(54) Title: COMPOSITE MATERIAL COMPRISING NANOMATERIAL OR MICROMATERIAL

(57) Abstract: Disclosed herein are composite materials formed by covalently bonding a nanomaterial or micromaterial with a macro-scale material.

Declarations under Rule 4.17:
  — as applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))
  — as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))

Published:
  — with international search report (Art. 21(3))
COMPOSITE MATERIAL COMPRISING NANOMATERIAL OR MICROMATERIAL

CROSS-REFERENCES TO RELATED APPLICATIONS

This application claims the benefit under 35 U.S.C. § 119(e) of U.S. Provisional Patent Application No. 62/141,192, filed March 31, 2015, which application is incorporated herein by reference in its entirety.

BACKGROUND

Technical Field

This disclosure relates to composite materials including one or more nanomaterial components.

Description of the Related Art

Many nanomaterials or micromaterial, such as carbon nanotubes (CNTs), graphene, metal or metal oxide nanostructures, have electrical, electroactive, semiconductive, mechanical, optical, or other material properties that could enable significant new applications. In spite of their properties at the nano-scale, such properties are often difficult to leverage when the nanomaterial is combined with macro-scale materials. One reason for this difficulty is the challenge in obtaining an effective and stable interface between the nanomaterial and the macro-scale material in which they are embedded.

BRIEF SUMMARY

Provided herein are functionalized substrate (e.g., nanomaterials), and a composite of the functionalized substrate covalently bonded to a bonding target material (e.g., macro-scale material).

One embodiment provides a functionalized substrate represented by the following Formula:

\[ A \left( L_1 \rightleftharpoons N \leftarrow L_2 \leftarrow N u \right)_{m} \]

1
wherein,

\( m \) is an integer \( \geq 1 \); \( A \) represents a substrate; \( N \) is a nucleophilic group; \( L_1 \) is a first linker covalently connecting the substrate to \(-N(R^1)\)-; \( R_1 \) is hydrogen or alkyl; and \( L_2 \) is a second linker represented by \(-(CH_2)_n\)-, wherein \( n \) is 2 or 3.

In various embodiments, the substrate is a nanomaterial or micromaterial. More specifically, the nanomaterial includes carbon nanotubes, graphene, buckyballs, carbyne, or a combination thereof, or the nanomaterial includes magnetite nanoparticles, metal nanoparticles, semiconductor nanoparticles, metal oxide nanoparticles, magnetic nanoparticles, or a combination thereof.

In other embodiments, the substrate is a surface of a macro-scale material.

A further embodiment provides a composite comprising a functionalized substrate covalently coupled to a bonding target material.

In various embodiments, the bonding target material may be a macro-scale material such as a polymer which acts a host matrix for incorporating the functionalized substrate. The bonding target material may also be a surface of a material and can be surface-functionalized by forming a covalent bond with the functionalized substrate.

BRIEF DESCRIPTION OF THE SEVERAL VIEWS OF THE DRAWINGS

Figure 1 shows an embodiment of the present disclosure wherein a functionalized nanomaterial (carbon nanotubes functionalized with hydroxyl groups undergoes an enhanced nucleophilic reaction to form covalent bonds with a macro-scale material (polylactide).

Figure 2 shows another embodiment of the present disclosure wherein a functionalized nanomaterial (carbon nanotubes functionalized with secondary amine groups) undergoes an enhanced nucleophilic reaction to form covalent bonds with a macro-scale material (polylactide).
DETAILED DESCRIPTION

Disclosed herein are embodiments directed to composite materials in which a functionalized substrate (such as a functionalized nanomaterial) and a bonding target material (such as a macro-scale material) form a strong interface by creating covalent bonding. In particular, the functionalized substrate comprises one or more activated nucleophilic groups. Advantageously, the activated nucleophilic group can form covalent bonds with a bonding target material, e.g., a polyester, at mild conditions. Moreover, the nucleophilic reaction can advantageously take place at melt temperature of the polymeric bonding target material without a solvent or the need for catalysts.

Functionalized Substrate

A "substrate" is any material capable of being functionalized via the formation of one or more carbon-substrate covalent bonds. Preferably, the functionalization may be carried out by a tris(trimethylsilyl)silane (TTMSS) - mediated reaction as described in PCT/US2015/018197, in the name of Functionalize Inc., the assignee of the present application.

In certain embodiments, the substrate is a nanomaterial and comprises one or more nanoparticles. As used herein, nanoparticles are particles having at least one dimension in the nanometer range (i.e., less than 1 micron). In other embodiments, the substrate may be a nanomaterial that comprises one or more microparticles. The substrate may also be a micro-scale material such as microparticles, which are particles in which the smallest dimension is in the micrometer range (i.e., 1 micron to less than 1 millimeter). The nanoparticles or microparticles can be sphere or elongated (e.g., in the shapes of wires, tubes, or rods). Examples of nano- or micro-scale substrates include, without limitation, carbon nanotubes, nanoparticles or microparticles of graphene, buckyballs, carbyne, nano-diamonds, nanoparticles or microparticles of titanium dioxide, silica, magnetite, metal nanoparticles or microparticles, semiconductor nanoparticles or microparticles, and metal oxide nanoparticles or microparticles.
Nanomaterials or micromaterial, including carbon nanotubes, graphene, or other carbon allotropes, can be chemically functionalized by one or more functional groups that will facilitate charge-based or covalent bonding and interface with a bonding target material, which may be a macro-scale material that can act as a host material matrix of the nanomaterial or micromaterial. As used herein, any disclosure related to nanomaterial applies equally to micromaterial.

In certain embodiments, the substrate may include a combination of nanoparticles and microparticles.

In various embodiments, the substrate may be a macro-scale material. The macro-scale substrate may be the whole or a portion of a device, an apparatus or any objects in which the smallest dimension is at least 1 millimeter. The substrate may be metallic, metal oxide, semiconductive, polymeric, dielectric material, the surface of which may be functionalized. More specific examples of macro-scale substrates include, without limitation, silicon, graphene, polymers, metal-plated surfaces, or complex fluids.

The functionalized substrate, such as functionalized nanomaterial or micromaterial, comprises a nucleophilic group (Nu) for further bonding with a bonding target material. Typically, a bonding target material can be any material comprising one or more electrophilic moieties that are receptive to the nucleophilic attack from the nucleophilic group (Nu). As discussed in further detail below, the bonding target material may have functional groups itself and thereby add further functionalization to the substrate or may be a host polymer matrix for incorporating the substrate (e.g., a nanomaterial) via covalent bonds. Advantageously, the functionalized substrate further comprises an electron-rich or electron-donating moiety adjacent to the nucleophilic group, thereby providing a catalytic effect or activating the nucleophilic attack to the appropriate moiety of the bonding target. Typically, the electron-donating group is a secondary or preferably tertiary amine group. Thus, in certain embodiments, the functionalized nanomaterial can be represented by the following Formula:
wherein,

\[ m \text{ is an integer } \geq 1; \]

\[ A \text{ is a substrate,} \]

\[ L_1 \] is a first linker that covalently connects the nanomaterial to the nucleophilic group (Nu), via the electron-donating amine moiety. There is no particular limitation to the structure of the \( L_1 \). Thus, \( L_1 \) may have 1-30 non-hydrogen atoms selected from the group consisting of C, N, O, P, and S; and are composed of any combination of ether, thioether, amine, ester, carboxamide, sulfonamide, hydrazide bonds and aromatic or heteroaromatic bonds. The covalent linkage can be linear or cyclic, or a combination thereof. The linear linkages can be derived from, for example, polymethylene, polyethyleneglycol, alkylsulfonyl, alkylthio, amino alcohol and diol. "Amino alcohol" refers to a di-radical of the formula \( \text{–NH–Y–O–} \), wherein \( Y \) is an alkanediyl or substituted alkanediyl; alkanediyl refers to a divalent alkyl with two hydrogen atoms taken from different carbon atoms. "Diol" refers to a di-radical of the formula \( \text{–O–Y–O–} \), wherein \( Y \) is defined as above. Linkers having cyclic groups typically comprise an aryl group, heterocyclyl, heteroaryl, cycloalkyl or cycloalkenyl. Typically, \( L_1 \) is a \( C_2-C_{20} \) alkylene chain, or \( C_2-C_{10} \) alkylene chain, or \( C_2-C_{4} \) alkylene chain, wherein the alkylene chain may be further substituted with one or more substituents, such as oxo, hydroxyl, amine, alkoxide, and the like.

\[ R_1 \] is hydrogen or alkyl.

\[ L_2 \] is a second linker represented by \( -(\text{CH}_2)_n- \), wherein \( n \) is 2 or 3. \( L_2 \) covalently connects the nucleophilic group to the electron-donating amine moiety. The length of \( L_2 \) is important for the activation or enhancement of the nucleophilicity by the nearby electron-donating moiety. In particular, as a linear structure, \( L_2 \) has a length of 2 or 3 carbon atoms between the nitrogen of the
amine moiety and the nucleophilic group (Nu). In a preferred embodiment, L₂ is -(CH₂CH₂)-.

Nu is a nucleophilic group, and is preferably a hydroxyl, an amine (including primary or secondary amine), or a thiol group. Typically, a nucleophilic group is also electron rich. The reactivity of the nucleophilic group is further enhanced by the nearby electron-donating and basic amine moiety.

The functionalized substrate (e.g., nanomaterial) may be prepared by first functionalizing the nanomaterial via methods known to those skilled in the art to create the L₁ moiety, preferably according to but not limited to methods described in PCT/US2015/018197. More specifically, the nanomaterial may be functionalized by a tris(trimethylsilyl)silane (TTMSS)-mediated reaction that installs the first linker (L₁) connected to a reactive group (e.g., a halo group). The reactive group will be utilized in the subsequent attachment to the amine moiety, which is connected to the nucleophilic group by L₂.

A given substrate may be functionalized with any number (m≥1) of the functionalizing group having the nucleophilic groups.

In particularly preferred embodiments, the substrate is a nanomaterial or micromaterial including, for example, carbon nanotubes, nanoparticles of graphene, buckyballs, carbyne, magnetite, metal nanoparticles, semiconductor nanoparticles, and metal oxide nanoparticles (e.g., titanium dioxide), magnetic nanoparticles, and the like. In certain embodiments, the nanomaterial or micromaterial may be nanoparticles or microparticles of metals, metal complexes (oxide, carbides, sulfides, etc.) and metal alloys. As used herein, the term metal (as pure or ionic) include but are not limited to transition metals and metalloids, and more particularly to titanium, vanadium, chromium, manganese, cobalt, nickel, copper, zinc, zirconium, molybdenum, ruthenium, rhodium, palladium, cadmium, tungsten, rhenium, osmium, iridium, platinum, gold, aluminum, bismuth, zinc, gallium, lead, and silicon. Exemplary metal alloys include but are not limited to Pt₃Co, and other alloys of cobalt and alloys of copper.
Figures 1-2 are examples of constructing functionalized nanomaterials. As shown in Figure 1, nanomaterial (A) is shown schematically as a graphene structure (which can be a nanoparticle of graphene or a carbon nanotube, i.e., a rolled-up graphene). As shown, under a TTMSS-mediated reaction, 1-chloro-3-iodopropane is covalently coupled to a carbon atom of the nanomaterial to provide intermediate (A1). Subsequently, the chloro group of A1 is reactive toward the amino group of 1-methyl-2-aminoethanol to provide the functionalized nanomaterial (A2) having a nucleophilic group (i.e., hydroxy group). In particular, the tertiary amine moiety of A2 not only provides a point of attachment for constructing the functionalized nanomaterial, but is also an electron-donating group that boosts the nucleophilicity of the nearby hydroxy group.

Figure 2 demonstrates a further embodiment of functionalizing a nanomaterial with other nucleophilic groups, i.e., a secondary amino group. As shown, following the formation of the intermediate A1, A1 is coupled to a N,N'-dimethylenediamine to form a functionalized nanomaterial (A4) having a secondary amine group (a nucleophilic group).

**Bonding Target Material**

According to various embodiments, the functionalized nanomaterial having one or more nucleophilic groups (e.g., A2 or A4) is capable of forming covalent bonds with one or more bonding target materials. A bonding target material may be polymeric, metallic, metal oxide, semiconductive, dielectric material, the surface of which may be functionalized. A bonding target can also take the form of a powder, melt, and the like. The bonding target may be a nano-scale or macro-scale material.

In preferred embodiments, the bonding target material is a polymer, e.g., a thermoplastic polymer. In preferred embodiments, the polymer contains one or more carboxylic, ester, or amide moieties, which are points of covalent attachments in a nucleophilic substitution reaction with the functionalized substrate, including functionalized nanomaterial.
In certain embodiments, the bonding target is a polyester. Non-limiting examples include polylactic acid, polyethylene terephthalate, or other thermoplastics containing ester bonds and/or carboxyl terminal groups. In other embodiments, the macro-scale material is an amide, imide, or ketone based polymers, such as ULTEM, NYLON, KAPTON, PEEK, or PEKK.

The carbonyl group in an ester, amide, or imide is susceptible to some forms of nucleophilic attack. However, catalysts are generally required to complete the reaction. In accordance with the embodiments disclosed herein, because the functionalized nanomaterial comprises nucleophilic groups that are activated by a nearby electron-donating and basic group, the nucleophilicity is substantially enhanced. As a result, the nucleophilic reaction between the functionalized nanomaterial and the polymeric material can take place efficiently, often without a catalyst.

**Composite**

As discussed above, carbonyl groups of an ester, or amide bond in a polymer chain (including the terminus) are susceptible to nucleophilic attack, resulting in new ester or amide bond formation. As a result of the trans-esterification or trans-amidation reaction, the functionalized substrate (e.g., a nanomaterial) and the bonding target (e.g., a macro-scale material) are covalently bonded, thereby strengthening the interface between the two materials. Numerous other moieties, including but not limited to ketones and imides are also susceptible to nucleophilic attack and undergo reactions, which covalently bond with the nucleophilic group, activated by the nearby electron-donating moiety.

Bonding reactions can take place by blending the functionalized nanomaterial with a thermoplastic polymer at melt temperature. The relative amounts of the nanomaterial and polymer (macro-scale material) are not particularly limited and can be determined by the desired properties of the resulting composite. For example, functionalized conductive nanomaterials (e.g., CNTs) may be blended in with a polylactic acid powder at various stoichiometric ratio. Above the percolation threshold, the higher the ratio of the
nanomaterial, the higher the conductivity can be expected in the resulting composite. Due to the covalent bonding with the bonding target material, nanomaterial can be well distributed through shear forces generated by compounding and efficiently transferred to the bonding target material through the covalent bonds.

Figure 1 shows that functionalized nanomaterial (A2) is coupled to a macro-scale material, i.e., polylactic acid (PLA) by an enhanced nucleophilic reaction. The resulting composite has a strong interface between the nanomaterial and the macro-scale material due to the formation of ester bonds between the hydroxyl group and PLA.

Figure 2 shows another embodiment whereby a functionalized nanomaterial (A4) is coupled to PLA by forming an amide bond with PLA.

As a result of the covalent bond formation (e.g., ester or amide bond), the polymer (as a matrix) and the nanomaterial (as a filler) can be strongly interfaced, better enabling leverage of nanoscale properties, such as strength, electrical or optical characteristics in macro-scale materials.

EXAMPLES

EXAMPLE 1

COMPOSITE OF CNT AND PLA

In a specific example, CNTs were functionalized and coupled to PLA according to the scheme shown in Figure 1.

More specifically, to a sonicating flask, multi-wall CNTs(MWCNTS) or graphene(12g, 1 mol) and 1-chloro-3-iodopropane (1.074ml, 0.01 mol) were added in 800ml of cyclopentyl methyl ether (CPME). Alternated sonication for 5 minutes and stirring for 5 minutes for half of an hour before transferring the reaction mixture to a reactor. The reaction mixture was purged with nitrogen under stirring. To the purged and stirred reaction mixture, tris(trimethylsilyl)silane (TTMSS) (3.4ml, 0.011 mol) was added and exposed to air. The reaction was allowed to react for about 3 hours at room temperature to provide A1, which was dried.
Thereafter, the dried A1 was combined with 1-ethyl-2-aminoethanol (0.02 mol) and Hunig's base (0.04 mol) in 800ml of methanol. Under reflex, the reaction was carried out for 3 hours to afford the functionalized CNTs (A2).

The functionalized CNTs (A2) may be further blended with polylactic acid (PLA) in a twin screw extruder at hot melt temperature (e.g., 175-205°C) to produce a highly conductive (owing to the presence of the CNTs which are electrically conductive) polymer blend with improved tensile strength (owing in part to the covalently bonded interface with the PLA polymer). The loading of the functionalized CNTs can vary and will affect the electrical and mechanical property of the resulting polymer blend.
CLAIMS

1. A functionalized substrate represented by the following formula:

\[
\begin{array}{c}
\text{A} \quad \text{L}_1 \quad \text{N} \quad \text{L}_2 \quad \text{Nu}
\end{array}
\]

wherein,

- \( m \) is an integer \( \geq 1 \);
- \( A \) represents a substrate,
- \( \text{Nu} \) is a nucleophilic group;
- \( \text{L}_1 \) is a first linker covalently connecting the substrate to \( -\text{N}(\text{R}^1)\); 
- \( \text{R}^1 \) is hydrogen or alkyl; and
- \( \text{L}_2 \) is a second linker represented by \( -(\text{CH}_2)_n\), wherein \( n \) is 2 or 3.

2. The functionalized substrate of claim 1 wherein the substrate is a nanomaterial or micromaterial.

3. The functionalized substrate of claim 2 wherein the nanomaterial includes carbon nanotubes, graphene, buckyballs, carbyne, or a combination thereof, or the nanomaterial includes magnetite nanoparticles, metal nanoparticles, semiconductor nanoparticles, metal oxide nanoparticles, magnetic nanoparticles, or a combination thereof.

4. The functionalized substrate of claim 1 wherein the substrate is a surface of a macro-scale material.

5. The functionalized substrate of any one of claims 1-4 wherein \( \text{L}_1 \) is an alkylene chain represented by \( -(\text{CH}_2)_n\), wherein \( n \) is an integer between 2 and 10.
6. The functionalized substrate of claim 5 wherein n is 2, 3 or 4.

7. The functionalized substrate of any one of claims 1-6 wherein $L_2$ is $-(\text{CH}_2\text{CH}_2)\text{-}$.

8. The functionalized substrate of any one of claims 1-7 wherein $R^1$ is methyl.

9. The functionalized substrate of any one of claims 1-8 wherein the nucleophilic group is hydroxyl, thiol, primary amine or secondary amine.

10. The functionalized substrate of any one of claims 1-9 wherein the nanomaterial is carbon nanotubes or graphene and the functionalize nanomaterial is represented by:

11. A composite comprising the functionalized substrate of any one of claims 1-10 covalently coupled to a bonding target material.
12. The composite of claim 11 wherein the bonding target material is a polymer or a surface thereof.

13. The composite of claim 12 wherein the polymer is polyester or polyamide.

14. The composite of any one of claims 11-13 wherein the nanomaterial and the bonding target material are coupled by one of more covalent bonds selected from ester and amide bonds.

15. The composite of claim 14 wherein the polymer is polylactic acid and the nanomaterial includes CNTs, graphene, nanoparticles, or a combination thereof.
Fig. 1
Fig. 2
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
IPC(8) - C08J 7/12; B05D 3/10; B28B 3/00; B28Y 30/00, 40/00 (2016.01)
CPC - C08J 7/12; B05D 3/10; B28B 3/0095; B28Y 30/00, 40/00

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)
IPC(8): C08J 7/12; B05D 3/10; B28B 3/00; B28Y 30/00, 40/00 (2016.01)
CPC: C08J 7/12; B05D 3/10; B28B 3/0095; B28Y 30/00, 40/00

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)
PatSeek (US, EP, WO, JP, DE, GB, CN, FR, KR, ES, AU, IN, CA, INPADOC Data); IP.com; Google/Google Scholar; EBSCO, functionalize, functionalise, surface modification, coupling, linker, ligand, substrate, nanoparticle, microparticle, nanotube, graphene, buckyball, carbine, alkylene, ethylene, propylene, nitrogen, nucleophilic amine, amino, thiol, hydroxyl, aminosilane, ethylenediamine

C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>X</td>
<td>US 6,097,742 B2 (YING, JY et al.) 17 January 2012; abstract; figures 3B, 5; column 4, lines 16-27, 49-51</td>
<td>1-3, 5/1-3, 6/1-6/3</td>
</tr>
<tr>
<td>Y</td>
<td>US 2010/0080932 A1 (KIM, AS et al.) 01 April 2010; figures 1, 3; paragraph [0017]</td>
<td>4, 5/4, 6/5/4</td>
</tr>
<tr>
<td>A</td>
<td>US 7,794,683 B1 (FOROHAR, F et al.) 14 September 2010; entire document</td>
<td>1-4, 5/1-4, 6/1-6/4</td>
</tr>
</tbody>
</table>

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

Date of the actual completion of the international search
19 May 2016 (19.05.2016)

Date of mailing of the international search report
20 JUN 2016

Name and mailing address of the ISA/
Mail Stop PCT, Attn: ISA/US, Commissioner for Patents
P.O. Box 1450, Alexandria, Virginia 22313-1450
Facsimile No. 571-273-8300

Form PCT/ISA/210 (second sheet) (January 2015)

Authorized officer
Shane Thomas
PCT Helpdesk: 571-272-4300
PCT OGP: 571-272-7774
INTERNATIONAL SEARCH REPORT

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.:  
   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:

3.  ☒ Claims Nos.: 7-15  
   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 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.

Form PCT/ISA/210 (continuation of first sheet (2)) (January 2015)