INVENTION

The present invention is directed to methods of dispersal of CNTs into one or more solvents with or without carrier compounds and the dispersion containing CNTs is then integrated with a polymer and to the CNT-polymer composites produced by such methods. Integration of CNTs with one or more polymers is augmented through improved dispersal of the CNTs, with or without covalent bonding with the molecules of the polymer matrix during the curing process. In general, the methods comprise the steps of: (a) dispersing CNTs in a solvent with the addition of a carrier compound; (b) adding one or more polymer matrices to the dispersion, forming a mixture; (c) removing the solvent and the carrier compound from the mixture to form a largely solvent- and carrier-free mixture; (d) adding a curing agent to the solvent- and carrier-free mixture; and (d) curing the solvent- and carrier-free mixture, forming a CNT-polymer composite, wherein the CNTs are dispersed and integrated into the polymer mixture. Alternatives in the methods include replacing a single solvent with a plurality of solvents and/or not including a carrier compound.

One embodiment of the present invention is directed towards a method of dispersion

where the CNTs are added to a solvent comprising largely an alkaline carbonate, which is a class of epoxy reactive diluents. Examples of alkaline carbonates include butylene carbonate, propylene carbonate or ethylene carbonate. The CNTs are dispersed in the alkaline carbonate solvent in the presence of a carrier compound, such as a titanate coupling agent, zirconate coupling agent or glycol ester. The carrier compound addition to the propylene carbonate solvent can include a carrier solvent, such as dimethyl sulfide. Alternatively, the CNTs can be added to the alkaline carbonate without the carrier compound and carrier solvent, thus achieving a stable dispersion of CNTs.

Another embodiment of the present invention is directed towards a method of dispersion where the CNTs are added to an alcohol, such as isopropyl alcohol, in the presence of a carrier compound, such as a titanate, zirconate or glycol ester. The CNT dispersion is further combined with an alkaline carbonate to achieve a stable dispersion of CNTs.

The present invention includes a method of dispersion of CNTs in a hydrocarbon solvent, such as toluene, Dowanol PMA (propylene glycol methyl ether acetate), Dowanol EPh (ethylene glycol phenyl ether) or Dowanol PPh (propylene glycol phenyl ether), in the presence of a carrier compound. The CNT dispersion is then mixed with an alkaline carbonate, thus creating a stable dispersion of CNTs.

The present invention includes a method of dispersion of CNTs in water in an emulsion of a titanate coupling agent or zirconate coupling agent. The present invention also includes a method of dispersion of CNTs in n-methylpyrrolidone in the presence of a titanate coupling agent or zirconate coupling agent.

For each dispersion method, the final CNT dispersed mixture is added to a polymer

matrix, such as an epoxy resin. The solvents and carrier compounds are removed from the CNT dispersed mixture plus polymer matrix either before or after the addition of a curing agent, thus leaving the dispersed CNTs in the polymer plus curing agent matrix. Removal of the solvents and carrier compounds is accomplished by vacuum distillation, fine filtration or organic solvent nano-filtration using an Evonik Duramem membrane, defined here as "OSN." A review of OSN can be found in White, L., *J. Membrane Science*, 2006, 286, 26 and Volkov, A., et al., *Russian Chemical Reviews*, 2008, 77, 983. The CNT-slurry can be combined with an epoxy resin without sonication.

DESCRIPTION

The present invention is directed to methods of dispersal of CNTs into one or more solvents with or without carrier compounds, where the CNTs are non-functionalized or non-covalently functionalized, the dispersion is then integrated with a polymer. The present invention is also directed to the CNT-polymer composites produced by such methods. The CNTs and polymer interface through the greatly improved dispersion of the CNTs and the non-covalent interactions between the CNTs and the polymer. The scope of the invention includes polymer composites that include one or more reinforcing compounds. In general, the disclosed methods involve manipulating the non-covalent interactions, such as the van der Waals and electrostatic forces, between the CNTs and the polymer matrix or even the curing agent to not only increase the dispersion of the CNTs but also to increase the interactions between the CNTs and the polymer matrices.

While various embodiments of the present invention are discussed below, one skilled in the art will understand and it will be apparent that a variety of modifications can be made within the scope of this disclosure. Such modifications form a part of the present

application and are embraced by the claims of this application. All patents and publications and disclosures referenced in this application are incorporated by reference in their entireties.

The methods of the present invention generally comprise the steps of: (a) dispersing CNTs in a solvent with the addition of a carrier compound; (b) adding one or more polymer matrices to the dispersion, forming a mixture; (c) removing the solvent and the carrier compound from the mixture to form a largely solvent- and carrier-free mixture; (d) adding a curing agent to the solvent- and carrier-free mixture; and (d) curing the solvent- and carrier-free mixture, forming a CNT-polymer composite, wherein the CNTs are dispersed and integrated into the polymer matrix.

CNTs of the present application include single-wall carbon nanotubes (SWCNTs), multi-wall carbon nanotubes (MWCNTs), double-walled carbon nanotubes, buckytubes, fullerene tubes, tubular fullerenes, graphite fibrils, vapor grown carbon fibers, inorganic/organic nanotube hybrids and combinations thereof. In some embodiments of the present invention, the CNTs are separated based on a characteristic inherent in a CNT, such as, but not limited to, chirality, electrical conductivity, thermal conductivity, diameter, length, number of nested tubes, and combinations thereof. In some embodiments, the CNTs are purified using techniques that include, but are not limited to, Chiang et al., *J. Phys. Chem, B*, 2001, 105, 1157-1161 and 8297-8301. The terms “CNT,” “CNTs,” and “nanotube(s)” are used synonymously herein.

Polymers of the present invention include epoxies and polymer resins, such as an alkyd resin, a polyester resin, vinyl resin (epoxy resin combined with an unsaturated monocarboxylic acid) or a silicone resin. Epoxies of the present invention are cross-linked

polymeric species, where the cross-linking is between epoxy resin species comprising epoxide groups and a curing agent. Curing is defined as the process of cross-linking of the epoxy resin species and the curing agent. Suitable epoxy resins include, but are not limited to, diglycidyl ether of bis-phenol-A, Nov lac epoxy, cycloaliphatic epoxy, brominated epoxy, aliphatic amines, aromatic amines, and combinations thereof. Epoxies may further comprise additives such as, but not limited to, plastisizers, anti-degradation agents, diluents, toughening agents, pigments, clay fillers and combinations thereof.

As to each embodiment, the general step of dispersal of the CNTs in a solvent can require selection of a suitable solvent for dispersing the CNTs with a particular group. Dispersal can include mixing, agitation, and sonication for assistance in dispersal.

In the general step of adding the polymer to the dispersion to form a CNT-polymer mixture, the level of homogeneity of the mixture can be variable initially or varied in subsequent processing steps.

In the general step of removal of the solvent and carrier compounds from the CNT-polymer mixture to form a largely solvent-free mixture, the removal can be an evaporative process, a vacuum removal process or other enhanced evaporative removal process or a filtration process.

The following examples are provided to more fully illustrate some of the embodiments of the present invention. One skilled in the art will appreciate that the techniques disclosed in the examples can be altered or varied and still obtain a like or similar result without departing from the scope of the invention. For each of the below Examples, dispersion-resin mixture process was adding the epoxy resin to the dispersion mixture and stirring the solution for at least 10 min. and up to and including 30 min. in a

low powered ultrasonic bath. Removal of the solvent from the dispersion-resin mixture was completed by organic solvent nano-filtration ("OSN"). White, L.J. *Membrane Science*, 2006, 286, 26.

EXAMPLE 1

This Example illustrates dispersion of SWCNTs in an alkaline carbonate in the presence of a titanate compound.

SWCNTs of 95% or greater purity with a diameter of 8-15 nm and a length of 10-50 μm were obtained by a variety of sources. A titanate compound (Neoalkoxy Titanate LICA-09) was added to propylene carbonate via the carrier solvent dimethyl sulfide.

Concentration of CNTs added to the titanate-containing solvent was 0.01% up to and including 5.5% by weight and the titanate ranged from 0.2% up to and including 20% weight percent of the weight of the CNT concentration. The CNT-solvent mixture was mixed by sonication. The sonication process used a 3/16 inch diameter tapered ultrasonic probe coupled to a Sonics and Materials VCX 750 Sonicator, where the Sonicator was at 25% power. The sonication process consisted of repeated cycle of 5 sec. on and 5 sec. off for a total of 15 minutes. Dispersion of SWCNTs remained stable at least 3 months. Complete dispersion of SWCNTs were found at SWCNT concentrations up to and including 0.05 g per liter.

EXAMPLE 2

This Example illustrates dispersion of MWCNTs in an alkaline carbonate in the presence of a titanate compound.

MWCNTs of 95% or greater purity with a diameter of 8-15 nm and a length of 50-80 μm were obtained by a variety of sources. A titanate compound (Neoalkoxy Titanate LICA-

09) was added to propylene carbonate via the carrier solvent dimethyl sulfide.

Concentration of CNTs added to the titanate-containing solvent was 0.01% up to and including 5.5% by weight and the titanate ranged from 0.2% up to and including 20% weight percent of the weight of the CNT concentration. The CNT-solvent mixture was mixed by sonication. The sonication process used a 3/16 inch diameter tapered ultrasonic probe coupled to a Sonics and Materials VCX 750 Sonicator, where the Sonicator was at 25% power. The sonication process consisted of repeated cycle of 5 sec. on and 5 sec. off for a total of 15 minutes. Dispersion of SWCNTs remained stable for at least 3 months.

EXAMPLE 3

This Example illustrates dispersion of MWCNTs in an alkaline carbonate in the presence of a titanate compound.

MWCNTs of 95% or greater purity with a diameter of 8-15 nm and a length of 50-80 μm were obtained by a variety of sources. A titanate compound (Neoalkoxy Titanate LICA-09), concentration of titanate ranging from 0.2% up to and including 20% as weight percent of the weight of the MWCNTs, was added to isopropyl alcohol. Concentration of CNTs added to the titanate-containing solvent ranged from 0.01% up to and including 5.5% by weight and the titanate ranged from 0.2% up to and including 20% weight percent of the weight of the CNT concentration. The CNT-solvent mixture was mixed by sonication. The sonication process used a 3/16 inch diameter tapered ultrasonic probe coupled to a Sonics and Materials VCX 750 Sonicator, where the Sonicator was at 25% power. The sonication process consisted of repeated cycle of 5 sec. on and 5 sec. off for a total of 15 minutes. Dispersion of SWCNTs remained stable for at least 3 months. Sonication process used a 3/16 inch diameter tapered ultrasonic probe coupled to a Sonics and Materials VCX 750

Sonicator, where the Sonicator was at 25% power. The sonication process consisted of repeated cycle of 5 sec. on and 5 sec. off for a total of 15 minutes. Dispersion of SWCNTs remained stable for at least 3 months.

CLAIMS:

What is claimed is:

1. A method comprising the steps of:
 - dispersing CNTs in a solvent to form a dispersion in the presence of at least one carrier compound, wherein the solvent is selected from the group consisting of an alkaline carbonate epoxy reactive diluent, a hydrocarbon, or an alcohol;
 - adding an epoxy resin to the dispersion to form a mixture;
 - removing the solvent from the mixture wherein the CNTs and the epoxy resin form a substantially solvent-free mixture;
 - adding a curing agent to the substantially solvent-free mixture; and
 - curing the substantially solvent-free mixture to form a CNT-epoxy composite, wherein the CNTs are dispersed and interface with the epoxy resin in the CNT-epoxy composite.
2. The method of claim 1, wherein the dispersing step comprises ultrasonication.
3. The method of claim 1, wherein the alkaline carbonate epoxy reactive diluent is propylene carbonate.
4. The method of claim 1, wherein the alkaline carbonate epoxy reactive diluent is ethylene carbonate.
5. The method of claim 1, wherein the alkaline carbonate epoxy reactive diluent is butylene carbonate.
6. The method of claim 1, wherein the CNTs comprise a carbon nanotube type selected from the group consisting of single-wall carbon nanotubes, multi-wall carbon nanotubes (MWCNTs), double-walled carbon nanotubes, buckytubes, fullerene tubes,

tubular fullerenes, graphite fibrils, vapor grown carbon fibers, and inorganic/organic nanotube hybrids.

7. The method of claim 1, wherein the hydrocarbon chosen is toluene.
8. The method of claim 1, wherein the hydrocarbon chosen is propylene glycol methyl ether acetate.
9. The method of claim 1, wherein the hydrocarbon chosen is propylene glycol phenyl ether.
10. The method of claim 1, wherein the alcohol is isopropyl alcohol.
11. The method of claim 1, wherein the carrier compound is a titanate coupling agent.
12. The method of claim 1, wherein the carrier compound is a zirconate coupling agent.
13. The method of claim 1, wherein the carrier compound is a glycol ester.
14. The method of claim 1, further comprising purifying the CNTs before the dispersing step.
15. The method of claim 1, further comprising a selection step before the dispersing step where the selection step comprises the selection of the CNTs by a property, wherein the property is selected from the group consisting of length, diameter, chirality, conductivity, Young's modulus, tensile strength, elongation-to-break, and combinations thereof.
16. A method comprising the steps of:
 - dispersing CNTs in a solvent to form a dispersion in the presence of at least one carrier compound, wherein the solvent is selected from the group consisting of an alkaline carbonate epoxy reactive diluent, a hydrocarbon, or an alcohol;
 - adding a polymer resin to the dispersion to form a mixture; and

removing the solvent from the mixture wherein the CNTs and the polymer resin form a substantially solvent-free mixture, wherein the substantially solvent-free mixture forms a CNT-polymer resin composite antifouling coating.

17. The method of claim 16, wherein the dispersing step comprises ultrasonication.
18. The method of claim 16, wherein the alkaline carbonate is a propylene carbonate.
19. The method of claim 16, wherein the alkaline carbonate is an ethylene carbonate.
20. The method of claim 16, wherein the alkaline carbonate is a butylene carbonate.
21. The method of claim 16, wherein the CNTs comprise a carbon nanotube type selected from the group consisting of single-wall carbon nanotubes, multi-wall carbon nanotubes (MWCNTs), double-walled carbon nanotubes, buckytubes, fullerene tubes, tubular fullerenes, graphite fibrils, vapor grown carbon fibers, and inorganic/organic nanotube hybrids.
22. The method of claim 16, wherein the hydrocarbon chosen is toluene.
23. The method of claim 16, wherein the hydrocarbon chosen is propylene glycol methyl ether acetate.
24. The method of claim 16, wherein the hydrocarbon chosen is propylene glycol phenyl ether.
25. The method of claim 16, wherein the alcohol is isopropyl alcohol.
26. The method of claim 16, wherein the carrier compound is a titanate coupling agent.
27. The method of claim 16, wherein the carrier compound is a zirconate coupling agent.
28. The method of claim 16, wherein the carrier compound is a glycol ester.
29. The method of claim 16, further comprising purifying the CNTs before the

dispersing step.

30. The method of claim 16, further comprising adding a pigment to CNT-polymer resin composite antifouling coating.

31. A CNT-epoxy polymer composite prepared by a process comprising the steps of:

- dispersing CNTs in a solvent to form a dispersion, wherein the solvent contains a carrier compound;
- adding an epoxy resin to the dispersion to form a mixture;
- removing the solvent and the carrier compound from the mixture to form a substantially solvent-free mixture;
- adding a curing agent to the substantially solvent-free mixture; and
- curing the substantially solvent-free mixture to form the CNT-epoxy polymer composite.

32. A CNT-polymer antifouling coating prepared by a process comprising the steps of

- dispersing CNTs in a solvent to form a dispersion, wherein the solvent contains a carrier compound;
- adding a polymer resin to the dispersion to form a mixture; and
- removing the solvent and the carrier compound from the mixture to form a substantially solvent-free mixture.