MULTIPURPOSE GRAPHENE-BASED COMPOSITE

FIELD OF THE INVENTION

The present invention relates in general to graphene-based materials. In particular, the invention relates to a graphene-based composite, a substrate comprising the composite, a method of preparing the composite and applications of the composite.

BACKGROUND OF THE INVENTION

The protection of objects such as construction and industrial substrates against everyday use and environmental conditions presents a considerable challenge in modern day society. For example, many objects can be detrimentally affected by factors such as corrosion, abrasion induced wear, bacterial fouling and fire damage, to name but a few.

In response to that challenge, considerable research has been directed toward developing means for protecting objects. A common approach to providing such protection is to coat or treat the object with a protective material. For example, objects are commonly coated with various paint products that can protect an object from corrosion, abrasive wear or bacteria fouling. Objects can also be treated with fire retardants to improve their fire resistance properties.

While state of the art techniques for protecting objects have proven effective, many of the protective systems employed are now proving an environmental concern in their own right. For example, tin-based antibacterial fouling coatings and halogenated fire retardant compounds, while being effective in application, their use is now raising considerable environmental concern.

Furthermore, conventional protective systems are typically application specific in the sense the protective system lacks versatility for use in numerous different applications.

The diverse properties of graphene (Gr) are only now just being realised. Graphene is an

allotrope of carbon having a one atom thick planar sheet structure of typically sp^2-bonded carbon atoms that are densely packed in a honeycomb to D crystal ladders. The covalently bonded carbon atoms typically form repeating units that comprise 6-membered rings, but can also form 5-membered rings and/or 7-membered rings. A layer of such covalently bonded carbon atoms is commonly referred to as a graphene "sheet". Graphene may conveniently prepared synthetically or by exfoliation of graphite.

The unique properties of graphene are now being applied in protection systems that promote, for example, improved gas impermeability, chemical resistance, fire retardant and antibacterial effects, and super-lubricity.

However, despite graphene showing much promise for use in protective systems, many of the graphene-based protective systems developed to date fail to meet the quality demands of the conventional protective systems. Many graphene-based protective systems have therefore not been successfully translated into commercially viable products.

Accordingly, there remains an opportunity to develop new graphene-based materials with diverse utility, for example in protective applications.

SUMMARY OF THE INVENTION

The present invention therefore provides a graphene-based composite comprising graphene-based material intercalated with hydrated sodium metaborate.

The present invention also provides a method of preparing a graphene-based composite, the method comprising (i) providing a liquid composition comprising graphene-based material and hydrated sodium metaborate, and (ii) evaporating liquid from the composition so as to retain the graphene-based material and hydrated sodium metaborate in the composition, wherein the process of evaporating liquid in step (ii) promotes intercalation of the hydrated sodium metaborate in the graphene-based material to afford the graphene-based composite.

The present invention further provides a substrate comprising a graphene-based composite,

the graphene-based composite comprising graphene-based material intercalated with hydrated sodium metaborate.

The graphene-based composite in accordance with the invention has surprisingly been found to exhibit characteristics capable of imparting numerous improved properties to a substrate. The composite demonstrates a unique ability to protect a variety of substrates from a range of different environmental/use conditions. Such improved properties imparted to the substrate are surprisingly superior to properties imparted to the substrate by each of the constituent components of the composite when used alone.

For example, substrates comprising the graphene-based composite can advantageously exhibit improved fire retardant properties, improved abrasion resistance and/or improved antimicrobial properties.

The present invention therefore further provides a substrate with improved fire retardant properties, the substrate comprising a graphene-based composite, wherein the graphene-based composite comprises graphene-based material intercalated with hydrated sodium metaborate.

The present invention also provides a substrate with improved abrasion resistance, the substrate comprising a graphene-based composite, wherein the graphene-based composite comprises graphene-based material intercalated with hydrated sodium metaborate.

The present invention further provides a substrate with improved antimicrobial properties, the substrate comprising a graphene-based composite, wherein the graphene-based composite comprises graphene-based material intercalated with hydrated sodium metaborate.

While the present invention will be described with an emphasis on use of the graphene-based composite to provide for improved fire retardant properties, improved abrasion resistance and/or improved antimicrobial properties, it is to be understood the invention is not to be limited to such applications.

Accordingly, the present invention further provides a substrate with one or more improved properties, the substrate comprising a graphene-based composite, wherein the graphene-based composite comprises graphene-based material intercalated with hydrated sodium metaborate.

The present invention also provides a method of improving one or more of fire retardant properties abrasion resistance properties and antimicrobial properties of a substrate, the method comprising coating or impregnating the substrate with a liquid composition comprising a graphene-based composite, wherein the graphene-based composite comprises graphene-based material intercalated with hydrated sodium metaborate, said improved properties being relative to the substrate absent the graphene-based composite.

The substrate may comprise or be provided with the graphene-based composite by any suitable means. For example the substrate may be coated, impregnated, blended and/or compounded with the graphene-based composite.

The present invention also provides a method of improving one or more fire retardant properties, abrasion resistance properties and antimicrobial properties of a thermoplastic polymer substrate comprises melt processing the thermoplastic polymer substrate with a graphene-based composite, wherein the graphene-based composite comprises graphen-based material intercalated with hydrated sodium metaborate, said improved properties being relative to the substrate absent the graphene-based composite.

The present invention also provides method of improving one or more fire retardant properties, abrasion resistance properties and antimicrobial properties of a thermoset polymer substrate comprises blending a graphene-based composite with precursor materials used to make the thermoset polymer substrate, wherein the graphene-based composite comprises graphene-based material intercalated with hydrated sodium metaborate, said improved properties being relative to the substrate absent the graphene-based composite.

The present invention also provides a use of a graphene-based composite to improve one or

more of fire retardant properties, abrasion resistance properties and antimicrobial properties of a substrate, wherein the graphene-based composite comprises graphene-based materials intercalated with hydrated sodium metaborate, said improved properties being relative to the substrate absent the graphene-based composite.

While the various improved properties imparted to a substrate by the graphene-based composite may operate through different mechanisms, without wishing to be limited by theory it is believed a common feature of most if not all of such improved properties stems from the composite not only being able to form an excellent bond with the substrate, but also the composite *per se* having a strong internal bonded structure. Again without wishing to be limited by theory, it is believed the hydrated sodium metaborate plays an important role in promoting such bonding characteristics.

The graphene-based composite may comprise graphene-based material selected from graphene, graphene oxide, reduced graphene oxide, partially reduced graphene oxide and combinations thereof.

Substrates suitable for use in accordance with the invention include those comprising cellulosic material, polymer, metal, ceramic, glass and combinations thereof.

Further aspects and embodiments of the invention are described in more detail below.

BRIEF DESCRIPTION OF THE DRAWINGS

The invention will herein be described with reference to the following non-limiting drawings in which:

Figure 1 shows a schematic illustration of the graphene-based composite used in accordance with the invention;

Figure 2 shows a schematic illustration of (a) substrate provided with the graphene-based composite in accordance with the invention, and (b) fire retardant features afforded by the

graphene-based composite used in accordance with the invention;

Figure 3 shows flammability testing of (a) paper, (b) paper treated with reduced graphene oxide, and (c) paper treated with a reduced graphene oxide/hydrated sodium metaborate composite in accordance with the invention;

Figure 4 shows a pine wood slat being subjected to a burn test (exposed to a butane flame for 12 seconds at a distance of 20mm), where (a) employs a pine wood slat and (b) employs a pine wood slat coated with a reduced graphene oxide/hydrated sodium metaborate composite in accordance with the invention; and

Figure 5 shows a pellet formed from saw dust being subjected to a vertical burn test (UL-94), where (a) employs a pellet formed from saw dust and (b) employs a pellet formed from saw dust provided with a reduced graphene oxide/hydrated sodium metaborate composite in accordance with the invention;

Figure 6 shows bacteria colonies at time zero and 24 hours presented on petri-dished coated with nothing (glass control), graphene oxide (GO control), reduced graphene oxide (rGO by N_2H_2) (also a control), and the graphene-based composite according to the invention (rGO/SMB); and

Figure 7 shows comparative characterization of adhesion and abrasion characteristics of the graphene-based composite according to the invention (rGO/SMB) relative to graphene oxide (GO-control) and reduced graphene oxide (rGO-control) on Cu and glass substrates.

Figure 8 shows polymer (water soluble - PVA) sample being subjected to a burning test (UL-94), where (top) employs a non-treated sample, and (bottom) employs a polymer sample impregnated with a reduced graphene oxide/hydrated sodium metaborate composite in accordance with the invention.

Figure 9 shows polymer (oil soluble - polystyrene) sample being subjected to a burning test (UL-94), where (top) employs a non-treated sample, and (bottom) employs a polymer

sample impregnated with a reduced graphene oxide/hydrated sodium metaborate composite in accordance with the invention.

Some figures have been filed in colour and are available on request.

DETAILED DESCRIPTION OF THE INVENTION

The present invention provides a unique graphene-based composite. The graphene-based composite comprises graphene-based material intercalated with hydrated sodium metaborate.

In the context of the present invention the expression "graphene-based" composite is intended to mean the composite has a composition comprising graphene, graphene oxide, partially reduced graphene oxide, reduced graphene oxide or a combination of two or more thereof. The expression "graphene-based" material may therefore be used herein as a convenient reference to graphene (material or sheets), graphene oxide (material or sheets), partially reduced graphene oxide (material or sheets), reduced graphene oxide (material or sheets) or a combination of two or more thereof.

A brief discussion on the nature of graphene is provided above.

Graphene oxide is an oxygenated form of graphene that is typically prepared by exfoliation of graphite oxide. Graphene oxide is considered to have a graphene-based structure that is substituted with oxygenated groups such as hydroxyl and epoxide. Graphene oxide may be prepared using a number of techniques such as the so called Brodie, Staudenmaier or Hummers methods.

Graphene oxide may be reduced so as to form a reduced form of graphene oxide. Reduced graphene oxide is both chemically and physically different to graphene oxide due to the loss of its oxygenated groups. The degree to which graphene oxide is reduced can be varied, with that variation being reflected in the amount of oxygenated groups remaining. Where graphene oxide is not fully reduced it is often referred to in the art as partially reduced

graphene oxide. Reduced and partially reduced graphene oxide are less hydrophilic than graphene oxide. Reduced graphene oxide is sometimes referred to in the art simply as graphene as an indication that substantially all oxygenated groups have been removed. Techniques for reducing or partially reducing graphene oxide are well known in the art. For example, graphene oxide can be reduced or partially reduced by chemical or thermal reduction.

Graphene oxide, partially reduced graphene oxide and reduced graphene oxide have a covalently bonded carbon atom sheet structure similar to graphene.

The graphene-based composite comprises graphene-based material intercalated with hydrated sodium metaborate. The composite *per se* will therefore comprise a plurality of graphene-based material sheets having intercalated there between hydrated sodium metaborate. A schematic illustration of the graphene-based composite is presented in Figure 1 which highlights the layered sheet structure of the graphene-based material and the hydrated sodium metaborate ($NaBO_2.xH_2O$) intercalated within the layered sheet structure.

By the graphene-based material being "intercalated" with hydrated sodium metaborate is meant the hydrated sodium metaborate resides as a solid in between and on layers of the graphene-based material sheet structure. In other words, the graphene-based material is intercalated with solid hydrated sodium metaborate.

For avoidance of any doubt, the graphene-based composite *per se* also presents as a solid.

The layered sheet structure of the graphene-based material may comprise graphene, graphene oxide, partially reduced graphene oxide, reduced graphene oxide or a combination of two or more thereof.

In one embodiment, the graphene-based composite comprises one or both of graphene and reduced graphene oxide intercalated with hydrated sodium metaborate.

Sodium metaborate used in accordance with the invention is "hydrated". By the sodium

metaborate being hydrated is meant the sodium metaborate contains physically and/or chemically absorbed and/or bonded water such as water of crystallisation. Hydrated compounds are typically identified with the indicator .xH_2O.

Provided the hydrated sodium metaborate can be intercalated within the graphene-based material, there is no particular limitation on the physical form which the hydrated sodium metaborate may take.

In one embodiment, the graphene-based material is intercalated with hydrated sodium metaborate in the form of microparticles, nanoparticles, a film, a sheet or combinations thereof.

As used herein, reference to "nanoparticles" are particles having a largest dimension of no more than 100nm.

As used herein, reference to "microparticles" are particles having a largest dimension of no more than 1000nm.

When in particle form, the largest dimension of the hydrated sodium metaborate will generally range from about 50-500nm.

Generally, the graphene-based composite will comprise about 20 wt% to about 80 wt% graphene-based material and about 20 wt% to about 80 wt% intercalated hydrated sodium metaborate.

The graphene-based composite may comprise one or more other components. In that case, the wt. % of the graphene-based material and/or the intercalated inorganic metal hydrate will be adjusted accordingly.

The graphene-based material and hydrated sodium metaborate used in accordance with the invention can be sourced commercially or made by techniques known in the art.

The graphene-based composite can conveniently be prepared by a method comprising (i) providing a liquid composition comprising graphene-based material and hydrated sodium metaborate, and (ii) removing liquid from the composition so as to retain the graphene-based material and hydrated sodium metaborate in the composition, wherein the process of removing liquid in step (ii) promotes intercalation of the hydrated sodium metaborate in the graphene-based material to afford the graphene-based composite.

By providing a liquid composition comprising graphene-based material and hydrated sodium metaborate, the composition will of course also comprise a liquid. The liquid may be organic (solvent), aqueous or a combination thereof.

Those skilled in the art will appreciate that graphene-based material is substantially insoluble in most liquids, but can be readily dispersed within a liquid.

The hydrated sodium metaborate may be soluble or insoluble in the liquid composition.

In one embodiment, the method of preparing the composite comprises (i) providing an aqueous liquid composition comprising graphene-based material and hydrated sodium metaborate, and (ii) removing water from the composition.

Including hydrated sodium metaborate within a liquid dispersion of graphene-based material and removing liquid from the resulting composition (so as to retain the graphene-based material and hydrated sodium metaborate in the composition) allows for the hydrated sodium metaborate to become intercalated within the layered structure of the graphene-based material.

Provided the graphene-based material and hydrated sodium metaborate are retained in the composition, liquid may be removed from the composition by any suitable means.

In one embodiment, liquid is removed from the composition by evaporation. If required, heat may be applied to the composition to promote such evaporation.

Where the hydrated sodium metaborate is soluble in the liquid used for the composition, removing the liquid from the composition will promote formation of hydrated sodium metaborate particles or crystals that intercalate within the layered structure of the graphene-based material.

Where the hydrated sodium metaborate is insoluble in the liquid used for the composition, removing the liquid from the composition will simply promote intercalation of the pre-existing hydrated sodium metaborate particles within the layered structure of the graphene-based material. In that case, the sodium metaborate particles used will of course be of a suitable size for such intercalation to occur.

The hydrated sodium metaborate used to form the graphene-based composite may itself be pre-formed and introduced to the liquid composition provided for preparing the graphene-based composite. Alternatively, the hydrated sodium metaborate may be prepared *in situ* as part of the method of preparing the graphene-based composite.

Accordingly, the liquid composition comprising graphene-based material and hydrated sodium metaborate may be provided by an aqueous liquid composition comprising graphene oxide and sodium borohydride, wherein the graphene oxide is reduced by the sodium borohydride to afford reduced graphene oxide and the hydrated sodium metaborate.

In one embodiment, the graphene-based composite is produced by (i) providing an aqueous liquid composition comprising graphene oxide and sodium borohydride, wherein the sodium borohydride reduces the graphene oxide to afford reduced graphene oxide and hydrated sodium metaborate, and (ii) removing water from the so formed composition so as to retain the graphene-based material and hydrated sodium metaborate in the composition, wherein the process of removing water in step (ii) promotes intercalation of the hydrated sodium metaborate in the graphene-based material to afford the graphene-based composite.

The present invention provides a substrate with one or more improved properties, the substrate comprising a graphene-based composite, wherein the graphene-based composite comprises graphene-based material intercalated with hydrated sodium metaborate.

The present invention also provides a method of improving one or more properties of a substrate, the method comprising providing the substrate with a graphene-based composite, wherein the graphene-based composite comprises graphene-based material intercalated with hydrated sodium metaborate.

The one or more improved properties include, but are not limited to, improved fire retardant properties, improved abrasion resistance, improved antimicrobial properties.

Reference to "improving", "improved" or "to improve" properties in the context of the present invention is intended to mean an improvement of a property of a substrate relative to that substrate not comprising the graphene-based composite in accordance with the invention.

The graphene-based composite can advantageously provide improved properties to a variety of substrates.

Substrates suitable for use in accordance with the invention include those comprising cellulosic material, polymer, metal, ceramic, glass and combinations thereof.

Examples of cellulosic material include, but are not limited to, wood, paper, saw dust, and natural fibres.

Examples of polymer include, but are not limited to, thermoset and thermoplastic polymers.

Specific examples of polymer include, but are not limited to, polyolefins, polyamides, polyesters, polyvinyl alcohols, polystyrenes, polyacrylates, polyurethanes, polycarbonates, epoxy resins.

Examples of metal include, but are not limited to, steel, copper, and aluminium.

There is no particular limitation on the physical form in which the substrate can take. For

example, the substrate can be in the shape of a sheet, film, plate, beam, particles, powder, plank or any formed product.

By the substrate "comprising" the graphene-based composite, or "providing" the substrate with the composite, is meant the composite is suitably physically associated with the substrate so as to impart an improved property. In other words, the substrate comprises or is provided with a graphene-based composite such that the composite is physically associated with the substrate.

The graphene-based composite may be located on a surface of the substrate and/or within the substrate matrix. The substrate may comprise or be provided with the composite by the composite being coated on, absorbed or impregnated in and/or compounded with the substrate material.

For example, the composite may present as a coating on a surface of a substrate and/or the composite may be distributed throughout the substrate matrix material.

The substrate may be provided with the graphene-based composite by any suitable means.

When providing the substrate with the graphene-based composite, the graphene-based composite may be used in a pre-formed state (i.e. in the form of the composite *per se*). For example, the graphene-based composite may form part of a liquid composition that is coated on or impregnated in the substrate using application techniques well known to those skilled in the art. In that case, the liquid composition may comprise the graphene-based composite in the form of a dispersion within a liquid (organic (solvent), aqueous or a combination thereof).

As a pre-formed material the graphene-based composite may also be used in the form of a solid (e.g. powder) and combined with substrate material, with the resulting blend of the substrate material and graphene-based composite optionally processed so as to provide for a product made of the substrate material comprising the graphene-based composite. For example, the substrate may be in the form of a thermoplastic polymer whereby the

thermoplastic polymer is melt processed with the graphene-based material so as to provide for a thermoplastic polymer product comprising the graphene-based composite distributed throughout the thermoplastic polymer matrix.

As a pre-formed material the graphene-based composite may also be blended with cellulosic material such as saw dust and the resulting blend compressed so as to form a so called reconstituted wood product comprising the graphene-based composite distributed throughout the product.

Alternatively, the graphene-based composite can be prepared *in situ* using precursor components as part of the process of providing it to the substrate. For example, graphene-based material may be dispersed in a liquid which also comprises the hydrated sodium metaborate. The resulting liquid composition can then be used to coat or impregnate the substrate. Removing liquid from the coated or impregnated liquid composition, while retaining the graphene-based material and hydrated sodium metaborate in the composition, can promote formation of the composite *in situ*.

In one embodiment, the substrate is provided with the graphene-based composite using precursor components of the graphene-based composite.

Reference herein to "precursor components" of the graphene-based composite is intended include graphene-based material and hydrated sodium metaborate. As a "precursor component", the hydrated sodium metaborate may not be intercalated with the graphene-based material but rather that intercalation occurs as part of the process of providing the substrate with the graphene-based composite.

The graphene-based composite or precursor components thereof may be provided in the form of a coating composition which is applied to the substrate using conventional techniques such as spraying, dip coating, doctor blade and/or brushing.

The coating composition may be in the form of a paint composition.

Where the substrate is suitably absorbent, a liquid composition comprising the graphene-based composite or precursor components thereof may be used to impregnate the substrate.

Alternatively, the graphene-based composite *per se* may be blended with the substrate material, with that resulting blend optionally being further processed such as being compressed or extruded.

In one embodiment, the substrate is provided with the graphene-based composite by coating the substrate with a composition comprising the graphene-based composite or precursor components thereof. Coating the substrate with the composition may be performed by techniques such as spraying, dip coating, doctor blade and/or brushing.

In another embodiment, the substrate is provided with the graphene-based composite by impregnating the substrate with a composition comprising the graphene-based composite or precursor components thereof. Impregnation of the substrate with the composition may be performed by soaking the substrate in the composition.

The composition comprising the graphene-based composite for coating or impregnating the substrate may be a liquid composition. The liquid component of the composition may be organic (solvent), aqueous or a combination thereof. That composition may comprise other components such as polymer.

In a further embodiment, the substrate is a thermoplastic polymer and it is provided with the graphene-based composite by melt processing the polymer with the graphene-based composite.

In yet a further embodiment, the substrate is a thermoset polymer and it is provided with the graphene-based composite by blending the graphene-based composite with precursor materials used to make the thermoset polymer. Precursor materials used to make thermoset polymer include monomer and pre-polymer that is polymerised and crosslinked to form the thermoset polymer matrix.

In one embodiment the substrate is provided with the graphene-based composite by coating or impregnating the substrate with a liquid composition comprising the graphene-based composite.

In another embodiment the substrate is provided with the graphene-based composite by (i) coating or impregnating the substrate with a liquid composition comprising the graphene-based material and the hydrated sodium metaborate, and (ii) removing liquid from the coated or impregnated liquid composition while retaining the graphene-based material and hydrated sodium metaborate in the composition so as to form and provide the graphene-based composite.

In further embodiment, the substrate is provided with the graphene-based composite by (i) coating or impregnating the substrate with an aqueous composition comprising the graphene-based material and hydrated sodium metaborate, and (ii) removing water from the coated or impregnated liquid composition so as to form and provide the graphene-based composite.

As described herein, the hydrated sodium metaborate used to form the graphene-based composite may be pre-formed and introduced to the liquid composition provided for preparing the graphene-based composite. Alternatively, the hydrated sodium metaborate may be prepared *in situ* as part of the process of preparing or forming the graphene-based composite.

Accordingly, "precursor components" of the graphene-based composite can also include a precursor compound(s) for preparing the hydrated sodium metaborate. Precursor compounds to hydrated sodium metaborate can include sodium borohydride which is oxidised, sodium carbonate in combination with borax, and sodium tetraborate in combination with sodium hydroxide.

In one embodiment, the substrate is provided with the graphene-based composite by (i) providing an aqueous liquid composition comprising graphene oxide and sodium borohydride, wherein the graphene oxide is reduced by the sodium borohydride to afford

reduced graphene oxide and hydrated sodium metaborate, (ii) coating or impregnating the substrate with the aqueous liquid composition provided for in step (i), and (iii) removing water from the coated or impregnated aqueous liquid composition so as to form and provide the graphene-based composite.

The invention may further comprise providing the substrate with hydrated sodium metaborate that does not form part of the graphene-based composite *per se*. In that case, the substrate will comprise the graphene-based composite and also hydrated sodium metaborate that does not form part of the graphene-based composite.

For example, in one embodiment the substrate used is impregnated with hydrated sodium metaborate. In that case, the substrate is impregnated with hydrated sodium metaborate and can then also be impregnated and/or coated with the graphene-based composite.

Providing the substrate with hydrated sodium metaborate that does not form part of the graphene-based composite *per se* can further enhance fire retardant properties of the substrate.

As a coating on a substrate, the graphene composite may be provided in the form of film of average thickness depending on the desired application. For example, the graphene composite film may have a thickness of up to 500 microns.

<u>Improved fire retardant properties of a substrate</u>

The graphene-based composite according to the present invention can impart improved fire retardant properties to a substrate.

The substrate can comprise or be provided with the graphene-based composite as herein described.

Relevant fire retardant properties are those well known in the art and include ignitability and burn rate of a substrate, release of toxic/flammable volatiles from a substrate upon the

substrate being exposed to an ignition source such as fire or extreme heat, self-extinguishing and intumescent properties, char formation/yield and oxygen barrier properties.

For example, a substrate provided with the graphene-based composite in accordance with the invention has been found to exhibit one or more of reduced ignitability, a lower burn rate, a pronounced intumescent effect, and reduced release of toxic/flammable volatiles upon being exposed to an ignition source, relative to the same substrate that has not been provided with the graphene-based composite according to the invention.

Fire retardant properties of a substrate can be determined using techniques know in the art. Such techniques include TGA, STA, UL-94, calorimeter, limiting oxygen index (LOI) measurements.

A substrate that exhibits the improved fire retardant properties according to the present invention will of course be a substrate that in its own right is flammable. In other words, the present invention can provide a flammable substrate with improved fire retardant properties.

Examples of such flammable substrates include those comprising cellulosic material, polymer and combinations thereof.

Examples of cellulosic material include those herein described.

Examples of polymer include those herein described.

In one embodiment, the flammable substrate comprises cellulosic material, polymeric material or a combination thereof.

The excellent fire retardant properties imparted to the substrate by the graphene-based composite are believed to operate through a number of mechanisms.

Without wishing to be limited by theory, it is believed the hydrated sodium metaborate functions as a heat sink as it undergoes endothermic dehydration releasing water into the

surrounding environment. That in turn is believed to promote a unique intumescent effect.

The graphene-based material is believed to function synergistically to promote fire resistance by providing at least four combined functions, including (i) preventing access of oxygen to the flammable substrate, (ii) providing self-extinguishing properties, (iii) preventing escape of toxic and flammable volatiles from the substrate, and (iv) exhibiting char formation and an intumescent effect.

The graphene-based material is believed to also act as a carbon donor to create a physical barrier between the unburnt substrate and a flame to thereby protect the substrate.

Still further, the hydrated sodium metaborate is believed to promote a high degree of binding between layers of the graphene-based material and also between the substrate and the composite graphene-based composite, thereby providing for a robust fire retardant system. This is particularly useful where the composite is provided in the form of a coating on a substrate.

The unique fire retardant properties imparted by the graphene-based composite may be further explained with reference to Figure 2.

Figure 2 (a) represents a substrate coated with a graphene-based composite in accordance with the invention. The graphene-based composite coating can be seen as comprising the graphene-based material intercalated with hydrated sodium metaborate.

Figure 2 (b) illustrates the graphene-based composite coated substrate of Figure 2 (a) being exposed to fire. The graphene-based composite used in accordance with the invention is believed to provide numerous mechanisms by which improved fire retardant properties are imparted to the substrate. Firstly, and again without wishing to be limited by theory, the intercalated hydrated sodium metaborate is believed to not only facilitate good adhesion between the layers of the graphene-based material structure, but also facilitate adhesion of the graphene-based composite to the substrate. Such adhesive properties provide for a robust fire retardant system. The strongly adhered layered structure of the graphene-based

composite is believed to impede the transmission of oxygen to the substrate thereby reducing the potential for the substrate to catch fire. Similarly, the strongly adhered layered structure of the graphene-based composite is believed to impede the release of volatile components from the substrate (e.g. CH_4) that can be toxic and also fuel the fire. Furthermore, upon being exposed to fire the hydrated sodium metaborate can undergo endothermic dehydration thereby functioning as a heat sink and also releasing water into the surrounding environment. This in turn is believed to promote a unique intumescent effect. Such collective features of the graphene-based composite have been found to function as a highly effective, efficient and robust fire retardant system.

The excellent fire retardant properties imparted by the graphene-based composite are clearly illustrated in Figure 3 which presents results of a series of flame tests. In the flame tests a paper sample is exposed to a naked flame and its flammability is assessed as a function of time. Figure 3(a) tests the base paper sample, Figure 3(b) tests the base paper sample coated with only reduced graphene oxide, and Figure 3(c) tests the base paper sample coated with a graphene-based composite in accordance with the invention, the composite comprising reduced graphene oxide intercalated with hydrated sodium metaborate. As can be clearly seen from Figure 3, the base paper sample and the paper coated with reduced graphene oxide readily ignite and are fully combusted after about 10 seconds. However, the paper sample coated with graphene-based composite in accordance with the invention fails to ignite upon being exposed to a naked flame for at least 120 seconds.

Similarly, Figure 4 shows a pine wood slat being subjected to a burn test (exposed to a butane flame for 12 seconds at a distance of 20mm), where (a) employs a pine wood slat and (b) employs a pine wood slat coated with a reduced graphene oxide/hydrated sodium metaborate composite in accordance with the invention. The untreated pine wood slat can be seen to be almost completely combusted after 30 seconds, while the pine wood slat coated with the composite in accordance with the invention can be seen to only be effected by the flame at its point of contact, with the fire not propagating and the remainder of the slat being largely undamaged.

Also, Figure 5 shows a pellet formed from saw dust being subjected to a vertical burn test

(UL-94), where (a) employs a pellet formed from saw dust and (b) employs a pellet formed from saw dust provided with a reduced graphene oxide/hydrated sodium metaborate composite in accordance with the invention. The coated pellet (b) displayed excellent fire-retardancy with no flame propagation behaviour. No flaming or glowing combustion was observed for the composite treated sample, hence those samples were graded as V-0. The burning of the composite treated sample ceased instantly with no vertical lift of the flame, whereas the untreated sawdust pellet showed higher degree of flammable properties that continued till the end (up to the holding clamp) with an approximate linear burning rate of 0.5 mm/s.

Figures 8 and 9 show how flammable polymer (PVA and polystyrene - top) can be provided with fire retardant properties (bottom) by being compounded with a reduced graphene oxide/hydrated sodium metaborate composite in accordance with the invention.

Improved antimicrobial properties of a substrate

The graphene-based composite according to the present invention can impart improved antimicrobial properties, such as antibacterial and/or antifungal properties, to a substrate.

The substrate can be provided with the graphene-based composite as herein described.

Relevant antimicrobial characteristics are those well known in the art and include the prevention or reduction in the colonisation of microbes such as bacteria or fungi on the substrate.

For example, a substrate comprising the graphene-based composite in accordance with the invention has been found to prevent or reduce colonisation of microbes such as bacteria and fungi, relative to the same substrate that does not comprise the graphene-based composite according to the invention. In other words a substrate comprising the graphene-based composite in accordance with the invention has been found to exhibit microbicidal or microbiostatic properties, for example bacteriostatic, bactericidal, fungistatic and/or fungicidal properties.

Antimicrobial properties of a substrate can be determined by techniques know in the art.

A substrate that exhibits the improved antimicrobial properties according to the present invention will of course be a substrate that in its own right is susceptible to microbial colonisation. In other words, the present invention can provide a substrate that is susceptible to microbial colonisation with improved antibacterial properties.

Examples of substrates that are susceptible to microbial colonisation include those comprising cellulosic material, polymer, glass, metal, ceramic and combinations thereof.

Examples of cellulosic material include those herein described.

Examples of polymer include those herein described.

Examples of glass include those herein described.

Examples of metal include those herein described.

Examples of ceramic include those herein described.

In one embodiment, the antimicrobial properties of a substrate comprising the graphene-based composite in accordance with the invention are antibacterial and/or antifungal properties.

Reference herein to the term “microbe”, or associated terms such as “microbial” and “microbial organism”, is intended to mean any organism that exists as a microscopic cell that is included within the domains of archaea bacteria or eukarya. Accordingly, the term is intended to encompass prokaryotic or eukaryotic cells or organisms having a microscopic size and includes bacteria, archaea and eubacteria of all species as well as eukaryotic microorganisms such as yeast and fungi.

Relevant microbes also include Gram-positive bacteria and Gram-negative bacteria.

The excellent antimicrobial properties imparted to the substrate by the graphene-based composite are believed to operate through a number of mechanisms. Without wishing to be limited by theory, it is believed the antimicrobial properties relate to the destructive lipid extraction by the sharp edged graphene-based material which destroys the microbe membrane integrity and intertwining microbe pores that creates perturbation of the cell membrane, and charge transfer between the graphene-based material sheet and microbial cells causing DNA damage. Furthermore, the presence of the hydrated sodium metaborate in the composite is also believed to impart an antimicrobial effect in itself. Where the substrate is comes into contact with an aqueous environment, hydrated sodium metaborate can advantageously be slowly leached form the composite to impart such an antimicrobial effect. Accordingly, the composite as a whole is believed to impart effective antimicrobial character to the substrate.

The unique antimicrobial properties imparted by the graphene-based composite may be further illustrated with reference to Figure 6.

Figure 6 shows bacteria colonies at time zero and 24 hours presented on petri-dished coated with nothing (glass control), graphene oxide (GO control), reduced graphene oxide (rGO by N_2H_2), and the graphene-based composite according to the invention (rGO/SMB). Only the rGO/SMB sample showed a significant reduction in bacteria colonisation after 24 hours.

Improved abrasion resistance properties of a substrate

The graphene-based composite according to the present invention can impart improved abrasion resistance properties to a substrate.

The substrate can be provided with the graphene-based composite as herein described.

Relevant abrasion resistance characteristics are those well known in the art and include measuring the amount of wear upon being subjected to an abrasive force.

For example, a substrate comprising the graphene-based composite in accordance with the invention has been found to exhibit improved abrasive wear, relative to the same substrate that does not comprise the graphene-based composite according to the invention.

Abrasion resistance of a substrate can be determined by techniques know in the art. Such techniques include ASTM D4060.

A substrate that exhibits the improved abrasion resistance according to the present invention will of course be a substrate that in its own right is susceptible to abrasion. In other words, the present invention can provide a substrate that is susceptible to abrasion with improved abrasion resistance.

Examples of substrates that are susceptible to abrasion resistance include those comprising cellulosic material, polymer, glass, metal, ceramic and combinations thereof.

Examples of cellulosic material include those herein described.

Examples of polymer include those herein described.

Examples of glass include those herein described.

Examples of metal include those herein described.

Examples of ceramic include those herein described.

The excellent abrasion resistance imparted to the substrate by the graphene-based composite are believed to operate through a number of mechanisms. Without wishing to be limited by theory, it is believed the abrasion resistance operates through a combination of lubricity afforded by the graphene based material, the strong internal binding of the composite structure afforded by the hydrated sodium metaborate, and the strong binding of the graphene-based composite to the substrate also afforded by the hydrated sodium metaborate.

Accordingly, the composite as a whole is believed to impart a robust abrasion resistant system to the substrate.

The unique abrasion resistance imparted by the graphene-based composite may be further illustrated with reference to Figure 7.

Figure 7 shows comparative characterization of adhesion and abrasion characteristics of the graphene-based composite according to the invention (rGO/SMB) relative to graphene oxide (GO-control) and reduced graphene oxide (rGO-control) on Cu and glass substrates. Parts (a-d) show cross-cut scratch tape adhesion test (ASTM D3359-09e2) of coating deposited on the Cu and glass substrate, with (a & d) being GO (control), (b & e) being rGO (control), and (c & f) being rGO/SMB. Parts (a-d) illustrate the varied adhesion between graphene-based composite and the substrate, with parts (c & f) showing the best results with little if no damage to the graphene-based composite after the adhesion test. Part (g) shows abrasion type after abrasion test that combines micro dents and parallel groves identified on the coated surface, part (h) shows the weight loss behaviour with different abrasion length of the coated surface.

The present invention will herein after be described with reference to the following non-limiting examples.

EXAMPLES

Synthesis of Graphene Oxide (GO)

Graphite flakes (<45 μm) were chemically exfoliated following the improved Hummers method. The complete reaction was performed using a 9:1 ratio of H_2SO_4/H_3PO_4 (360:40 ml) with 18 g of $KMnO_4$ for the oxidation of 3 g of graphite flakes. Exfoliation proceeded at 50 °C while stirring for 12 h. The solution was then cooled to room temperature and poured onto ice cubes (300 ml) with 3 ml of 30% H_2O_2. Finally, the mixture was repeatedly centrifuged at 4000 rpm for 2 h for the purpose of washing with distilled water (twice), 32% of HCl (twice) and ethanol (twice) respectively to obtain GO, which was oven dried at 40 °C for 12 h.

Composite formulation-1

Reduction of Graphene Oxide (GO) and Formation of hydrated Sodium Meta-borate (SMB): Reduced-GO (rGO) was prepared by reducing 50 ml of aqueous dispersion of GO (3.5 mg/ml) with a certain amount of $NaBH_4$ as reducing agent to form a mixer of 0.1 mol L^{-1} $NaBH_4$ and then refluxed and stirred at 60 °C for 8 hr. The reaction simultaneously produced hydrated sodium metaborate resulted from the hydrolysis of $NaBH_4$ in the solution (shown in Equation 1).

$$NaBH_4 + (2 + x)H_2O \xrightarrow{\Delta} NaBO_2.xH_2O + 4H_2 + heat \quad (1)$$

The final solution contains rGO and hydrated-SMB that form the graphene based composite upon removing water by curing with heat.

Composite formulation-2

Graphene Oxide (GO) was chemically reduced following the methods provided in the literature using Hydrazine (N2H4) in aqueous solution of GO (1 µl for 3 mg of GO). Subsequently, hydrated-sodium metaborate was mixed from external sources to prepare aqueous solution of reduced-GO and dissolved hydrated-SMB varying the composition percentage between 40 to 80 wt%.

Preparation of graphene-based composite coatings

The prepared rGO/SMB solution was deposited on the substrate by drop casting or spraying method on copper flat plates (3 cm × 3 cm × 0.2 cm) and glass slides (2.5 cm X 3.5 cm) covering the entire area (from edge to edge) and then dried in the oven at 60 °C for 3 h. Comparative coatings with control solutions of GO, rGO and were prepared using the same conditions. For abrasion testing, the coated graphene-based surfaces were placed under Taber abrasion test (ASTM D4060).

Characterizations

Scanning electron microscope (SEM-FEI QUANTA 450, Japan) was used to analyze the GO and rGO surface morphology, as well as to measure the coating thickness of the vertically aligned sample at an accelerating voltage of 5 KV. The energy dispersive X-ray

(EDX) unit was used to capture the elemental peaks of rGO coatings containing sodium metaborate crystals at 5.0 KV. A high resolution Philips CM200, Transmission Electron Microscope (TEM), Japan was used for imaging the exfoliated GO flakes at 200 KV. TEM sample was prepared by dispersing the synthesized GO in ethanol to form a homogeneous dispersion. A Nikon Optical Petrographic Microscope (LV100 POL, USA) was used to analyze the cross-cut surfaces in order to mark the adhesion grade. Vibrational stretching mode of different oxygen functional groups in GO and rGO were studied by Fourier transform infrared spectroscopy (FTIR) (Nicolet 6700 Thermo Fisher, USA). TGA (Thermogravimetric analysis) and DTG (Derivative Thermogravimetry) of treated and untreated sawdust were analysed by a TA instruments (Q-500, Tokyo, Japan) in air atmosphere. The temperature was raised from ambient temperature to 600 °C at a rate of 5 °C/min for the combustion in air environment. Thermogravimetric analysis coupled with Fourier transform infrared (TGA-FTIR) for the real time analysis of multiple gas phase compounds released from the combustion samples were done by a PerkinElmer TG-IR EGA System connected to TL 8000 (TG-IR EGA, PerkinElmer Ltd, UK). The operation is accomplished in air atmosphere for an approximately sample mass of 16 mg at a rate of 6 °C/min.

Cross-cut adhesion test

The adhesion of rGO/SMB coatings to the metal (Cu) and glass (microscope slide) substrates were measured according to the standard tape test ASTM D3359-09e2. The cross-cut adhesion test kit (QFH-HG600) was purchased from Biuged Laboratory Instruments (Guangzhou, China). The cutting tool blade comprised eleven teeth spaced 1.0 mm apart. Coated substrates were placed on the lab bench supported by the guide rail before using the cutting tool. After the cross-cut pattern was applied (at approximately 90°) any detached flakes of the coating were removed with the kit's brush and scotch tape was placed over the cross-cut with gentle pressure. The cut samples were examined with a high magnification microscope (Nikon-Petrographic Microscope) and rated according to the ASTM rating scheme.

Abrasion resistance test

A standard (ASTM D4060) Taber abrasion (Dongguan Jianqiao Testing Equipment Co., LTD, Model JQ-802A) test was performed to evaluate the progressive wear of adhesive rGO/SMB coating under a pair of abrading wheels of 52 mm in dimeter at 250 g load. In order to run the test, the copper and glass coated specimen (10 cm × 10 cm) were placed and clumped on the stage to rotate at the constant speed of 60 rpm for 3000 cycles. The wear loss was measured by weighting the sample in every ≈300 cycles after a smooth brushing to remove loose particles on the abrasive surface. The worn sample was taken under SEM and Raman mapping system to observe wear mode and occupied molecular area percentage after abrasion.

Antibacterial test

A quantitative assessment of the antibacterial efficiency of GO, rGO and rGO/SMB coated glass swatches was done against gram-negative bacteria *E. coli* (ATCC 25922) according to the AATCC test method 100-2004. Bare glass slide and GO coated slides were performed as primary and secondary controls. Regarding the coated samples, the glass slides (2.5 cm × 2.0 cm) were drop cast with 0.8 ml solution at an original concentration of 3 mg/ml of graphene derivatives. Coated and uncoated samples were separately placed in a sterile micro plate (6 wells) and inoculated with 0.35 mL of overnight incubated bacterial suspension (10^7 CFU/mL). After inoculation, each sample was placed in a 50 mL of saline solution (0.85% (w/v)) and was strongly shaken for 1 min. To measure the number of bacteria at zero time, the samples were placed in saline solution immediately after inoculation. The total bacterial count was determined by serial dilution and pour plate method using Luria-Bertani agar medium plates (10 g peptone, 5 g yeast extract, 10 g NaCl and distilled water up to 1 L; pH-7) incubated at 37 °C for 48 h. The antibacterial efficiency of all samples was calculated using Equation (2):

$$R\% = \frac{C_0 - C_{24}}{C_0} \times 100 \qquad (2)$$

Where, R is the bacterial reduction percentage, C_0 and C_{24} are the bacterial count immediately after inoculation and after incubation for 24 h, respectively.

Borate Impregnation and Composite Coating

The prepared aqueous solution of rGO/SMB makes a homogeneous mixture where SMB is dissolved state. For impregnation, 2.6 g of purified pine sawdust (500 µm to 1 mm) were treated with the 50 ml of rGO/SMB into a beaker and kept stirring for 5 hour at 70 ^{0}C. The dried sawdust sample was impregnated with SMB and found well coated with the rGO/SMB composite.

Volatiles Suppression and Fire Retardant Tests

The test for smoke and volatiles suppression was carried out inside a one end closed glass cylinder of 4 cm inner diameter so that the smoke and volatiles can be visually observed. Two small beakers (10 ml) containing 300 mg of preheated (at 80 °C) sawdust (treated and untreated) were placed on a hot surface (300 °C). The hot plate was allowed to be thermally

stable at 300 °C for 10 min before placing the samples. The beakers with samples were covered by two similar glass cylinders for the observation. The instant reaction of samples placed on the hot plate was recorded for 30 min by a high definition video camera (Sony HDR-PJ260).

In order to carry out the test of self-ignition properties, both the untreated and treated sawdust (80 mg) were placed on a screen mesh well-set above a Bunsen burner (3 cm apart from the tip of burner) to be in contact to the flame. The flame height and gas flow of Bunsen burner was set by keeping a half quarterly opened air hole that is constant for both type of the samples and placed in the middle of the flame. The combustion phenomena (self-igniting, flame propagation) were recorded for further analysis by a high definition video camera (Sony HDR-PJ260).

The pellets of a dimension of 120 mm × 13 mm × 3.5 mm were made out of untreated and treated sawdust under a hydraulic pressure of 5 ton. The fire retardant behaviour of these pellets were assessed by UL-94 standardized vertical burning tests. Five specimens of each type of samples were measured to ensure reproducibility of data and to grade their flammability. The time until the flame extinguished itself and the distance the burn propagated have been measured, then figured out the linear burning rate in mm per minute.

To examine rag-paper flammability with the application of rGO/SMB material as coating, fibre based paper was dip coated and cured under 50^0 C for several time that increases the material loading up to 15 wt%. The samples with and without coating were subjected to a fire retardant test (see Figure 3).

Results

The exfoliation of GO sheets from graphite was determined by transmission electron microscope (TEM). The simultaneous reduction of GO and formation of SMB by hydrolysis of $NaBH_4$ forms an aqueous solution of rGO/SMB. The presence of hydrated-SMB between (intercalated) and on top of the rGO sheets was confirmed by TEM. EDX (Energy-dispersive X-ray) of the so formed graphene-based composite showed elemental peaks of boron (B), carbon (C), oxygen (O) and sodium (Na) at 0.185, 0.277, 0.523 and 1.040 KeV,

respectively confirming the existence of SMB on the rGO surfaces.

A sample of rGO/SMB composite was taken under FTIR spectroscopy to investigate the characteristic peaks of the synergy. The oxygen functional groups of GO are almost entirely removed during the reduction process using $NaBH_4$ indicating successful reduction of GO. The appearance of new peaks observed in the sample at 692 cm^{-1} and 783 cm^{-1} indicate O-B-O ring asymmetric bending. The ring B–O asymmetric stretching vibrations appear strongly at 932, 1083, 1248 and 1432 cm^{-1}. Furthermore, the peak at 3353 cm^{-1} indicates hydrogen bond between hydroxyl groups of metaborate anion and water.

Thermogravimetric analysis of GO and rGO/SMB composite (N_2 atmosphere, heating at 5 °C/min) shows significant difference in the mass loss profiles. The GO sample shows a first stage mass loss (14.45 %) from ambient temperature to 100 °C due to the evaporation of water molecules in the GO structure, which is slightly greater than rGO/SMB at this stage. In the second stage between 100 °C to 250 °C, the GO sample has a massive mass loss (54.68 %) principally attributed to the removal of oxygen functional groups, whereas the rGO/SMB shows 25.72 % loss caused by the release of additional water molecules from the hydrated-SMB. The anhydrous sodium metaborate and rGO exists when the temperature exceeds 350 °C.

Fire retardant properties

The modification and coating of pine-sawdust was achieved by a solution treatment of an aqueous-rGO that contains dissolved-SMB. The loading was performed by soaking sawdust into the rGO/SMB solution. The dried mass of the treated sample increased by ≈14.67 % which did not make a huge difference in the total heat released (≈ 460 Cal/gram) between the samples which was determined by a high pressure (3000 KPa) oxygenated combustion of both the untreated and treated sawdust in a bomb calorimeter.

The evolution of gaseous products and volatiles suppression was analysed by FTIR. The FTIR spectra (4000 – 500 cm^{-1}) at different selected temperatures (100 °C, 200 °C, 250 °C, 300 °C, 325 °C, 350 °C) during combustion of the untreated and treated pine sawdust exhibited evolution of gaseous products by temperature change. The presence of water above

250 °C was caused by the cleavage of aliphatic hydroxyl groups confirmed by the appearance of bands at 4000 – 3500 cm^{-1}. The characteristic peaks at 3000 – 2730 cm^{-1} indicated the existence of methane, which was evolved between 250 °C to 300 °C as a result of cracking methoxyl (OCH_3–) and methyl (CH_3–). The methylene group (– CH_2 –) at high temperature also generated methane (CH_4). As the temperature increases to 350 °C, the intensity peak of carbon dioxide (CO_2) enhances at 2400-2260 cm^{-1}. The large amount of CO_2 release is caused by the cracking of cellulose and lignin, and the carbonized char burning at this temperature. The incomplete combustion of the pine sawdust also generated carbon monoxide (CO) as identified at 2260 –1990 cm^{-1} between the temperatures from 300 °C to 350 °C. Absorption bands at 1900–1660 cm^{-1} and 1500 cm^{-1} were related to C=O stretching for aldehyde or ketone compounds, C–O–C bend stretching for the groups of phenols, respectively. Absorptions at 900 and 650 cm^{-1} were assigned to C–H stretching for aromatic hydrocarbons. At an increased temperature (350 °C) the organic volatile compounds (aldehyde or ketone, phenols, alkanes, alkenes and aromatic hydrocarbon) begin to release violently.

Water content was identified at 4000 – 500 cm^{-1} since the beginning of the heating process from 100 to 350 °C as the treated sawdust contained relatively more water molecules because of the presence of hydrated sodium metaborate. The bonded water molecules were released in two steps; once between 83 and 155 °C and second between 249 and 280 °C. However, the intensity of other gases (CH_4, CO_2, CO, organic compounds) released from the treated samples were significantly lower at the selected temperatures possibly attributed to the impermeable gaseous barrier effect from the graphene-base composite. The barrier effect of the graphene-base composite has also been realized by a visual inspection when the treated and untreated samples were placed on a hot plate set at 300 ˚C for 30 min after a preheating at 80 ˚C to ensure the loss of additional moisture. The untreated sawdust begun to release smoke (possibly CO_2) and moisture (from aliphatic hydroxyl groups) at 3 min and the release of other organic volatiles (yellow and brown) was also observed between 10 to 20 min, whereas, the treated sawdust showed no significant release of observable organic volatiles.

The coated and modified loose sawdust also exhibits outstanding performance to resist flame propagation, when 80 mg of samples were placed on the screen mesh above a Bunsen burner

at a distance of 3 cm from the tip of the burner. The untreated sawdust started to propagate a flame between 15 to 20 s that was reinforced at 25 s and finally burned out within 70 s. On the other hand, the treated sawdust samples showed no self-ignition behaviour during the burning for 100 s.

In addition, the fire-retardant behaviour was further assessed by vertical burning tests (UL-94) using the samples (120 mm × 13 mm × 3.5 mm) made from uncoated and coated sawdust. The coated wooden pellet displayed excellent fire-retardancy with no flame propagation behaviour for the wooden pellet made from the treated sawdust. No flaming and glowing combustion was observed for each of the five treated specimens; hence the material is graded as V-0. Each burning for the treated specimen ceased instantly with no vertical lift of the flame, whereas the untreated sawdust pellet showed higher degree of flammable properties that continued till the end (up to the holding clamp) with an approximate linear burning rate of 0.5 mm/s.

An experiment was also performed to demonstrate fire retardant properties of rGO/SMB coatings where the rag paper is used a model substrate. The impregnated rag paper samples were torched with a natural gas (methane) flame in comparative experiment with untreated pristine paper and paper treated with rGO prepared by N_2H_4 (see Figure 3). The pristine rag paper took maximum 20 sec to be completely burned leaving almost no trace of the sample while and the rGO loaded sample shows only a negligible resistance and structural integrity for few extended period of time during the fire. On the other hand, rGO/SMB sample showed no sign of flame propagation behaviour during the flame test. The sample restrained its structure and showed self- extinguishing properties with little emission of white smoke due to the release of extra water molecules bonded to hydrated-SMB. Total mass loss of the fire retardant samples were ≈25 % after introducing a natural gas flame for 60 sec. TGA in air atmosphere for coated and coated rag paper showed different mass loss profile. The mass loss profile of the untreated rag paper exhibited 78.69 % loss between 300 to 400 °C including initially vaporised moisture content during combustion, whereas the rGO/SMB treated rag paper lost only 43.81 % of its total mass despite losing additional water molecules bonded to SMB. Samples coated with rGO/SMB left around 14 % more residue in contrast to the untreated rag paper after ending the combustion process at 1000 °C.

After-flame char analysis revealed some additional fire retardant properties of the material. The originally compact fibrous rag paper becomes fluffy ash and could not hold its structural shape. On the other hand, rGO-containing SMB showed intumescent effect providing swelling properties principally attributed to the presence of hydrated-SMB in between the rGO layers. The material starts to release water molecules between 90 °C and 250 °C. The underneath free water molecules start to vaporise and grow in volume during the fire, which pushes through the impermeable graphene layers to go out that eventually causes the coating layer to swell. This swelling effect has been identified all over the surface of the rGO/SMB treated sample that enables the protection of the underneath fibrous paper from the flame.

The rGO/SMB composite is demonstrated to exhibit a very high degree of fire retardant properties when applied on a flammable rag paper. The hydrated-SMB with graphene showed efficient intumescent effect and self-extinguishing properties to protect the underneath flammable material from fire for an extended period of time. These outstanding fire retardant performance of can be explained by synergistic effect of fire-retardant properties of SMB nanocrystals with barrier properties of graphene film that prevent oxygen to come into contact with flammable part underneath coating.

Preparation of composite formulation-A (solution based)

Graphene material in two forms, namely reduced Graphene Oxide (GO) prepared by chemical, thermal reduction or any other process, or graphene prepared synthetically or from graphite by electrochemical, thermal/mechanical or any other process, were used to make graphene fire-retardant composite solution. Graphene aqueous solution with a concentration of 2-10% was mixed with hydrated-sodium metaborate to make dissolved hydrated-SMB varying the composition percentage between 10 to 80 wt%.

Preparation of composite formulation-B (powder based)

Composite formulation (powder based) were prepared using solution based formulation-A by drying followed by grinding the formed products by grinder or ball milling to form fine powder composed with graphene sheets decorated with inorganic metal hydrates such as SMB nanoparticles.

Preparation of non flammable polymer materials (part A)

Water soluble polymer materials (e.g. polyvinyl alcohol (PVA)) in the form of pellets, granules or powder was mixed with formulation-A or powder based formulation-B, and stirred at 90 °C for 3 hrs followed by casting or extrusion process to make non-flammable polymer (see Figure 8).

Preparation of non flammable polymer materials (part B)

Solvent soluble polymer materials (e.g. polystyrene) in the form of pellets, granules or powder was dissolved in DMF and mixed with formulation-A or powder based formulation-B, with concentration 20wt% to 50 wt% of the mixture. The mixture was stirred at 115 °C for 3 hours followed by casting or extrusion process to make non-flammable polymer (see Figure 9).

Mechanical adhesion and abrasion properties

The overall thickness of the rGO/SMB coatings fabricated for the cross-cut adhesion test was ≤ 2 μm as determined by optical profilometry and SEM. Table 1 shows the adhesion performance of the coated samples with different comparative coating formulations rated following the standard ASTM-class for both copper (Cu) and glass substrates. These results show that the rGO/SMB coating had the best adhesion to both the Cu and glass surfaces, also as shown in Figure 7 (b) and (e) as determined by the cross-cut adhesion test followed by the scotch tape procedure. Control (N_2H_4 reduced) rGO coatings were prepared to compare with the rGO/SMB coating to examine the inherent adhesion of the material to the Cu and glass substrates. The coatings made from the sample (rGO-N_2H_4) failed to show appreciable minimal adhesion (ASTM class 0B) to either of the Cu and glass substrates.

Table 1 Adhesion performance of coatings as determined by ASTM D-3359-02.

Substrate	GO	rGO/SMB	rGO- N_2H_4
Copper (ASTM-class)	0B	4B	0B
Microscope Glass (ASTM-class)	0B	4B	0B

The deposition of rGO with and without SMB revealed that the coating without SMB did not have any adhesion properties as determined by the cross-cut adhesion test. The ASTM adhesion of GO and rGO (reducing agent N_2H_4) on both the Cu and glass substrates was found to be 0B (considered as undefined or no adhesion), whereas the rGO/SMB sample showed an ASTM adhesion rating of 4B (less than 5 % cross cut area was demonstrated as affected) for both the Cu and glass substrate. Furthermore, the rGO/SMB coating was also applied to other metals (i.e. aluminium (Al), stainless steel) and results confirmed that the adhesion is independent to the metal substrate. The adhesion strength between the metal plate and coating is likely formed between the native metal oxide and borate interface.

The abrasion test results a minimal weight loss (6.33 mg/cm^2, max^m) after the completion of ≈3000 cycles under a load of 250 g of each wheel. The surface morphology of rGO/SMB sample before and after the abrasion test have been shown in Figure 7 (g and h) for the comparison where SMB-crystals were found to be homogeneously distributed on both the abrasive and non-abrasive surface. Patterns of the wear damage could be clearly classified as parallel grooves and multiple indentations as shown by the red arrows in Figure 7 (h). The micro indentation is created from the loss of SMB-crystal during the abrasion test. A Raman mapping of the abrasive surface was performed to analyse the area percentage of components occupied in the inner coating layers, which showed that about 71 % was occupied by rGO and 29 % for SMB-crystals.

Outstanding adhesion properties of the graphene-based composite film were determined by standard ASTM test to be 4B grade, with a high degree of abrasion resistance. The characterization results confirm the existence of SMB crystals at the interfaces and inside graphene-based layers which suggest to significantly promote the mechanical strength of the layered composite and adhesion to the external substrates (metal and glass). The possible mechanism of the enhanced adhesion between graphene film and surface (the metal plate) is likely result of strong binding interaction between the native metal oxide and borate (SMB nanocrystals).

Antibacterial properties

The antibacterial properties of the uncoated (glass slide) and coated (GO, rGO- N_2H_4 and rGO/SMB) samples were evaluated by AATCC Test Method 100-2004. The bacterial strain similarly grew well on all tested samples at zero time, while the growth was further enhanced only on the uncoated (control) sample after 24 h. Other samples containing graphene derivatives showed strong antibacterial activity at a uniform concentration of GO as the starting material (3 mg/ml) after 24 h (Figure 6). GO was found to reduce 85.34 % *E. coli* colonies, whereas rGO- N_2H_4 was less effective (54.47 %) than GO. The antibacterial ability of rGO/SMB (99.9%) outperformed the GO and rGO-N_2H_4 coatings.

SEM analysis was performed to qualitatively investigate the interaction between the coated surfaces and bacteria to confirm the potential antibacterial actions. Formation of a thick biofilm was identified on the glass slide where *E. Coli* had easily proliferated. GO coated surface was found to interact with the bacterial cells to reduce proliferation. At higher magnification, it was observed that the single bacterial cell was intertwined with GO sheets to cause membrane perturbation which was reported as one of few possible mechanisms for antibacterial properties of GO. Furthermore, bacterial membrane damage and cytoplasm leakage was observed for the sample containing rGO/SMB, where the bacterial cells were found to be randomly distributed.

The presence of SMB on/in the rGO sheets increases the wettability (≈32° WCA) of the rGO/SMB composite coating in comparison to the rGO-N_2H_4 coating ((≈84° WCA) that may reinforce the interaction between the graphene sheets and bacterium.

A strong antibacterial effect of the graphene-based composite has been demonstrated showing almost 100 % resistance against the colonization of *E.coli* bacteria with significantly better performance compared with the GO and the rGO used as a control. The results suggest that surface wettability should be taken as an active parameter that may affect the antibacterial properties the graphene based composite. Along with the intrinsic antibacterial properties of SMB, it is believed to increase hydrophilicity of the surface that possibly allows E. Coli cells to come into close contact with the sharp graphene sheets, thus leading bacterial cells towards an active membrane destruction.

Throughout this specification and the claims which follow, unless the context requires otherwise, the word "comprise", and variations such as "comprises" and "comprising", will be understood to imply the inclusion of a stated integer or step or group of integers or steps but not the exclusion of any other integer or step or group of integers or steps.

The reference in this specification to any prior publication (or information derived from it), or to any matter which is known, is not, and should not be taken as an acknowledgment or admission or any form of suggestion that that prior publication (or information derived from it) or known matter forms part of the common general knowledge in the field of endeavour to which this specification relates.

CLAIMS

1. A graphene-based composite comprising graphene-based material intercalated with hydrated sodium metaborate.

2. The graphene-based composite according to claim 1, wherein the graphene-based material comprises one or both of reduced graphene oxide and graphene.

3. The graphene-based composite according to claim 1, wherein the hydrated sodium metaborate is present in the form of nano-particles or a film.

4. A method of preparing a graphene-based composite, the method comprising (i) providing a liquid composition comprising graphene-based material and hydrated sodium metaborate, and (ii) evaporating liquid from the composition so as to retain the graphene-based material and hydrated sodium metaborate in the composition, wherein the process of evaporating liquid in step (ii) promotes intercalation of the hydrated sodium metaborate in the graphene-based material to afford the graphene-based composite.

5. The method according to claim 4, wherein the liquid composition is an aqueous liquid composition and in step (ii) water is evaporated from the composition.

6. The method according to claim 4 or 5 in which the liquid composition comprising graphene-based material and hydrated sodium metaborate is provided by an aqueous liquid composition comprising graphene oxide and sodium borohydride, wherein the graphene oxide is reduced by the sodium borohydride to afford reduced graphene oxide and the hydrated sodium metaborate.

7. A substrate comprising a graphene-based composite, the graphene-based composite comprising graphene-based material intercalated with hydrated sodium metaborate.

8. The substrate according to claim 7, wherein the graphene-based composite is coated on a surface of the substrate, distributed throughout the substrate matrix, or a combination thereof.

9. The substrate according to claim 7 or 8, wherein the substrate comprises cellulosic material, polymer, metal, ceramic, glass or a combination thereof.

10. The substrate according to any one of claims 7 to 9 which exhibits improved fire retardant properties, improved abrasion resistance, improved antimicrobial properties or a combination thereof, relative to the substrate absent the graphene-based composite.

11. A method of improving one or more of fire retardant properties, abrasion resistance properties and antimicrobial properties of a substrate, the method comprising coating or impregnating the substrate with a liquid composition comprising a graphene-based composite, wherein the graphene-based composite comprises graphene-based material intercalated with hydrated sodium metaborate, said improved properties being relative to the substrate absent the graphene-based composite.

12. The method according to claim 11, wherein the substrate is coated or impregnated with the graphene-based composite by (i) coating or impregnating the substrate with a liquid composition comprising the graphene-based material and the hydrated sodium metaborate, and (ii) evaporated liquid from the coated composition so as to retain the graphene-based material and the hydrated sodium metaborate in the coated or impregnated composition and form the graphene-based composite.

13. The method according to claim 12 in which the liquid composition comprising graphene-based material and hydrated sodium metaborate is provided by an aqueous liquid composition comprising graphene oxide and sodium borohydride, wherein the graphene oxide is reduced by the sodium borohydride to afford reduced graphene oxide and the hydrated sodium metaborate.

14. A method of improving one or more fire retardant properties, abrasion resistance properties and antimicrobial properties of a thermoplastic polymer substrate, the method comprising melt processing the thermoplastic polymer substrate with a graphene-based composite, wherein the graphene-based composite comprises graphen-based material intercalated with hydrated sodium metaborate, said improved properties being relative to the substrate absent the graphene-based composite.

15. A method of improving one or more fire retardant properties, abrasion resistance properties and antimicrobial properties of a thermoset polymer substrate, the method comprising blending a graphene-based composite with precursor materials used to make the thermoset polymer substrate, wherein the graphene-based composite comprises graphene-based material intercalated with hydrated sodium metaborate, said improved properties being relative to the substrate absent the graphene-based composite.

16. The method according to any one of claims 11 to 15, wherein the graphene-based material comprises one or both of reduced graphene oxide and graphene.

17. The method according to any one of claims 11 to 16, wherein the substrate comprises hydrated sodium metaborate that does not form part of the graphene-based composite.

18. Use of a graphene-based composite to improve one or more of fire retardant properties, abrasion resistance properties and antimicrobial properties of a substrate, wherein the graphene-based composite comprises graphene-based materials intercalated with hydrated sodium metaborate, said improved properties being relative to the substrate absent the graphene-based composite.