

Description

Title of Invention: A Modified Layered Clay Material And Composites Containing the Same

Technical Field

The present invention relates to a modified layered clay material and composites containing the same. The invention also relates to a method of preparing the modified layered clay material and composite.

Background Art

Inorganic-organic nanocomposites often exhibit properties exceeding those of macroscopic composites. For the generally accepted definition of nanocomposites, the inorganic component is inorganic filler which is no larger than 1 micron in size and the organic component is a polymer with continuous phase structure, that is, nanocomposites are highly dispersed systems of submicron-sized inorganic particles in a polymeric matrix.

Of the many inorganic nanomaterials known such as metal oxide, fumed silica, fibre glass, metal wires, etc., clays are particularly interesting because of their geometric platelet shapes and natural abundance. Clay (montmorillonite, bentonite or hectorite) has a naturally occurring layered structure in which negatively charged layered structures or sheets are held together by sodium, potassium, magnesium or other inorganic cations sitting in anionic galleries between the sheets. The sheet-to-sheet separation (or d spacing) is about 1.2 to 1.5 nm. To form nanocomposites, clay needs to be well exfoliated to make the use of its two dimensional platelet structure, i.e. high surface to volume feature.

Clay in the natural state is unsuitable for the preparation of nanocomposites because clay is too hydrophilic and the layers are bound too tightly, limiting the extent of interaction with hydrophobic polymer monomers, which in turns limit the extent of dispersion of clay with the polymer monomers. To make it more compatible with the polymers, clay is modified by an ion exchange method in which the inorganic cations (sodium, potassium, magnesium, etc.) that exist between the sheets are replaced with organic cations. The resulted product is called “modified clay” or “organoclay”.

Commonly, the organic cations used to make modified clay are cationic surfactants containing long alkyl chains, such as quaternary alkylammonium, trialkylimidazolium and tetraalkylphosphonium salts. For the organoclay, the content of organic surfactant is ~35-45 wt%. Due to the low thermal stability of the organic surfactant, the modified clay has a low decomposition temperature of ~250°C. Therefore, the organic modified clay filled nanocomposite usually has an unimproved or lower thermal stability, especially when compared with the ideal nanocomposite system without any existing surfactant. Furthermore, as the nanocomposite is usually prepared by melt blending modified clay with a polymer, in such cases, the modified layered clay needs to be stable at the processing temperature of the polymer. As conventional organic surfactant modified clay is stable only

up to about 250°C, it is thus not feasible to make nanocomposites which have high processing temperatures above 250°C.

There is therefore a need to provide a modified layered clay material that overcomes, or at least ameliorates, one or more of the disadvantages described above.

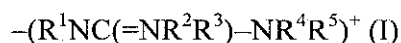
Summary

There is provided a modified layered clay material comprising a layered clay material modified by a functionalized silsesquioxane having a functional group with at least two conjugated amine groups.

In one aspect, there is provided a modified layered clay material comprising a layered clay material modified by a functionalized silsesquioxane having a functional group with at least two conjugated amine groups,

wherein said functional group having at least two amine groups is a triamine compound, wherein at least one amine group is positively charged, and

wherein the triamine compound is a guanidinium ion having the formula I



wherein R^1 , R^2 , R^3 , R^4 and R^5 are independently selected from hydrogen, alkyl, alkenyl, aryl, arylalkenyl, alkoxy, cycloalkyl, heteroaryl, heterocyclic or halogen.

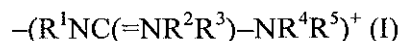
Advantageously, the at least two conjugated amine groups forming the functional group may be able to interact strongly with the layered clay material. Hence, the functional group may have a strong affinity with the layered clay material, resulting in modification of the layered clay material with high efficiency.

Still advantageously, the interaction between the functionalized silsesquioxane and the layered clay material may be enhanced due to the type of functional group on the silsesquioxane.

There is provided a composite comprising a polymer having a plurality of modified layered clay materials dispersed therein, where the modified layered clay material comprises a layered clay material modified by a functionalized silsesquioxane having a functional group with at least two conjugated amine groups.

In another aspect, there is provided a composite comprising a polymer having a plurality of modified layered clay materials dispersed therein, where the modified layered clay material comprises a layered clay material modified by a functionalized silsesquioxane having a functional group with at least two conjugated amine groups,

wherein said functional group having at least two amine groups is a triamine compound, wherein at least one amine group is positively charged, and wherein the triamine compound is a guanidinium ion having the formula I



wherein R^1 , R^2 , R^3 , R^4 and R^5 are independently selected from hydrogen, alkyl, alkenyl, aryl, arylalkenyl, alkoxy, cycloalkyl, heteroaryl, heterocyclic or halogen.

In order to have greater clay exfoliation in the composite, the functionalized silsesquioxane may be modified easily by altering the chain length of the functional group. Due to the higher tendency to be exfoliated and improved thermal stability as compared to a conventional organic surfactant modified clay, the modified layered clay material may be used as fillers to improve the mechanical and thermal properties of the composites.

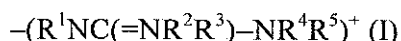
Still advantageously, the modified layered clay material can be used with polymers that have high processing temperatures (of for example above 250°C); in comparison, conventional organoclays would decompose at such temperatures and cannot be used as fillers where high processing temperature is required.

Further advantageously, the composite may exhibit increased strength, reduced vapor permeability, and improved thermal stability as compared to composites made from conventional organoclay fillers that usually display a decreased thermal stability.

There is provided a method of preparing a modified layered clay material comprising the step of mixing a layered clay material with a functionalized silsesquioxane having a functional group with at least two conjugated amine groups. Advantageously, this method does not require the use of complicated equipment or conditions and can be scaled up easily.

In another aspect, there is provided a method of preparing a modified layered clay material comprising the step of mixing a layered clay material with a functionalized silsesquioxane having a functional group with at least two conjugated amine groups,

wherein said functional group having at least two amine groups is a triamine compound, wherein at least one amine group is positively charged, and wherein the triamine compound is a guanidinium ion having the formula I

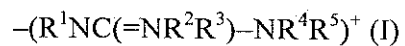


wherein R^1 , R^2 , R^3 , R^4 and R^5 are independently selected from hydrogen, alkyl, alkenyl, aryl, arylalkenyl, alkoxy, cycloalkyl, heteroaryl, heterocyclic or halogen.

There is provided a method of preparing a composite comprising a polymer having a plurality of modified layered clay materials dispersed therein, wherein the method comprising the step of passing a mixture of the polymer and the modified clay materials through an extruder.

In another aspect, there is provided a method of preparing a composite comprising a polymer having a plurality of modified layered clay materials dispersed therein, wherein the method comprising the step of passing a mixture of the polymer and the modified clay materials through an extruder,

wherein said modified layered clay material comprises a layered clay material modified by a functionalized silsesquioxane having a functional group with at least two conjugated amine groups, wherein said functional group having at least two amine groups is a triamine compound, wherein at least one amine group is positively charged, and wherein the triamine compound is a guanidinium ion having the formula I



wherein R^1 , R^2 , R^3 , R^4 and R^5 are independently selected from hydrogen, alkyl, alkenyl, aryl, arylalkenyl, alkoxy, cycloalkyl, heteroaryl, heterocyclic or halogen.

Definitions

The following words and terms used herein shall have the meaning indicated:

The term “silsesquioxane” may be interpreted broadly to refer to any organosilicon compound that contains cage-like or polymeric structures with Si-O-Si linkages and tetrahedral silicon vertices. The silsesquioxane generally has the chemical formula $[\text{RSiO}_{3/2}]_m$ in which R refers to hydrogen, alkyl, aryl, arylalkenyl, cycloalkyl, alkoxy, heteroaryl, heterocyclic or halogen and m is 6, 8, 10 or 12. The silsesquioxane includes polymeric silsesquioxane (commonly known as polyhedral oligomeric silsesquioxane or POSS) or hydridosilsesquioxane. The silsesquioxane may be functionalized with a functional group to thereby form a “functionalized silsesquioxane”.

The terms “nano” or “nano-scale” when used in conjunction with an object, may be interpreted broadly to refer to at least one dimension of that object to be less than one micrometer, or less than 1000 nm, less than 500 nm, less than 100 nm or less than 50 nm. Where the object fulfils this criteria, the object may be termed as a nano-object. For example, where the object is a composite, the nano-object may be termed as a nano-composite. For the avoidance of doubt, the object may have two or more dimensions that are in the micron range (such as 1 micron to 1000 microns) as long as at least one dimension of that object is in the nano range to be termed as a nano-object (such as a nano-composite).

As used herein, the term “composite” refers to a polymeric material which contains a dispersion of the modified layered clay material throughout the polymeric material. When the modified layered clay material is well dispersed, its size at one dimension is in the range of 1 to 10 nm, the composite may then be termed as a “nanocomposite”.

The term “clay” as used herein refers to a naturally occurring material composed primarily of fine-grained minerals, which depending on the water content, can deform when a stress is applied on the clay, and become harder and non-deformable when heat is applied to the clay. Clay can be generally divided into four groups depending on their structures and contents, such as kaolinite, montmorillonite-smectite, illite, or chlorite. Clay is made of clay minerals that are structured within the clay as planes of cations, arranged in sheets, which may be tetrahedrally or octahedrally coordinated (with oxygen), which in turn are arranged into layers of tetrahedral and/or octahedral sheets. As such, it is possible to introduce additives into the clay by intercalating such additives into the clay such that the cations existing naturally in the natural clays are replaced with the positively charged ion of the additive. Where the clay is intercalated with such additives, the clay can be termed as modified clay. Hence, the term “modified clay” as used herein can refer to clays whose existing cations are replaced synthetically with another positively charged ion.

The term “guanidinium” is to be interpreted broadly to refer to the conjugate acid of guanidine; an ionically charged, cationic, species. Guanidinium ion refers to a moiety having the formula: $-(\text{R}^1\text{NC}(=\text{NR}^2)-\text{NR}^3\text{R}^4\text{R}^5)^+$, where R^1 , R^2 , R^3 , R^4 and R^5 are independently selected from hydrogen, alkyl, alkenyl, aryl, arylalkenyl, alkoxy, cycloalkyl, heteroaryl, heterocyclic or halogen. Where the silsesquioxane is functionalized with the guanidinium ion, the nitrogen attached to R^1 is then the point of attachment of the

guanidinium ion to the silsesquioxane, forming a guanidinium functionalized silsesquioxane.

The term “amine” is intended to refer to a group containing -NH₂. The group may be a terminal group or a bridging group. The amine group may act as a base to attract a proton in order to achieve a positive charge, forming an ammonium ion.

The term “alkyl” as a group or part of a group refers to a straight or branched aliphatic hydrocarbon group having 1 to 12 carbon atoms, 1 to 10 carbon atoms, 1 to 6 carbon atoms, or 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11 or 12 carbon atoms. Examples of suitable straight and branched C₁-C₆ alkyl substituents include methyl, ethyl, n-propyl, 2-propyl, n-butyl, sec-butyl, t-butyl, hexyl, and the like. The group may be a terminal group or a bridging group.

The term “alkenyl” as a group or part of a group denotes an aliphatic hydrocarbon group containing at least one carbon-carbon double bond and which may be straight or branched having 2 to 12 carbon atoms, 2 to 10 carbon atoms, 2 to 6 carbon atoms, or 2, 3, 4, 5, 6, 7, 8, 9, 10, 11 or 12 carbon atoms in the chain. The group may contain a plurality of double bonds and the orientation about each double bond is independently *E* or *Z*. Exemplary alkenyl groups include, but are not limited to, ethenyl, propenyl, butenyl, pentenyl, hexenyl, heptenyl, octenyl and noneyl. The group may be a terminal group or a bridging group.

The term “aryl” as a group or part of a group denotes (i) an optionally substituted monocyclic, or fused polycyclic, aromatic carbocycle (ring structure having ring atoms that are all carbon) preferably having from 5 to 12, or 5, 6, 7, 8, 9, 10, 11, or 12 carbon atoms per ring. Examples of aryl groups include phenyl, naphthyl, and the like; (ii) an optionally substituted partially saturated bicyclic aromatic carbocyclic moiety in which a phenyl and a C₅₋₇-cycloalkyl or C₅₋₇-cycloalkenyl groups are fused together to form a cyclic structure, such as tetrahydronaphthyl, indenyl or indanyl. The group may be a terminal group or a bridging group. Typically an aryl group is a C₆-C₁₈ aryl group.

The term “arylalkenyl” means an aryl-alkenyl group in which the aryl and alkenyl are as defined herein. Exemplary arylalkenyl groups include phenylallyl. The group may be a terminal group or a bridging group. If the group is a terminal group, it is bonded to the remainder of the molecule through the alkenyl group.

The term “bond” refers to a linkage between atoms in a compound or molecule. The bond may be a single bond, a double bond, or a triple bond.

The term “cycloalkyl” refers to a saturated monocyclic or fused or spiro polycyclic, carbocycle preferably having 3 to 9, or 3, 4, 5, 6, 7, 8 or 9 carbon atoms per ring, such as cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl and the like, unless otherwise specified. It includes monocyclic systems such as cyclopropyl and cyclohexyl, bicyclic systems such as decalin, and polycyclic systems such as adamantane. The group may be a terminal group or a bridging group.

The term “alkoxy” as used herein refers to straight chain or branched alkyloxy groups. Examples include methoxy, ethoxy, n-propoxy, isopropoxy, tert-butoxy, and the like.

The term "heteroaryl" either alone or part of a group refers to groups containing an aromatic ring (preferably a 5- or 6- membered aromatic ring) having one or more heteroatoms as ring atoms in the aromatic ring with the remainder of the ring atoms being carbon atoms. Suitable heteroatoms include nitrogen, oxygen and sulphur. Examples of heteroaryl include thiophene, benzothiophene, benzofuran, benzimidazole, benzoxazole, benzothiazole, benzisothiazole, naphtha[2,3-b]thiophene, furan, isoindolizine, xantholene, phenoxatine, pyrrole, imidazole, pyrazole, pyridine, pyrazine, pyrimidine, pyridazine, tetrazole, indole, isoindole, 1H-indazole, purine, quinoline, isoquinoline, phthalazine, naphthyridine, quinoxaline, cinnoline, carbazole, phenantridine, acridine, phenazine, thiazole, isothiazole, phenothiazine, oxazole, isooxazole, furazane, phenoxazine, 2-, 3- or 4-pyridyl, 2-, 3-, 4-, 5-, or 8-quinolyl, 1-, 3-, 4-, or 5-isoquinolyl, 1-, 2-, or 3-indolyl, and 2-, or 3-thienyl. The group may be a terminal group or a bridging group.

The term "heterocyclic" refers to saturated, partially unsaturated or fully unsaturated monocyclic, bicyclic or polycyclic ring system containing at least one heteroatom selected from the group consisting of nitrogen, sulphur and oxygen as a ring atom. Examples of heterocyclic moieties include heterocycloalkyl, heterocycloalkenyl and heteroaryl.

The term "halogen" represents chlorine, fluorine, bromine or iodine. The term "halo" represents chloro, fluoro, bromo or iodo.

The word "substantially" does not exclude "completely" e.g. a composition which is "substantially free" from Y may be completely free from Y. Where necessary, the word "substantially" may be omitted from the definition of the invention.

Unless specified otherwise, the terms "comprising" and "comprise", and grammatical variants thereof, are intended to represent "open" or "inclusive" language such that they include recited elements but also permit inclusion of additional, unrecited elements.

As used herein, the term "about", in the context of concentrations of components of the formulations, typically means +/- 5% of the stated value, more typically +/- 4% of the stated value, more typically +/- 3% of the stated value, more typically, +/- 2% of the stated value, even more typically +/- 1% of the stated value, and even more typically +/- 0.5% of the stated value.

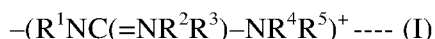
Throughout this disclosure, certain embodiments may be disclosed in a range format. It should be understood that the description in range format is merely for convenience and brevity and should not be construed as an inflexible limitation on the scope of the disclosed ranges. Accordingly, the description of a range should be considered to have specifically disclosed all the possible sub-ranges as well as individual numerical values within that range. For example, description of a range such as from 1 to 6 should be considered to have specifically disclosed sub-ranges such as from 1 to 3, from 1 to 4, from 1 to 5, from 2 to 4, from 2 to 6, from 3 to 6 etc., as well as individual numbers within that range, for example, 1, 2, 3, 4, 5, and 6. This applies regardless of the breadth of the range.

Certain embodiments may also be described broadly and generically herein. Each of the narrower species and subgeneric groupings falling within the generic disclosure also form part of the disclosure. This includes the generic description of the embodiments with a proviso or negative limitation removing any subject matter from the genus, regardless of whether or not the excised material is specifically recited herein.

Detailed Disclosure of Embodiments

Exemplary, non-limiting embodiments of a modified layered clay material will now be disclosed. The modified layered clay material comprises a layered clay material modified by a functionalized silsesquioxane having a functional group with at least two conjugated amine groups.

The at least two amine groups may be bonded to the same carbon atom. The functional group having at least two diamine groups may be a diamine compound or a triamine compound, wherein one amine group is bonded to the carbon via a carbon-carbon double bond. Where the functional group having at least two conjugated amine groups is a triamine compound, the triamine compound may be a guanidinium ion having the formula I



wherein

R^1 , R^2 , R^3 , R^4 and R^5 are independently selected from hydrogen, alkyl, alkenyl, aryl, arylalkenyl, alkoxy, cycloalkyl, heteroaryl, heterocyclic or halogen.

The guanidinium ion may be of the formula $-(HNC(=NH_2)-NH_2)^+$ (where all of R^1 , R^2 , R^3 , R^4 and R^5 are hydrogen).

Where the functional group having at least two conjugated amine groups is a diamine compound, the diamine compound may be an amidinium ion having the formula II

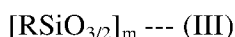


wherein

R^1 , R^2 , R^3 and R^6 are independently selected from hydrogen, alkyl, alkenyl, aryl, arylalkenyl, alkoxy, cycloalkyl, heteroaryl, heterocyclic or halogen.

The amidinium ion may be of the formula $-(HN-CH(=NH_2))^+$ (where all of R^1 , R^2 , R^3 and R^6 are hydrogen) and this ion is termed as formamidinium ion.

The silsesquioxane may be of the formula III



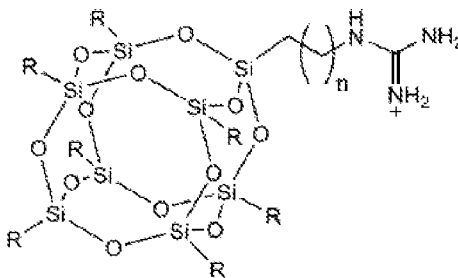
wherein

R refers to hydrogen, alkyl, aryl, arylalkenyl, cycloalkyl, alkoxy, heteroaryl, heterocyclic or halogen; and

m is 6, 8, 10 or 12.

The above functional group may be attached to one or more of the silicon atoms of the silsesquioxane, without compromising the structural stability of the silsesquioxane. Where more than one functional group is present, each or all of the functional groups may have the same or different structure. Where the functional group has the generic structure of Formula I or II, one or all of the functional groups can be same or different as long as all of them share the generic structure shown in Formula I or II above.

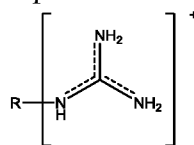
In the functionalised silsesquioxane, where m is 8, and the guanidinium ion is of the formula $-(HNC(=NH_2)-NH_2)^+$, the functionalized silsesquioxane has the following structure:

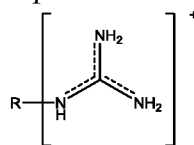


where n is 1 to 9, or 1, 2, 3, 4, 5, 6, 7, 8 or 9.

The silsesquioxane may be connected to the functional group with at least two conjugated amine groups via an aliphatic linker. The aliphatic linker may be a alkyl chain or an alkenyl chain, each having 1 to 10, 2 to 6, or 1, 2, 3, 4, 5, 6, 7, 8, 9 or 10 carbon atoms. The linker may also contain atom(s) other than carbon such as nitrogen, oxygen, sulfur, or mixture thereof. For example, the linker may be an amino alkyl group (such as dimethyl amine, diethyl amine, *N*-methylethyl amine, *N,N*-dimethylethyl amine, *N,N*-dimethylpropyl amine, *N*-ethyl-*N*-methylethyl amine).

The modification of silsesquioxane may be achieved by coupling silsesquioxane and an amino-conjugated compound that is a positively charged species regardless of the pH. This characteristic would result in a better performance as compared to a silsesquioxane coupled to just one ammonium ion. Unlike such ammonium coupled silsesquioxane, the silsesquioxane coupled with the at least two conjugated amine groups of the present disclosure carries a permanent charge that remains positively charged even in neutral pH. This permanent charge may be due to the sharing of electrons among the nitrogen atoms in the at least two conjugated amine groups that make up the functional group coupled to the



silsesquioxane (as shown in this structure ). With the coupled silsesquioxane of the present disclosure, it is possible to modify the layered clay material in neutral pH to minimize the negative competing effect with other co-existing cations.

The clay may be selected from the group consisting of montmorillonites, bentonite, kaolinite, hectorite, halloysite, beidellite, saponite, illites, glauconite, chlorites, vermiculite, fibrous clays and mixtures thereof. In the clay, the negatively charged structures are arranged in layers and are held together by one or more cations such as for example sodium, potassium, lithium, rubidium, caesium, beryllium, magnesium, calcium, strontium, barium ions. In order to form the modified layered clay material defined herein, any or all of the above cations are substituted with the functionalized silsesquioxane described above. Hence, the functionalized silsesquioxane may increase the spacing between the layers when being intercalated into the clay (thus forming the modified layered clay material). Due to inorganic/organic hybrid structure of the functionalized silsesquioxane, the modified layered clay material may have a higher thermal stability than conventional organoclays.

The modified layered clay material may be stable at a temperature of at least about 300°C, about 300°C to about 400°C, about 300°C to about 310°C, about 300°C to about 320°C, about 300°C to about 340°C, about 300°C to about 360°C, about 300°C to about 380°C,

about 310°C to about 320°C, about 310°C to about 340°C, about 320°C to about 360°C, about 320°C to about 380°C, about 320°C to about 400°C, about 340°C to about 360°C, about 340°C to about 380°C, about 340°C to about 400°C, about 360°C to about 380°C, about 360°C to about 400°C, or about 380°C to about 400°C.

The modified layered clay material may have an interspacing distance between the layers in the range from about 3.0 nm to about 5.0 nm, about 3.0 nm to about 3.5 nm, about 3.0 nm to about 4.0 nm, about 3.0 nm to about 4.5 nm, about 3.0 nm to about 5.0 nm, about 3.25 nm to about 3.5 nm, about 3.5 nm to about 3.75 nm, about 3.5 nm to about 4.0 nm, 3.5 nm to about 4.5 nm, about 3.5 nm to about 5.0 nm, about 4.0 nm to about 4.5 nm, about 4.0 nm to about 5.0 nm or about 4.5 nm to about 5.0 nm.

The modified layered clay material may have a particle size in the range of about 100 nm to about 20000 nm, about 100 nm to about 200 nm, about 100 nm to about 500 nm, about 100 nm to about 1000 nm, about 200 nm to about 500 nm, about 200 nm to about 1000 nm, about 500 nm to about 1000 nm, about 500 nm to about 20000 nm, or about 1000 nm to about 20000 nm.

When a water droplet is dispensed on the modified layered clay material, the contact angle between the water droplet and the surface of the modified layered clay material may be in the range of about 90° to about 150°, about 90° to about 100°, about 90° to about 110°, about 90° to about 120°, about 90° to about 150°, about 100° to about 110°, about 100° to about 120°, about 100° to about 150°, about 110° to about 120°, about 110° to about 150°, or about 120° to about 150°. Hence, the modified layered clay material may be liquidphobic and may be used as a self-cleaning surface or a liquid repellent surface.

Exemplary, non-limiting embodiments of a composite will now be disclosed. The composite comprises a polymer having a plurality of modified layered clay materials dispersed therein, where the modified layered clay material comprises a layered clay material modified by a functionalized silsesquioxane having a functional group with at least two amine groups.

In the composite, the polymer can be regarded as the continuous phase while the modified layered clay material is considered as the dispersed phase.

The polymer used to make the composites may generally include, but is not limited to, homopolymers, copolymers, such as, for example, block, graft, random and alternating copolymers, terpolymers, etc. and blends and modifications thereof. Polymers can include, but are not limited to, polylactides, polylactic acids, polyolefins, polyacrylonitrile, polyurethane, polycarbonate, polycaprolactone, polyvinyl alcohol (PVA), cellulose, chitosan nylon (e.g., nylon 6, nylon 406, nylon 6-6, etc.), polystyrene, and the like, or combinations thereof.

The polymers may be mixed with the modified layered clay material to make the composites at high processing temperature and may then be selected from crystalline polymers with high crystalline melting temperature (e.g., fluoroplastic) or amorphous polymer having a high glass transition temperature (e.g., polynorbornene). In contrast, a conventional organic surfactant modified layered clay is stable only up to about 250°C and cannot be used to make composites from polymers at high processing temperatures.

The composite may have better mechanical properties (for example tensile and flexural strengths), in comparison to the polymers without addition of the modified clay. Where the polymer in the composite is polyamide 11, the flexural strength of the composite may be in the range of about 70 MPa to about 80 MPa, or about 76 MPa. Where the polymer in the composite is polyamide 6, the flexural strength of the composite may be in the range of about 110 MPa to about 120 MPa, or about 118 MPa.

The composite may have a decomposition temperature in the range of about 300°C to about 450°C, about 300°C to about 325°C, about 300°C to about 350°C, about 300°C to about 375°C, about 300°C to about 400°C, about 300°C to about 450°C, about 325°C to about 350°C, about 325°C to about 375°C, about 325°C to about 400°C, about 325°C to about 450°C, about 350°C to about 375°C, about 350°C to about 400°C, about 350°C to about 450°C, about 375°C to about 400°C, about 375°C to about 450°C, or about 400°C to about 450°C. Generally, the decomposition temperature may be dependent on the type of polymer used in the composite.

The composite may have a particle size in the range of about 100 nm to about 20000 nm, about 100 nm to about 200 nm, about 100 nm to about 500 nm, about 100 nm to about 1000 nm, about 200 nm to about 500 nm, about 200 nm to about 1000 nm, about 500 nm to about 1000 nm, about 500 nm to about 20000 nm, or about 1000 nm to about 20000 nm.

Where the dispersed phase is in the nano-size range, the composite may be termed as a nanocomposite.

The amount of modified layered clay material dispersed in the polymer forming the composite may be in the range of 0.1 wt% to 20 wt%, or may be of 0.5 wt%, 1 wt%, 2 wt%, 3 wt%, 4 wt%, 4.5 wt%, 5 wt%, 5.5 wt%, 6 wt%, 7 wt%, 8 wt%, 9 wt%, 10 wt%, 11 wt%, 12 wt%, 13 wt%, 14 wt%, 15 wt%, 16 wt%, 17 wt%, 18 wt%, 19 wt%, or 20 wt% based on the weight of the composite.

Exemplary, non-limiting embodiments of a method of preparing a modified layered clay material will now be disclosed. The method comprises the step of mixing a layered clay material with a functionalized silsesquioxane having a functional group with at least two amine groups.

The method may be an ion-exchange method, in which the cation(s) in the clay is(are) exchanged with the functionalized silsesquioxane.

The method may further comprise, before the mixing step, the step of providing the functionalized silsesquioxane in an organic solvent. The organic solvent is not particularly limited and depends on the type of functionalized silsesquioxane used. As an example, a ketone such as acetone may be used to dissolve the functionalized silsesquioxane.

The functionalized silsesquioxane may be prepared by mixing a precursor of the functionalized silsesquioxane with a suitable salt (containing the desired functional group). The mixture may be stirred at room temperature for about 1 hour to about 24 hours, or about 1 hour, about 2 hours, about 3 hours, about 4 hours, about 5 hours, about 6 hours, about 7 hours, about 8 hours, about 9 hours, about 10 hours, about 11 hour, about 12 hours, about 13 hours, about 14 hours, about 15 hours, about 16 hours, about 17 hours, about 18 hours, about 19 hours, about 20 hours,

about 21 hour, about 22 hours, about 23 hours, or about 24 hours. After solvent removal, the functionalized silsesquioxane is obtained.

Where the functionalized silsesquioxane is guanidinium ion functionalized silsesquioxane, the guanidinium ion functionalized silsesquioxane may be prepared by mixing an amino functionalized silsesquioxane dissolved in a suitable organic solvent (such as tetrahydrofuran) with a compound containing the guanidinium ion group (also dissolved in a suitable organic solvent such as dimethyl sulfoxide). It is to be appreciated that the type of solvent used is dependent on the type of reactants used and is not limited to the above. The compound containing the guanidinium ion group may have a counter ion that is selected from the group consisting of chloride, fluoride, bromide, oxide, sulfide, hydroxide, sulphate, nitrate, phosphate, sulfite, phosphite, HPO_3^{2-} , $\text{HP}(\text{O})_2\text{OH}^-$, $\text{H}_2\text{P}_2\text{O}_5^{2-}$, H_2PO_2^- and any combinations thereof. Accordingly, the anion of the guanidinium ion functionalized POSS is the same as that of the counter ion mentioned above and will be removed when the guanidinium ion functionalized POSS is intercalated in the clay.

The step of mixing the layered clay material with the functionalized silsesquioxane may be undertaken at a temperature in the range of about 20°C to about 80 °C, or about 20°C, about 25°C, about 30°C, about 35°C, about 40°C, about 50°C, about 60°C, about 70°C, or about 80°C.

The step of mixing the layered clay material with the functionalized silsesquioxane may be undertaken for a time period in the range of 1 hour to 12 hours, or about 1 hour, about 2 hours, about 3 hours, about 4 hours, about 5 hours, about 5.5 hours, about 6 hours, about 6.5 hours, about 7 hours, about 8 hours, about 9 hours, about 10 hours, about 11 hours, or about 12 hours.

Exemplary, non-limiting embodiments of a method of preparing a composite comprising a polymer having a plurality of modified layered clay materials dispersed therein will now be disclosed. The method comprises the step of passing a mixture of the polymer and the modified clay materials through an extruder.

The passing step may be undertaken at a temperature in the range of about 100°C to about 400°C, or about 100°C, about 150°C, about 175°C, about 200°C, about 225°C, about 250°C, about 300°C, about 350°C, about 400°C.

The type of extruder used is not particularly limited and may be selected from single screw extruder, twin or multiple screw extruder or ram extruder.

Brief Description of Drawings

The accompanying drawings illustrate a disclosed embodiment and serves to explain the principles of the disclosed embodiment. It is to be understood, however, that the drawings are designed for purposes of illustration only, and not as a definition of the limits of the invention.

Fig. 1

[Fig. 1] is a schematic diagram showing the structure of guanidium-functionalized POSS modified clay made in accordance with Example 2.

Fig. 2

[Fig. 2] is a schematic diagram showing the preparation of POSS modified clay made in accordance with Example 2.

Fig. 3

[Fig. 3] is a graph showing the thermal gravimetric analysis (TGA) of POSS modified clay made in accordance with Example 2 and organoclay.

Fig. 4

[Fig. 4] is a picture showing the water contact angle of POSS modified clay prepared in accordance with Example 2 and organoclay.

Fig. 5

[Fig. 5] is a graph of the XRD pattern of POSS modified clay prepared in accordance with Example 2, in comparison with the XRD pattern of organoclay and unmodified clay.

Fig. 6

[Fig. 6] is a histogram showing the thermal stability of Composite A prepared in accordance with Example 3, in comparison with the thermal stability of PA11, organoclay/PA11 and POSS/PA11.

Fig. 7

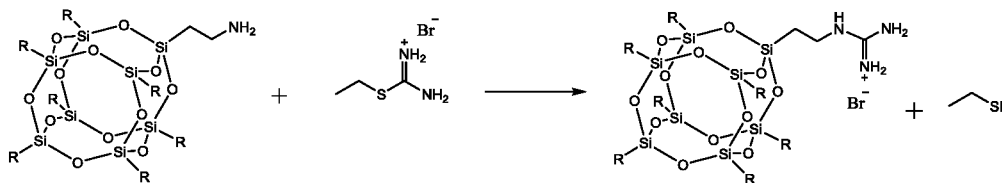
[Fig. 7] is a histogram showing the thermal stability of Composite B prepared in accordance with Example 4, in comparison with the thermal stability of PA6 and organoclay/PA6.

Examples

Non-limiting examples of the invention will be further described in greater detail by reference to specific Examples, which should not be construed as in any way limiting the scope of the invention.

Example 1: Preparation of guanidinium-functionalized POSS

A guanidinium ion functionalized silsesquioxane was prepared based on the chemical reaction as illustrated in Scheme 1 below. The silsesquioxane used in this reaction was an octahedral oligomeric silsesquioxane with R is *tert*-butyl group and n is 2.



Scheme 1

Here, 16.6 g aminopropyl functionalized POSS (Hybrid Plastics Inc. of Hattiesburg of Mississippi of the United States of America) was dissolved in 100 ml tetrahydrofuran (THF) (Merck & Co. Inc. of Kenilworth of New Jersey of United States of America) while 3.5 g ethyl-2-thiopseudourea hydrobromide (Tokyo Chemical Industry Co., Ltd. of Japan) was dissolved in 10 ml dimethyl sulfoxide (DMSO) (Merck & Co. Inc. of Kenilworth of New Jersey of United States of America). The ethyl-2-thiopseudourea hydrobromide solution was then slowly added to the aminopropyl functionalized POSS solution forming a mixture. The mixture was then stirred at room temperature for 12 hours. After removal of the solvent, the guanidinium ion functionalized POSS was obtained.

Example 2: Preparation of Guanidinium functionalized POSS modified clay

Clay (montmorillonite) was obtained from Nanocor Inc. of Illinois of United States of America. First, 10 g of clay was suspended in 1 L deionized water by magnetic stirring for 12 hours to make a 1wt% fine suspension. 8.0 g of guanidinium functionalized POSS was then dissolved in 400 ml of acetone (Merck & Co. Inc. of Kenilworth of New Jersey of United States of America) and the solution was added dropwise to the 1 L clay suspension. The resulting mixture was magnetically stirred for 6 hours at a rotation speed of 500 rpm, followed by washing in acetone using Soxhlet extractor for another 6 hours. After being dried at 60°C to remove acetone, the modified clay were ground to a fine powder with white color. The structure of the resulting guanidinium functionalized POSS is depicted in Fig. 1. In this figure, guanidinium functionalized POSS have displaced the inorganic cations that may be present in the interspacing layers of clay structure. The reaction scheme of preparation of guanidinium functionalized POSS modified clay is summarized in Fig. 2.

The properties of the guanidinium functionalized POSS modified clay was then analysed and compared with those of organic surfactant modified clay (or herein termed as “organoclay”). The organoclay used for comparison purposes with the commercial name Nanomer ®I.34TCN was modified by quaternary alkylammonium and obtained from Nanocor Inc. (from Illinois, of the United States of America). The properties of both types of clays are shown in Table 1 below.

The thermal stability of guanidinium functionalized POSS modified clay was evaluated using thermal gravimetric analysis (TGA). Fig. 3 showing the TGA curves of modified clay materials reveals that guanidinium functionalized POSS modified clay displays higher thermal stability as compared to the organoclay. Therefore, the guanidinium functionalized POSS modified clay may be used in applications that require higher processing temperature. Further, in comparison to organoclay, the guanidinium functionalized POSS modified clay had a larger d spacing, and lower interlayer binding force. As can be seen from Fig. 4, the guanidinium functionalized POSS modified clay also has a higher water contact angle which may aid in the compatibility of the guanidinium functionalized POSS modified clay with polymers, leading to better dispersion in a composite (which is made up of the guanidinium functionalized POSS modified clay dispersed in the polymer). The d spacings of the unmodified and modified clay were characterized by X-ray diffraction (XRD) measurements using Bruker D8 General Area Detector Diffraction System (GADDS) (Bruker). Fig. 5 shows the effect of surfactant chemistry on the X-ray diffraction patterns of clays. The shifting of the peak to the lower angle manifests the increase of the layer separation of the clay. It was found the guanidinium functionalized POSS modified

clay has a layer separation of 3.5 nm, which is much higher than the layer separation for the organoclay of 1.9 nm.

Table 1. Comparisons between organoclay and guanidinium functionalized POSS modified clay

	Organoclay	Guanidinium functionalized POSS modified clay
Layer separation (nm)	1.9	3.5
Degradation temperature ^a (°C)	264	313
Water contact angle (°)	77	120

^a Degradation temperature is defined as the temperature at which the modified clay lose 2% of its weight and is determined by the TGA curves shown in Fig. 3 (which was obtained under air flow of 20 ml/min with a heating rate of 10°C/minute) .

Example 3: Preparation of Composite A

Here, the guanidinium functionalized POSS modified clay from Example 2 was used to prepare a nanocomposite (herein termed “Composite A”) from polyamide 11 (PA11) (with trade name of Rilsan® from Arkema SA. of Colombes of France). Guanidinium functionalized POSS modified clay was blended with PA11 at loading rate of 5 wt% using a twin-screw extruder (Eurolab®, Haake) at temperature of 200°C. The blend material in the pellet form was then subjected to injection molding (MiniJet®, Haake) to make Composite A. The properties of the formed Composite A are listed in Table 2. In the same table, the properties of PA11 and organoclay /PA11 composite are shown for comparative purposes while non-functionalized POSS/PA11 was used as a control. Here, the organoclay used was Nanomer ®I.34TCN obtained from Nanocor Inc. PA11 was made by injection molding of the raw PA11 material and the organoclay/PA11 and non-functionalized POSS/PA11 composites were made by extruding and injection molding using the same methods as those for Composite A. Fig. 6 shows the comparison of the thermal stability of composite A and organoclay/PA11. It can be seen that composite A displays higher thermal stability as compared to organoclay/PA11.

Table 2. Mechanical properties and thermal stability

	PA11	Composite A (5 wt%)	Organoclay/PA11 (5 wt%)	POSS/PA11 (5 wt%)
Tensile modulus (GPa)	3.7	4.3	4.6	4.0
Tensile strength (MPa)	42.8	43.6	46.4	41.8
Flexural modulus (GPa)	2.3	3.3	3.3	3.1
Flexural strength (MPa)	66.6	76.9	75.5	72.3
Degradation temperature ^a (°C)	358	388	342	355

^a Degradation temperature is defined as the temperature at which the composite lose 2% of its weight.

Composite A obtained according to this Example exhibited improved mechanical properties and thermal stability. In contrast, the incorporation of organoclay into PA11 decreased the thermal stability, which limited its application in high temperature environments.

Example 4: Preparation of Composite B

Here, the guanidinium functionalized POSS modified clay from Example 2 was used to prepare a nanocomposite (herein termed “Composite B”) from polyamide 6 (PA6, trade name Zytel® obtained from Du Pont Inc. of Wilmington of Delaware of United States of America). Guanidinium functionalized POSS modified clay was blended with PA6 at loading rate of 5 wt% using a twin-screw extruder (Eurolab®, Haake) at a temperature of 270°C. The blend material in the pellet form was then subjected to injection molding (MiniJet®, Haake) to make Composite B. The properties of the formed Composite B are listed in Table 3. In the same table, the properties of PA6 and organoclay/PA6 are shown for comparative purposes. PA6 was made by injection molding of the raw PA6 material and the organoclay/PA6 composite was made by extruding and injection molding using the same methods as those for Composite B.

Table 3. Mechanical properties and thermal stability

	PA6	Composite B (5 wt%)	Organoclay/PA6 (5 wt%)
Tensile modulus (GPa)	7.3	8.6	8.0
Tensile strength (MPa)	65.6	72.9	71.0
Flexural modulus (GPa)	3.1	4.1	4.0
Flexural strength (MPa)	101	118	115
Degradation temperature ^a (°C)	325	374	321

^a Degradation temperature is defined as the temperature at which the composite lose 2% of its weight.

As shown in Table 3, with the addition of a small amount of the guanidinium functionalized POSS modified clay of 5 wt%, a substantial increase in the degradation temperature of PA6 can be obtained in which the degradation temperature increased by about 50°C. Further, Fig. 7 depicts the increased thermal stability of composite B in comparison to the organoclay/PA6. Hence, the guanidinium functionalized POSS modified clay can be used as a multi-functional filler to simultaneously improve the mechanical property and thermal stability of PA6.

Example 5: Preparation of Composite C

Here, guanidinium functionalized POSS modified clay according to the structure below (where R is *tert*-butyl and n is 5) was used to prepare a nanocomposite (herein termed “Composite C”) from PA6. The chemical structure of the guanidinium functionalized POSS modified clay used is depicted below. Guanidinium functionalized POSS modified clay was blended with PA6 at loading rate of 5 wt% using a twin-screw extruder (Eurolab®, Haake) at a temperature of 270°C. The blend material in the pellet form was then subjected to injection molding (MiniJet®, Haake) to make Composite C. The properties of the formed Composite C are listed in Table 4. In the same table, the properties of PA6 and organoclay/PA6 are shown for comparative purposes. PA6 was made by injection molding of the raw PA6 material and the organoclay/PA6 composite was made by extruding and injection molding using the same methods as those for Composite C.

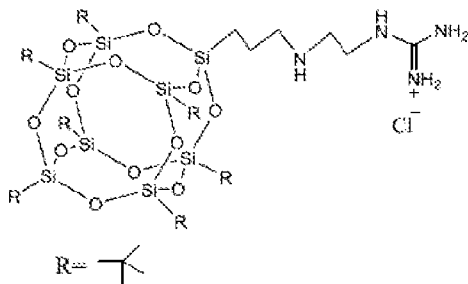


Table 4. Mechanical properties and thermal stability

	PA6	Composite C (5 wt%)	Organoclay/PA6 (5 wt%)
Tensile modulus (GPa)	7.3	8.1	8.0
Tensile strength (MPa)	65.6	71.2	71.0
Flexural modulus (GPa)	3.1	3.8	4.0
Flexural strength (MPa)	101	112	115
Degradation temperature ^a (°C)	325	360	321

^a Degradation temperature is defined as the temperature at which the composite lose 2% of its weight.

As shown in Table 4, with the addition of a small amount of the guanidinium functionalized POSS modified clay of 5 wt%, a substantial increase in the degradation temperature of PA6 can be obtained in which the degradation temperature increased by about 35°C. Hence, the guanidinium functionalized POSS modified clay can be used as a multi-functional filler to simultaneously improve the mechanical property and thermal stability of PA6.

Industrial Applicability

In the present disclosure, the composites comprising modified layered clay materials may be used in manufacturing pipings or pipelines (such as attached risers, pull tube risers, steel catenary risers, top-tensioned risers, riser towers and flexible riser configurations, as well as drilling risers). The composites may be used as laminate boards in the electronics industry that are suitable for high temperature soldering (such as tin soldering which occurs at a temperature more than 230°C). In addition, the composites may be used in crude oil pipeline cleaning. Further, the modified layered clay materials may be used as fillers to improve the strength and thermal stability of composites for other harsh environments such as aerospace, oil and gas industry.

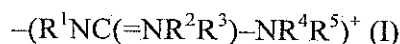
It will be apparent that various other modifications and adaptations of the invention will be apparent to the person skilled in the art after reading the foregoing disclosure without departing from the spirit and scope of the invention and it is intended that all such modifications and adaptations come within the scope of the appended claims.

Claims

1. A modified layered clay material comprising a layered clay material modified by a functionalized silsesquioxane having a functional group with at least two conjugated amine groups,

wherein said functional group having at least two amine groups is a triamine compound, wherein at least one amine group is positively charged, and

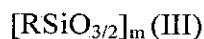
wherein the triamine compound is a guanidinium ion having the formula I



wherein

R^1 , R^2 , R^3 , R^4 and R^5 are independently selected from hydrogen, alkyl, alkenyl, aryl, arylalkenyl, alkoxy, cycloalkyl, heteroaryl, heterocyclic or halogen.

2. The modified layered clay material according to claim 1, wherein the silsesquioxane is of the formula III

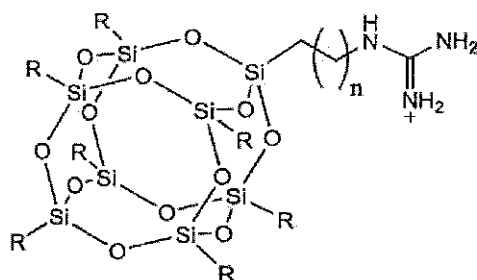


wherein

R refers to hydrogen, alkyl, aryl, arylalkenyl, cycloalkyl, alkoxy, heteroaryl, heterocyclic or halogen; and

m is 6, 8, 10 or 12.

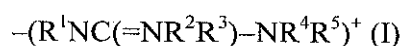
3. The modified layered clay material according to any one of the preceding claims, wherein the silsesquioxane is connected to the functional group with at least two amine groups via an aliphatic linker.
4. The modified layered clay material according to any one of the preceding claims, wherein when m is 8, the functionalized silsesquioxane is of the following structure:



where

n is 1 to 9.

5. The modified layered clay material according to any one of the preceding claims, wherein the modified layered clay material is stable at a temperature of at least 300°C.
6. The modified layered clay material according to any one of the preceding claims, wherein the modified layered clay material has an interspacing distance between the layers in the range from 3.0 nm to 5.0 nm.
7. The modified layered clay material according to any one of the preceding claims, having a particle size in the range of 100 nm to 20000 nm.
8. A composite comprising a polymer having a plurality of modified layered clay materials dispersed therein, where the modified layered clay material comprises a layered clay material modified by a functionalized silsesquioxane having a functional group with at least two conjugated amine groups, wherein said functional group having at least two amine groups is a triamine compound, wherein at least one amine group is positively charged, and wherein the triamine compound is a guanidinium ion having the formula I

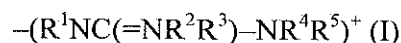


wherein R^1 , R^2 , R^3 , R^4 and R^5 are independently selected from hydrogen, alkyl, alkenyl, aryl, arylalkenyl, alkoxy, cycloalkyl, heteroaryl, heterocyclic or halogen.

9. The composite according to claim 8, having a decomposition temperature in the range of 300°C to 450°C.
10. The composite according to claim 8 or 9, having a particle size in the range of 100 nm to 20000 nm.
11. The composite according to any one of claims 8 to 10, wherein the amount of modified layered clay material dispersed in the polymer is in the range of 0.1 wt% to 20 wt%, based on the weight of the composite.
12. The composite according to any one of claims 8 to 11, wherein the polymer is selected from the group consisting of polylactides, polylactic acids,

polyolefins, polyacrylonitrile, polyurethane, polycarbonate, polycaprolactone, polyvinyl alcohol, cellulose, chitosan nylon, polystyrene, fluoroplastic polynorbornene and mixtures thereof.

13. A method of preparing a modified layered clay material comprising the step of mixing a layered clay material with a functionalized silsesquioxane having a functional group with at least two conjugated amine groups, wherein said functional group having at least two amine groups is a triamine compound, wherein at least one amine group is positively charged, and wherein the triamine compound is a guanidinium ion having the formula I

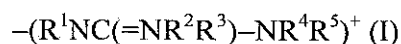


wherein R^1 , R^2 , R^3 , R^4 and R^5 are independently selected from hydrogen, alkyl, alkenyl, aryl, arylalkenyl, alkoxy, cycloalkyl, heteroaryl, heterocyclic or halogen.

14. The method of claim 13, further comprising, before said mixing step, the step of providing said functionalized silsesquioxane in an organic solvent.

15. The method of claim 13 or 14, wherein said mixing step is undertaken at a temperature in the range of 20°C to 80°C.
16. The method of any one of claims 13 to 15, wherein said mixing step is undertaken for a time period in the range of 1 hour to 12 hours.
17. A method of preparing a composite comprising a polymer having a plurality of modified layered clay materials dispersed therein, wherein the method comprising the step of passing a mixture of the polymer and the modified clay materials through an extruder,

wherein said modified layered clay material comprises a layered clay material modified by a functionalized silsesquioxane having a functional group with at least two conjugated amine groups, wherein said functional group having at least two amine groups is a triamine compound, wherein at least one amine group is positively charged, and wherein the triamine compound is a guanidinium ion having the formula I



wherein R¹, R², R³, R⁴ and R⁵ are independently selected from hydrogen, alkyl, alkenyl, aryl, arylalkenyl, alkoxy, cycloalkyl, heteroaryl, heterocyclic or halogen.

18. The method according to claim 17, wherein said passing step is undertaken at a temperature in the range of 100°C to 400°C.