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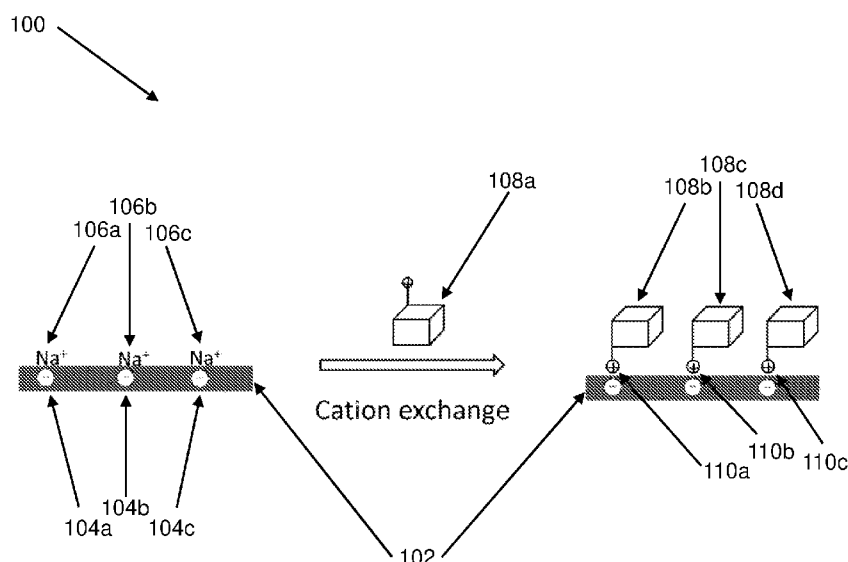


FIG. 1

(57) Abstract: There is provided a modifier for modifying a clay material, the modifier comprising a functionalized silsesquioxane having one or more epoxide group(s) and one or more organocation group(s); a modified clay material comprising a clay material that is modified by or that comprises said modifier; and a composite comprising an epoxy matrix and a filler comprising said modified clay material. Also provided are methods of preparing said modifier, said modified clay material and said composite.



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MODIFIER, MODIFIED CLAY MATERIAL, COMPOSITE, AND RELATED METHODS

TECHNICAL FIELD

5 The present disclosure relates broadly to a modifier for modifying clay material, a modified clay material and a composite. The present disclosure also relates to methods of preparing said modifier, said modified clay material and said composite.

BACKGROUND

10 Epoxy is a thermoset polymer showing some desirable chemical characteristics. For example, little or no byproducts or volatiles are released during curing reactions of epoxy. In addition, epoxy has curability over a wide temperature range and exhibits low shrinkage upon curing. Moreover, epoxy has excellent material properties, such as excellent chemical and heat resistance, high strength, high electrical insulation and high adhesive strength. All of these characteristics make epoxy a very useful material in a wide variety of industries, which include aerospace, electronics, automotive, construction, etc.

20 However, due to its high crosslink density, epoxy is still considered to be fundamentally brittle with relatively low toughness. Its widespread adoption is hence restricted. Epoxy also has low crack initiation as void growth due to plastic deformation is largely constrained. Therefore, it is important to improve the toughness of epoxy in order to broaden its suitability to more applications, such as for use in structural materials.

30 Different strategies based on composite technology have been developed to toughen epoxy. A conventional method is to use rubber particle as a second phase for toughening. The rubbers employed in the art include carboxylic nitrile-butadiene (NR), carboxyl-terminated butadiene acrylonitrile (CTBN) and hydroxyl

terminated polybutadiene (HTPB). These rubbers are usually used at a loading ratio of about 5-20 vol%. With the introduction of the rubber phase, a substantial increase in fracture toughness can be achieved. However, it was discovered that the stiffness and strength of the cured epoxy also decreased at the same time. In addition, the rubber particles also caused the thermal properties of epoxy to deteriorate.

Another approach of epoxy toughening is through the use of thermoplastic polymers. In this approach, high performance thermoplastics such as poly(phenylene oxide) (PPO), polysulfone (PSF) and polyetherimide (PEI) are added to epoxy resin to serve as a rigid toughening phase. When compared to the rubber toughening approach, the introduction of thermoplastics having high glass transition temperature (T_g) offers the advantages of increasing the toughness of epoxy without compromising the mechanical or thermal properties. However, processing of the thermoplastic/epoxy bend is generally very difficult due to the high melting point and insolubility of such engineering plastics in common solvents. This drawback discourages the adoption of the thermoplastic toughening method in many industries.

To overcome the drawbacks of both the rubber and thermoplastics toughening methods, another alternative method which involves the use of polymer composites such as polymer nanocomposites as a filler material (e.g. nanometer-scaled fillers stands) has been explored. Examples of nanofillers used for toughening epoxy include carbon nanotube (CNT), graphene, nanosilica and nanoclay. However, the use of some of these fillers presents new problems. For example, some of these fillers (e.g. nanoclay) are inherently incompatible with organic polymer matrix as they are hydrophilic in nature. As such, these fillers are required to be modified to change their surface chemistry from being hydrophilic to being hydrophobic so as to improve their compatibility with polymer matrix.

The current modifiers used to modify fillers are still far from being satisfactory and these modifiers include surfactants such as octadecyl ammonium (Nanomer® I.30E, Nanocor Inc.), octadecyl trimethyl ammonium (Nanomer® I.28E, Nanocor Inc.), methyl tallow bis-2-hydroxyl quaternary ammonium (Cloisite® 30B, BYK Inc.), cetylpyridinium chloride and stearylbenzyltrimethyl-ammonium chloride. Problems arising from the use of current modifiers include the lowering of the glass transition temperature (T_g) of epoxy, which results in reduced thermal stability and/or insufficient assimilation of the fillers and epoxy.

Other methods to modify fillers include using silanization techniques. However, such techniques still suffer from drawbacks such as the fillers eventually forming aggregates due to the crosslinking that occurs between themselves, which is encouraged by the crosslinking nature of silane molecules.

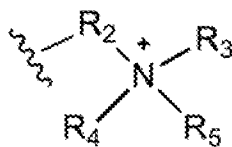
In view of the above, there is a need to address or at least ameliorate the above-mentioned problems. In particular, there is a need to provide a modifier for modifying clay material, a modified clay material and an epoxy composite containing the modified clay material that address or at least ameliorate the above-mentioned problems.

SUMMARY

In one aspect, there is provided a modifier for modifying clay material, the modifier comprising a functionalized silsesquioxane having one or more epoxide group(s) and one or more organocation group(s).

In one embodiment, the organocation group comprises a quaternary ammonium group.

In one embodiment, the quaternary ammonium group is represented by general Formula (I):

Formula (I)

wherein

R₂ is selected from the group consisting of a single bond, alkyl, alkylphenyl, cycloalkyl, alkenyl, cycloalkenyl, alkynyl, alkoxy, ether (or alkyloxyalkyl), alkoxyalkyl, alkylcarbonyl, alkoxycarbonyl, alkylphenyloxyalkyl, aryl, aryloxy, arylalkenyl and heteroaryl;

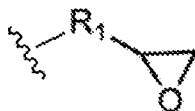
R₃, R₄ and R₅ are each independently selected from the group consisting of hydroxy, hydroxyalkyl, halogen, haloalkyl, cyano, cyanoalkyl, nitro, nitroalkyl, carboxyl, alkyl, alkylphenyl, cycloalkyl, alkenyl, cycloalkenyl, alkynyl, alkoxy, ether (or alkyloxyalkyl), alkoxyalkyl, alkylcarbonyl, alkoxycarbonyl, alkylphenyloxyalkyl, aryl, aryloxy, arylalkenyl and heteroaryl;

wherein one or more hydrogen atom(s) is/are optionally replaced by hydroxy, hydroxyalkyl, halogen, haloalkyl, cyano, cyanoalkyl and nitro, and

wherein one or more carbon atom(s) is/are optionally replaced by heteroatom(s) selected from the group consisting of O, S, S=O and C=O.

In one embodiment, the quaternary ammonium group comprises a hydroxyl group.

In one embodiment, the epoxide group is represented by general Formula (II):

Formula (II)

wherein R₁ is selected from the group consisting of a single bond, alkyl, alkylphenyl, cycloalkyl, alkenyl, cycloalkenyl, alkynyl, alkoxy, ether (or

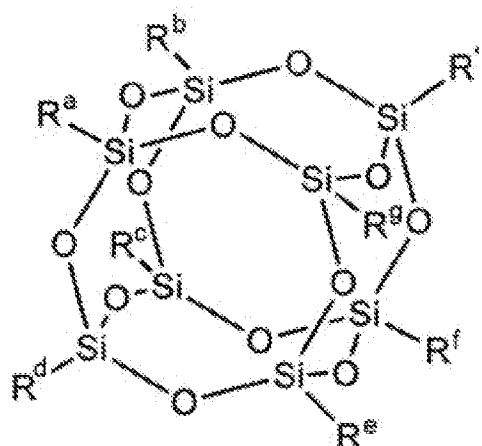
alkyloxyalkyl), alkoxyalkyl, alkylcarbonyl, alkoxyalkyl, alkylphenyloxyalkyl, aryl, aryloxy, arylalkenyl and heteroaryl;

wherein one or more hydrogen atom(s) is/are optionally replaced by hydroxy, hydroxyalkyl, halogen, haloalkyl, cyano, cyanoalkyl and nitro, and

5 wherein one or more carbon atom(s) is/are optionally replaced by heteroatom(s) selected from the group consisting of O, S, S=O and C=O.

In one embodiment, the epoxide group comprises a glycidyl group.

10 In one embodiment, the functionalized silsesquioxane is represented by general Formula (III):



Formula (III)

15 wherein R^a , R^b , R^c , R^d , R^e , R^f , R^g and R' are each independently selected from the group consisting of hydrogen, general Formula (I) and general Formula (II), with at least one of R^a , R^b , R^c , R^d , R^e , R^f , R^g and R' having general Formula (I) and at least one of R^a , R^b , R^c , R^d , R^e , R^f , R^g and R' having general Formula (II).

20 In one embodiment, the molar ratio of the one or more organocation group(s) to the one or more epoxide group(s) ranges from 1:7 to 1:1.

In one aspect, there is provided a modified clay material comprising a clay material that is modified by or that comprises a modifier as disclosed herein.

In one embodiment, the clay material comprises a layered clay material.

5 In one embodiment, the modified clay material comprises said modifier intercalated between layers of said layered clay material.

In one embodiment, the d-spacing of modified clay material is no less than 3 nm.

10 In one embodiment, the clay material is coupled to the modifier through at least ionic interactions.

In one embodiment, the clay material comprises a nanoclay.

15 In one aspect, there is provided a composite comprising: (i) an epoxy matrix; and (ii) a filler comprising a modified clay material as disclosed herein.

In one embodiment, the filler is no more than 3 wt% of the composite.

20 In one embodiment, the composite has a tensile strength and/or tensile modulus that is higher than the epoxy matrix alone.

In one aspect, there is provided a method of preparing a modifier as disclosed herein, the method comprising: a) reacting a silsesquioxane having one or more epoxide group(s) with an organocation precursor having an organic functional group to obtain a silsesquioxane having one or more epoxide group(s) and one or more of the organic functional group(s); and b) converting one or more of the organic functional group(s) obtained in a) to the corresponding organocation group(s) to obtain a functionalized silsesquioxane having one or more epoxide group(s) and one or more organocation group(s).

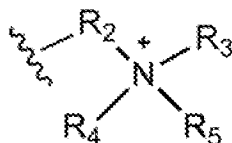
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In one embodiment, the organocation precursor in a) comprises a secondary amine precursor and the silsesquioxane obtained in a) has one or more epoxide group(s) and one or more tertiary amine group(s).

5 In one embodiment, b) comprises converting one or more tertiary amine group(s) obtained in a) to the corresponding quaternary ammonium cation(s) to obtain a functionalized silsesquioxane having one or more epoxide group(s) and one or more quaternary ammonium group(s).

10 In one embodiment, the quaternary ammonium group is represented by general Formula (I):



Formula (I)

wherein

15 R₂ is selected from the group consisting of a single bond, alkyl, alkylphenyl, cycloalkyl, alkenyl, cycloalkenyl, alkynyl, alkoxy, ether (or alkyloxyalkyl), alkoxyalkyl, alkylcarbonyl, alkoxy carbonyl, alkylphenyloxyalkyl, aryl, aryloxy, arylalkenyl and heteroaryl;

20 R₃, R₄ and R₅ are each independently selected from the group consisting of hydroxy, hydroxyalkyl, halogen, haloalkyl, cyano, cyanoalkyl, nitro, nitroalkyl, carboxyl, alkyl, alkylphenyl, cycloalkyl, alkenyl, cycloalkenyl, alkynyl, alkoxy, ether (or alkyloxyalkyl), alkoxyalkyl, alkylcarbonyl, alkoxy carbonyl, alkylphenyloxyalkyl, aryl, aryloxy, arylalkenyl and heteroaryl;

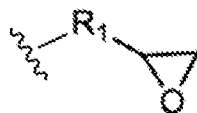
25 wherein one or more hydrogen atom(s) originally present is/are replaced by hydroxy, hydroxyalkyl, halogen, haloalkyl, cyano, cyanoalkyl and nitro, and

wherein one or more carbon atom(s) is/are optionally replaced by heteroatom(s) selected from the group consisting of O, S, S=O and C=O.

In one embodiment, the quaternary ammonium group comprises a hydroxyl group.

In one embodiment, the epoxide group is represented by general Formula

5 (II):



Formula (II)

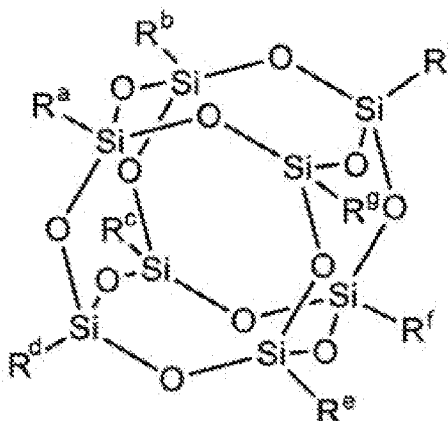
wherein R_1 is selected from the group consisting of a single bond, alkyl, alkylphenyl, cycloalkyl, alkenyl, cycloalkenyl, alkynyl, alkoxy, ether (or alkyloxyalkyl), alkoxyalkyl, alkylcarbonyl, alkoxyalkyl, alkylphenyloxyalkyl, aryl, aryloxy, arylalkenyl and heteroaryl;

wherein one or more hydrogen atom(s) originally present is/are replaced by hydroxy, hydroxyalkyl, halogen, haloalkyl, cyano, cyanoalkyl and nitro, and

15 wherein one or more carbon atom(s) is/are optionally replaced by heteroatom(s) selected from the group consisting of O, S, S=O and C=O.

In one embodiment, the epoxide group comprises a glycidyl group.

20 In one embodiment, the functionalized silsesquioxane is represented by general Formula (III):



Formula (III)

wherein R^a , R^b , R^c , R^d , R^e , R^f , R^g and R' are each independently selected from the group consisting of hydrogen, general Formula (I) and general Formula (II), with at least one of R^a , R^b , R^c , R^d , R^e , R^f , R^g and R' having general Formula (I) and at least one of R^a , R^b , R^c , R^d , R^e , R^f , R^g and R' having general Formula (II).

In one aspect, there is provided a method of preparing a modified clay material as disclosed herein, the method comprising: mixing a clay material with a modifier as disclosed herein to obtain a modified clay material.

In one embodiment, the method comprises intercalating the modifier into the clay material.

In one embodiment, the step of intercalating the modifier into the clay material comprises exchanging a cation in the clay material with an organocation of the modifier.

In one aspect, there is provided a method of preparing a composite as disclosed herein, the method comprising: mixing an epoxy matrix with a filler comprising a modified clay material as disclosed herein.

In one embodiment, the mixing step is carried out in the presence of a hardener.

In one embodiment, the filler is added in an amount that is no more than 3 wt% of the final composite product.

In one embodiment, the epoxy resin and hardener are mixed in a weight ratio in a range of from 5:1 to 2:1.

DEFINITIONS

The term "silsesquioxane" as used herein is to be interpreted broadly to refer to any organosilicon compound that contains cage-like or polymeric structures with Si–O–Si linkages and silicon vertices. The silsesquioxane may generally have 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 may include polymeric silsesquioxane (commonly known as polyhedral oligomeric silsesquioxane or POSS). The silsesquioxane may be functionalized with a functional group to thereby form a "functionalized silsesquioxane".

The term "composite" as used herein refers to a material that is formed from the combination of two or more constituent materials with significantly different physical or chemical properties. Generally, the composite may have characteristics different from the individual constituent materials. In various embodiments of the present disclosure, the composite includes a matrix material in combination with a filler material. For example, the composite may include a polymeric material which contains a dispersion of clay material (for e.g. a modified clay material) throughout the polymeric material. If the composite has a size at one dimension in the range of 1 nm 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. Depending on the water content, a clay may 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 may be

arranged into layers of tetrahedral and/or octahedral sheets. The term "modified clay" as used herein can refer to clays whose existing cations are replaced synthetically with another positively charged ion.

5 The term "amine group" or the like is intended to broadly refer to a group containing $-NR_2$, where R is independently a hydrogen or an organic group. 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.

10

 The term "ammonium group" or the like is intended to broadly refer to positively charged or protonated substituted amines $(NR_4)^+$, where one or more hydrogen atoms are replaced by organic groups (indicated by R). The terms "quaternary ammonium" or "quaternary ammonium cation" as used herein refer
15 to ammonium group whose hydrogen atoms are all replaced with organic groups i.e. all the four Rs are organic groups.

 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
20 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 C_1 - C_6 alkyl substituents include methyl, ethyl, n-propyl, 2-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, t-butyl, hexyl, amyl, 1,2-dimethylpropyl, 1,1-dimethylpropyl, pentyl, isopentyl, hexyl, 4-methylpentyl, 1-methylpentyl, 2-methylpentyl, 3-methylpentyl, 2,2-
25 dimethylbutyl, 3,3-dimethylbutyl, 1,2-dimethylbutyl, 1,3-dimethylbutyl, 1,2,2-trimethylpropyl, 1,1,2-trimethylpropyl, 2-ethylpentyl, 3-ethylpentyl, heptyl, 1-methylhexyl, 2,2-dimethylpentyl, 3,3-dimethylpentyl, 4,4-dimethylpentyl, 1,2-dimethylpentyl, 1,3-dimethylpentyl, 1,4-dimethylpentyl, 1,2,3-trimethylbutyl, 1,1,2-trimethylbutyl, 1,1,3-trimethylbutyl, 5-methylheptyl, 1-methylheptyl, octyl,
30 nonyl, decyl and the like. The group may be a terminal group or a bridging group.

The term "alkylphenyl" 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 attached to a phenyl group ($-C_6H_5$). Examples of alkylphenyl substituents include, but are not limited to, benzyl, methylphenyl, ethylphenyl, propylphenyl 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, vinyl, allyl, 1-methylvinyl, 1-propenyl, 2-propenyl, 2-methyl-1-propenyl, 2-methyl-1-propenyl, 1-butenyl, 2-butenyl, 3-butenyl, 1,3-butadienyl, 1-pentenyl, 2-pentenyl, 3-pentenyl, 4-pentenyl, 1,3-pentadienyl, 2,4-pentadienyl, 1,4-pentadienyl, 3-methyl-2-butenyl, 1-hexenyl, 2-hexenyl, 3-hexenyl, 1,3-hexadienyl, 1,4-hexadienyl, 2-methylpentenyl, 1-heptenyl, 2-heptenyl, 3-heptenyl, 1-octenyl, 1-nonenyl, 1-decenyl. 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 20, or 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19 or 20 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 $-C_{5-7}$ -cycloalkyl or $-C_{5-7}$ -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 C_6 - C_{18} 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.

5

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. 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.

15

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 may include nitrogen, oxygen and sulfur. 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, phenanthridine, acridine, phenazine, thiazole, isothiazole, phenothiazine, oxazole, isooxazole, furazane, phenoxazine, 2-, 3- or 4-pyridyl, 2-, 3-, 4-, 5-, or 8-quinolyl,

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1-, 3-, 4-, or 5-isoquinoliny 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, sulfur 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 term "micro" as used herein is to be interpreted broadly to include dimensions from about 1 micron to about 1000 microns.

The term "nano" as used herein is to be interpreted broadly to include dimensions less than about 1000 nm, less than about 500 nm, less than about 100 nm or less than about 50 nm.

The term "particle" as used herein broadly refers to a discrete entity or a discrete body. The particle described herein can include an organic, an inorganic or a biological particle. The particle used described herein may also be a macro-particle that is formed by an aggregate of a plurality of sub-particles or a fragment of a small object. The particle of the present disclosure may be spherical, substantially spherical, or non-spherical, such as irregularly shaped particles or ellipsoidally shaped particles. The term "size" when used to refer to the particle broadly refers to the largest dimension of the particle. For example, when the particle is substantially spherical, the term "size" can refer to the diameter of the particle; or when the particle is substantially non-spherical, the term "size" can refer to the largest length of the particle.

The terms "coupled" or "connected" as used in this description are intended to cover both directly connected or connected through one or more intermediate means, unless otherwise stated.

5 The term "associated with", used herein when referring to two elements refers to a broad relationship between the two elements. The relationship includes, but is not limited to a physical, a chemical or a biological relationship. For example, when element A is associated with element B, elements A and B may be directly or indirectly attached to each other or element A may contain
10 element B or vice versa.

 The term "adjacent" used herein when referring to two elements refers to one element being in close proximity to another element and may be but is not limited to the elements contacting each other or may further include the elements
15 being separated by one or more further elements disposed therebetween.

 The term "and/or", e.g., "X and/or Y" is understood to mean either "X and Y" or "X or Y" and should be taken to provide explicit support for both meanings or for either meaning.

20

 Further, in the description herein, the word "substantially" whenever used is understood to include, but not restricted to, "entirely" or "completely" and the like. In addition, terms such as "comprising", "comprise", and the like whenever used, are intended to be non-restricting descriptive language in that they broadly
25 include elements/components recited after such terms, in addition to other components not explicitly recited. For example, when "comprising" is used, reference to a "one" feature is also intended to be a reference to "at least one" of that feature. Terms such as "consisting", "consist", and the like, may in the appropriate context, be considered as a subset of terms such as "comprising",
30 "comprise", and the like. Therefore, in embodiments disclosed herein using the terms such as "comprising", "comprise", and the like, it will be appreciated that these embodiments provide teaching for corresponding embodiments using

terms such as "consisting", "consist", and the like. Further, terms such as "about", "approximately" and the like whenever used, typically means a reasonable variation, for example a variation of +/- 5% of the disclosed value, or a variance of 4% of the disclosed value, or a variance of 3% of the disclosed value, a
5 variance of 2% of the disclosed value or a variance of 1% of the disclosed value.

Furthermore, in the description herein, certain values may be disclosed in a range. The values showing the end points of a range are intended to illustrate a preferred range. Whenever a range has been described, it is intended that the
10 range covers and teaches all possible sub-ranges as well as individual numerical values within that range. That is, the end points of a range should not be interpreted as inflexible limitations. For example, a description of a range of 1% to 5% is intended to have specifically disclosed sub-ranges 1% to 2%, 1% to 3%, 1% to 4%, 2% to 3% etc., as well as individually, values within that range such
15 as 1%, 2%, 3%, 4% and 5%. The intention of the above specific disclosure is applicable to any depth/breadth of a range.

Additionally, when describing some embodiments, the disclosure may have disclosed a method and/or process as a particular sequence of steps.
20 However, unless otherwise required, it will be appreciated that the method or process should not be limited to the particular sequence of steps disclosed. Other sequences of steps may be possible. The particular order of the steps disclosed herein should not be construed as undue limitations. Unless otherwise required, a method and/or process disclosed herein should not be limited to the steps being
25 carried out in the order written. The sequence of steps may be varied and still remain within the scope of the disclosure.

Furthermore, it will be appreciated that while the present disclosure provides embodiments having one or more of the features/characteristics
30 discussed herein, one or more of these features/characteristics may also be disclaimed in other alternative embodiments and the present disclosure provides support for such disclaimers and these associated alternative embodiments.

DESCRIPTION OF EMBODIMENTS

Exemplary, non-limiting embodiments of a modifier for modifying clay material, a modified clay material, a composite and related methods are disclosed hereinafter.

Modifier

There is provided a modifier for modifying clay material, the modifier comprising a functionalized silsesquioxane having one or more epoxide group(s) and one or more organocation group(s). Advantageously, the presence of epoxide groups renders the clay material modified by said modifier to have a high reactivity with an epoxy matrix. For example, clay surface may be functionalized with the epoxide groups when treated with the modifier via a cation exchange process. Without being bound by theory, it is believed that owing to the similarity in chemistry and polarity between epoxy resin and the epoxide groups, the epoxide-functionalized clay has high compatibility with epoxy so that it can be readily dispersed and exfoliated in an epoxy composite. Without being bound by theory, it is also believed that the epoxide group(s) can react with a hardener to form chemical bonds with the epoxy polymer matrix. The energy reduction that has resulted from this chemical reduction is believed to provide a driving force for the entering of the epoxide polymer chain into the interlayer regions of clay, leading to the exfoliation of the clay in the composite. Advantageously, this allows strong filler-matrix interface to be formed in the composite, leading to a composite with very favourable mechanical properties.

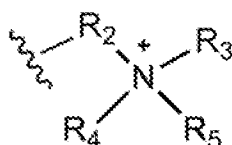
In various embodiments, the functionalized silsesquioxane comprises a polyhedral oligomeric silsesquioxane (POSS) core. Advantageously, incorporation of POSS group into the modifier may provide a clay material modified by the modifier a long interplanar distance (d spacing), thus promoting the intercalation of polymer chains. Even more advantageously, the use of the POSS based modifier enhances the thermal stability of clay modified by said modifier.

In various embodiments, the one or more epoxide group(s) are pendant groups that are disposed at the corners of the silsesquioxane cage. In various embodiments, the one or more organocation group(s) are pendant groups that are disposed at the corners of the silsesquioxane cage.

In various embodiments, the organocation group comprises ammonium group, phosphonium group, sulfonium group and/or pyridinium group.

In various embodiments, the organocation group comprises an ammonium group. In various embodiments, the ammonium group is a quaternary ammonium group or quaternary ammonium cation. Advantageously, the quaternary ammonium ion is a permanently charged cation and thus has a high ion exchange capability with clay. In comparison, primary, secondary or tertiary amines are weak bases so their corresponding ammonium cations are not permanently charged but are pH-dependent. For example, under normal pH conditions, such ammonium cations are only partially dissociated and thus have lower ion exchange capability with clay, as compared to quaternary ammonium cation. In various embodiments, the modifier comprises at least 1, at least 2, at least 3, at least 4, at least 5, at least 6 or at least 7 organocation groups or quaternary ammonium groups or cations.

The quaternary ammonium group may be represented by general Formula (I):



Formula (I)

wherein

R_2 is selected from the group consisting of a single bond, alkyl, alkylphenyl, cycloalkyl, alkenyl, cycloalkenyl, alkynyl, alkoxy, ether (or alkyloxyalkyl),

alkoxylalkyl, alkylcarbonyl, alkoxycarbonyl, alkylphenyloxyalkyl, aryl, aryloxy, arylalkenyl and heteroaryl;

R₃, R₄ and R₅ are each independently selected from the group consisting of hydroxy, hydroxyalkyl, halogen, haloalkyl, cyano, cyanoalkyl, nitro, nitroalkyl,
 5 carboxyl, alkyl, alkylphenyl, cycloalkyl, alkenyl, cycloalkenyl, alkynyl, alkoxy, ether (or alkyloxyalkyl), alkoxyalkyl, alkylcarbonyl, alkoxycarbonyl, alkylphenyloxyalkyl, aryl, aryloxy, arylalkenyl and heteroaryl;

wherein one or more hydrogen atom(s) originally present is/are replaced by hydroxy, hydroxyalkyl, halogen, haloalkyl, cyano, cyanoalkyl and nitro, and

10 wherein one or more carbon atom(s) is/are optionally replaced by heteroatom(s) selected from the group consisting of O, S, S=O and C=O.

In various embodiments, at least one of R₂, R₃, R₄ and R₅ is a hydroxy or hydroxyalkyl.

15

In various embodiments, the quaternary ammonium group comprises a hydroxyl group. Advantageously, the presence of hydroxyl group may (1) increase the binding interaction between modifier and clay and (2) catalyze the reaction between epoxide group(s) of the modified clay material and a hardener.

20 The quaternary ammonium group may comprise 1, 2, 3 or 4 hydroxyl groups.

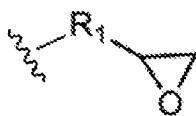
In various embodiments, R₂ is ether (or alkyloxyalkyl). In various embodiments, R₂ is ether (or alkyloxyalkyl) and at least one of the hydrogen atoms originally present in R₂ is replaced by hydroxy. For example, R₂ may be –
 25 (CH₂)_x–O–(CH₂)_yCH(OH)CH₂–. In one embodiment, R₂ is –(CH₂)₃–O–CH₂–CH(OH)CH₂–.

In various embodiments, at least one of R₃ and R₄ is hydroxyalkyl. In various embodiments, R₃ and R₄ are each hydroxyalkyl. For example, R₃ and R₄
 30 may be independently selected from hydroxymethyl, hydroxyethyl, hydroxypropyl, hydroxybutyl, hydroxypentyl or the like. In one embodiment, R₃ and R₄ are each 2-hydroxyethyl or –CH₂CH₂OH.

In various embodiments, R_5 is alkylphenyl. For example, R_5 may be benzylphenyl, ethylphenyl, propylphenyl or the like. In one embodiment, R_5 is benzyl or $-\text{CH}_2\text{C}_6\text{H}_5$.

In various embodiments, the modifier comprises at least 1, at least 2, at least 3, at least 4, at least 5, at least 6, or at least 7 epoxide groups.

The epoxide group may be represented by general Formula (II):



Formula (II)

wherein R_1 is selected from the group consisting of a single bond, alkyl, alkylphenyl, cycloalkyl, alkenyl, cycloalkenyl, alkynyl, alkoxy, ether (or alkyloxyalkyl), alkoxylalkyl, alkylcarbonyl, alkoxycarbonyl, alkylphenyloxyalkyl, aryl, aryloxy, arylalkenyl and heteroaryl;

wherein one or more hydrogen atom(s) originally present is/are replaced by hydroxy, hydroxyalkyl, halogen, haloalkyl, cyano, cyanoalkyl and nitro, and

wherein one or more carbon atom(s) is/are optionally replaced by heteroatom(s) selected from the group consisting of O, S, S=O and C=O.

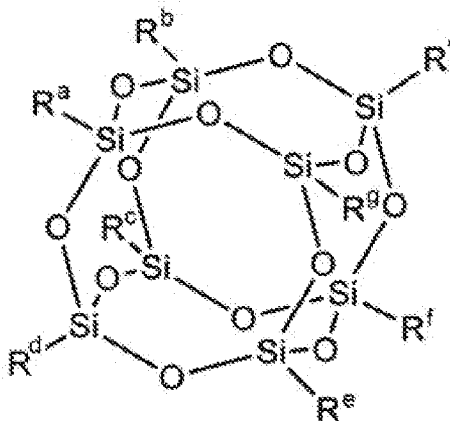
In various embodiments, the epoxide group comprises a glycidyl group.

In various embodiments, R_1 is ether (or alkyloxyalkyl). For example, R_1 may be $-(\text{CH}_2)_x-\text{O}-(\text{CH}_2)_y-$. In one embodiment, R_1 is $-(\text{CH}_2)_3-\text{O}-\text{CH}_2-$. Accordingly, Formula (II) may be $-(\text{CH}_2)_3-\text{O}-\text{CH}_2-\text{C}_2\text{H}_3\text{O}$.

In various embodiments, Formula (II) is glycidoxymethyl, glycidoxyethyl, glycidoxypropyl, glycidoxybutyl, glycidoxypentyl or the like.

In various embodiments, the functionalized silsesquinoxane is selected from the group consisting of $(\text{SiO}_{3/2})_6$, $(\text{SiO}_{3/2})_8$, $(\text{SiO}_{3/2})_{10}$, $(\text{SiO}_{3/2})_{12}$. In various embodiments, the functionalized silsesquinoxane is $(\text{SiO}_{3/2})_8$.

- 5 In various embodiments, the functionalized silsesquinoxane is represented by general Formula (III):



Formula (III)

- 10 wherein R^a , R^b , R^c , R^d , R^e , R^f , R^g and R^h are each independently selected from the group consisting of hydrogen, general Formula (I) and general Formula (II), with at least one of R^a , R^b , R^c , R^d , R^e , R^f , R^g and R^h having general Formula (I) and at least one of R^a , R^b , R^c , R^d , R^e , R^f , R^g and R^h having general Formula (II).
- 15 In various embodiments, the molar ratio of the one or more organocation group(s) to the one or more epoxide group(s) is between about 1:1 to about 1:7. In various embodiments, the molar ratio of the one or more organocation group(s) to the one or more epoxide group(s) is about 1:7, about 1:6, about 1:5, about 1:4, about 1:3, about 1:2, about 1:1.67 or about 1:1. In various embodiments, the
- 20 molar ratio of the one or more organocation group(s) to the one or more epoxide group(s) is about 1:7, 2:6, 3:5 or 4:4.

In one embodiment, R^h is general Formula (I) and R^a , R^b , R^c , R^d , R^e , R^f , R^g are each general Formula (II).

In various embodiments, the modifier is substantially devoid of conjugated amine groups.

Modified Clay Material

5

There is also provided a modified clay material comprising a clay material that is modified by or that is coupled to or that comprises a modifier disclosed herein. Advantageously, embodiments of the modified clay material disclosed herein have a long interplanar distance, high thermal stability and excellent
10 chemical compatibility with epoxy. When incorporated into epoxy (resin), embodiments of the modified clay may be fully exfoliated in the resin due to the formation of strong filler-matrix interfaces via covalent bonding. Embodiments of the modified nanoclay are thus very effective toughening agents for epoxy. For example, some embodiments of the epoxy composite containing the modified
15 clay exhibit 58% increase in K_{ic} (as compared to epoxy composite alone) at a clay loading of 0.8 wt% based on the resin mixture.

In various embodiments, the clay material and/or the clay material disclosed herein comprises a layered clay material. The modified clay material
20 may comprise the modifier disclosed herein intercalated between layers of said layered clay material. Advantageously, due to inorganic/organic hybrid structure of the modifier or functionalized silsesquioxane, the modified layered clay material may have a higher thermal stability than conventional organoclays. Even more advantageously, the thermal stability of the modified clay material allows
25 the modified clay material to be suitable for use at high composite processing temperatures.

In various embodiments, the modified clay material has a thermal degradation temperature above about 100°C, above about 150°C, above about
30 200°C, above about 250°C, above about 260°C, above about 270°C, above about 280°C, above about 290°C, above about 300°C, above about 310°C,

above about 320°C, above about 330°C, above about 340°C, or above about 350°C.

The modified clay material may be coupled to the modifier through at least
5 ionic interactions. For example, the clay material may contain negatively charged structure(s) that bind to one or more cation(s) of the modifier through ionic interactions. Notwithstanding the above, the unmodified clay material may initially also contain cations such as inorganic/metal cations (e.g. Na⁺, Mg²⁺, Al³⁺ or the like). These inorganic cations in the unmodified clay material may be exchanged
10 with organocations of the modifier during modification to eventually obtain a modified clay material modified by the disclosed modifier such that modified clay material may be coupled to the modifier through ionic interactions between negatively charged structure(s) of the clay material and one or more positively charged organocation(s) of the modifier. It will be appreciated that other
15 interactions such as Van der Waals interactions may also be present between the modifier and the clay material.

The clay may be selected from the group consisting of montmorillonites, bentonite, kaolinite, hectorite, halloysite, beidellite, saponite, illites, glauconite,
20 chlorites, vermiculite, fibrous clays and mixtures thereof. In the clay, negatively charged structures may be arranged in layers and are held together by one or more cations such as sodium, potassium, lithium, rubidium, caesium, beryllium, magnesium, calcium, strontium, barium ions. In various embodiments, the clay comprises sodium montmorillonite (Na-MMT).

25

The clay material disclosed herein may comprise a nanoclay. In various embodiments, the nanoclay is layered silicate that is a naturally occurring mineral product with a structure of stacked platelets. The thickness of the individual platelet may be around 1 nm and the lateral dimensions may vary from about 30
30 nm to several microns or larger. Unmodified nanoclay are typically hydrophilic and are generally incompatible with an organic polymer matrix. Advantageously,

nanoclay has several benefits over other materials as fillers in a composite and these benefits includes its high aspect ratio, ease of availability and low cost.

As mentioned above, the modified clay material disclosed herein may be
5 obtained when any or all of the cations in the unmodified clay material are substituted with the modifier or the functionalized silsesquioxane described herein.

Hence, in various embodiments, the modifier or functionalized
10 silsesquioxane may increase the spacing between the layers when being intercalated into the clay (thus forming the modified clay material). The modified layered clay material may have an interspacing distance or d-spacing between the layers of no less than 3.0 nm, no less than 4.0 nm or no less than 5.0 nm. The interspacing distance or d-spacing between the layers may be in the range
15 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
20 nm.

The modified clay material may have a particle size in the range of about 100 nm to about 20,000 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,
25 about 200 nm to about 1000 nm, about 500 nm to about 1000 nm about 500 nm to about 20,000 nm, or about 1000 nm to about 20,000 nm.

In various embodiments, the modified clay material is not or has not been modified by surfactants based modifiers such as octadecyl ammonium
30 (Nanomer® I.30E, Nanocor Inc.), octadecyl trimethyl ammonium (Nanomer® I.28E, Nanocor Inc.), methyl tallow bis-2-hydroxyl quaternary ammonium (Cloisite® 30B, BYK Inc.), cetylpyridinium chloride and stearylbenzyltrimethyl-

ammonium chloride. As compared to surfactants based modified clay, embodiments of the modified clay disclosed herein do not require a high level of modifiers to achieve the desired results. In various embodiments, the amount of modifier used to obtain the modified clay disclosed herein is much lower than the
5 general range of 25-40 wt% surfactant content used to obtain conventional modified nanoclay. In addition, in relation to using surfactants based modifiers to obtain surfactants based modified clay, without being bound by theory, it is believed that while the interplanar distance can be enlarged to promote the intercalation of polymer chains during the preparation of the composite, the
10 inclusion of an organic surfactant normally leads to lower glass transition temperature (T_g) of epoxy and reduce thermal stability. Furthermore, it is believed that due to the lack of strong interaction between the surfactant and epoxy matrix, such surfactant based modified nanoclay usually stays in an intercalated state in the epoxy composites.

15 In various embodiments, the modified clay disclosed herein can be fully exfoliated in epoxy to form strong filler-matrix interface, thereby allowing fabrication of epoxy composites with high toughness and simultaneously high tensile strength and high glass transition temperature. Without being bound by
20 theory, it is believed that full exfoliation of the modified clay material in epoxy resin/matrix is due to the modified clay's long interplanar distance and the strong driving force derived from its high reactivity of its epoxide group with the epoxy resin/matrix.

25 Composite

There is also provided a composite comprising an epoxy matrix; and a filler comprising a modified clay material disclosed herein. Accordingly, in various
30 embodiments, the composite is an epoxy composite. In various embodiments, the filler used is a nanofiller and the modified clay material is a nanoclay. Advantageously, the deterioration in properties through interfacial incompatibility

between the micrometer-scaled filler and the organic matrix could be avoided with the use of nanofillers.

In various embodiments, the composite is a nanocomposite. Advantageously, the nanocomposites are capable of showing an enhanced thermal and mechanical properties at much lower loadings (< 5 wt%) as compared to conventional polymer composites which usually require a high content (> 10 wt%) of inorganic fillers to impart the desired properties.

In various embodiments, the filler or the modified clay material is less than about 3 wt%, no more than about 2.5 wt%, no more than about 2 wt%, no more than about 1.5 wt%, or no more than about 1 wt % of the composite. In various embodiments, the composite has a tensile strength and/or tensile modulus that is higher than the epoxy matrix alone. In various embodiments, the composite has a tensile strength of no less than about 50 MPa, no less than about no less than about 52 MPa, no less than about 54 MPa, no less than about 56 MPa, no less than about 58 MPa, no less than about 60 MPa, no less than about 62 MPa, no less than about 64 MPa, no less than about 66 MPa, no less than about 68 MPa or no less than about 70 MPa. Therefore, in various embodiments, the use of the modified clay material in the composite has a high effectiveness in toughening epoxy due to the low filler loading required.

In various embodiments, the composite has a glass transition temperature (T_g) that is comparable or similar to that of the epoxy matrix alone. For example, the difference in the T_g of the composite and the epoxy matrix alone may be no more than about 5°C , no more than about 4°C , no more than about 3°C , no more than about 2°C , no more than about 1°C or no more than about 0.5°C .

In various embodiments, the composite further comprises a hardener/curing agent. In various embodiments, the hardener/curing agent is an amine hardener/curing agent. The amine hardener may be aliphatic amines, cycloaliphatic amines, amidoamines, polyamide, tertiary amines and aromatic

amines such as diethylenetriamine (DETA), triethylenetetraamine (TETA), tetraethylenepentamine (TEPA) and aminoethylpiperazine (AEP), bis(4-aminocyclohexyl)-methane, aminoethylpiperazine (AEP), isophorone diamine (IPDA), 1,2- diaminocyclohexane (DACH), 4,4'-diaminodiphenylmethane (MDA),
5 4,4'- diaminodiphenylsulfone (DDS), m-phenylenediamine (MPD), diethyltoluenediamine (DETDA), meta-xylene diamine (MXDA) and 1,3-bis(aminomethyl)cyclohexane (1,3-BAC).

Advantageously, in various embodiments, the disclosed epoxy composites
10 exhibit high tensile strength and high T_g. Accordingly, embodiments of the disclosed epoxy composite may be useful as resins for fibre reinforced composites for load bearing applications, flame retardant epoxy composites for aerospace, construction, electronics, etc, and/or low coefficient of thermal expansion (CTE) epoxy composites for electronic packaging.

Methods

There is also provided a method of making/preparing a modifier disclosed herein, the method comprising a) reacting a silsesquioxane having one or more
20 epoxide group(s) with an organocation precursor having an organic functional group to obtain a silsesquioxane having one or more epoxide group(s) and one or more of the organic functional group(s); and b) converting one or more of the organic functional group(s) obtained in a) to the corresponding organocation group(s) to obtain a functionalized silsesquioxane having one or more epoxide
25 group(s) and one or more organocation group(s). In various embodiments, the organocation precursor is a precursor for forming the organocation disclosed herein but may not be a cation on its own. In various embodiments, the organic functional group comprises an amine functional group. The functionalized silsesquioxane, epoxide group(s) and/or quaternary ammonium group(s) may
30 have one or more of the properties/characteristics described herein.

In various embodiments, the organocation precursor in a) comprises a secondary (2°) amine precursor. The secondary amine precursor may be dialkanolamines such as diethanolamine, dipropanolamine, methylethanolamine, ethylethanolamine or the like. Advantageously, the use of secondary amine as an organocation precursor for the attachment of ammonium ion to the modifier avoids the possibility of an undesirable crosslinking which would otherwise occur if a primary amine is used (due to formation of two bonds between the primary amine and epoxy). In various embodiments therefore, the organocation precursor in a) is substantially devoid of a primary amine. In various embodiments, the silsesquioxane obtained in a) has one or more epoxide group(s) and one or more tertiary (3°) amine group(s).

In various embodiments, step b) comprises converting one or more tertiary amine group(s) obtained in a) to the corresponding quaternary ammonium cation(s) to obtain a functionalized silsesquioxane having one or more epoxide group(s) and one or more quaternary ammonium group(s). Step b) may be undertaken in the presence of or an alkylating agent/quaternizing agent. In various embodiments, the alkylating agent/quaternizing agent comprises alkyl halides, alkylphenyl halides, alkyl sulfates, alkylphenyl sulfates, trialkylphosphates, haloesters, sulfonic esters, mixtures thereof. The alkylating agent/quaternizing agent may be methyl chloride, butyl bromide, ethyl bromide, ethyl iodide, benzyl chloride, benzyl bromide, benzyl iodide, dodecylbenzyl chloride, stearyl chloride, oleyl chloride, dimethyl sulfate, diethyl sulfate, triethyl phosphate, methyl chloroacetate, methyl-p-toluenesulfonate, ethylene chlorhydrin, epichlorohydrin or the like.

In various embodiments, step a) and/or step b) is/are carried out in the presence of an organic solvent. The organic solvent may be an aprotic solvent. In various embodiments, the organic solvent(s) for step a) and step b) is independently selected from the group consisting of tetrahydrofuran (THF), dichloromethane (DCM), acetonitrile (ACN), dimethyl sulfoxide (DMSO), γ -valerolactone (GVL), propylene carbonate (PC), dimethylcarbonate (DMC),

dioxane, dioxolane, diglyme, acetone, methyl ethyl ketone (MEK) and the like and combinations thereof. 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.

5 In various embodiments, step a) and/or step b) is/are carried out or undertaken at a temperature in the range of about 20°C to about 80 °C. The temperature(s) at which step a) and step b) is carried out may be independently selected from a temperature of 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.

10

 In various embodiments, the step a) of reacting a silsesquioxane having one or more epoxide group(s) with an organocation precursor having an organic functional group comprises stirring or mixing the silsesquioxane having one or more epoxide group(s) and the organocation precursor having an organic functional group. The step b) of converting one or more of the organic functional group(s) obtained in a) to the corresponding organocation group(s) to obtain a functionalized silsesquioxane having one or more epoxide group(s) and one or more organocation group(s) may also comprise a step of stirring or mixing the reactants.

20

 The step of stirring or mixing may be undertaken for a time period in the range of 1 hour to 20 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, about 12 hours, about 13 hours, about 14 hours, about 15 hours, about 16 hours, about 17 hours, about 18 hours, about 19 hours or about 20 hours.

25

 There is also provided a method of preparing a modified clay material disclosed herein. In various embodiments, the method comprises mixing clay material disclosed herein with the modifier disclosed herein. The method may comprise intercalating the modifier into the clay material. The step of intercalating the modifier into the clay material may comprise exchanging a cation in the clay

30

material with an organocation of the modifier. The modifier may be added to the clay material in a dropwise manner during mixing. The dropwise addition of the modifier to the clay material may allow expansion (e.g. higher d-spacing between layers) and chemically modification of the clay material. The mixing of the modifier with the clay material may allow for ion exchange between the cation(s) inherently present in the unmodified clay material and the organocation group(s) of the modifier. The mixing may be carried out for a time period in the range of 1 hour to 10 hours, or about 1 hour, about 2 hours, about 3 hours, about 4 hours, about 5.5 hours, about 5 hours, about 6 hours, about 6.5 hours, about 7 hours, about 8 hours, about 9 hours or about 10 hours to allow the ion exchange to be substantially completed. The mixing may also be carried out while the mixture is being stirred for example at a speed in the range of from about 300 rpm to about 800 rpm, about 400 rpm, about 500 rpm, about 550 rpm, about 600 rpm, about 650 rpm, about 700 rpm, or about 800 rpm.

The method of preparing a modified clay material may further comprise centrifuging the mixture to remove excess modifier. The centrifuging step may be carried out at a centrifugation speed in the range of from about 3000 rpm to about 8000 rpm, about 4000 rpm, about 5000 rpm, about 5500 rpm, about 6000 rpm, about 6500 rpm, about 7000 rpm, or about 8000 rpm. The centrifuging step may be carried out for a time duration of about 5 minutes, about 10 minutes, about 15 minutes or about 20 minutes.

In various embodiments, the method of preparing a modified clay material further comprise washing the modified clay material at least once, at least twice, at least thrice or at least four times with an organic solvent to purify the product. The organic solvent may be an aprotic solvent. In various embodiments, the organic solvent is selected from the group consisting of tetrahydrofuran (THF), dichloromethane (DCM), acetonitrile (ACN), dimethyl sulfoxide (DMSO), γ -valerolactone (GVL), propylene carbonate (PC), dimethylcarbonate (DMC), dioxane, dioxolane, diglyme, acetone, methyl ethyl ketone (MEK) and the like and combinations thereof. It is to be appreciated that the type of solvent used is

not limited to the above so long as it does not react with or is substantially non-reactive to the modified clay material and yet effectively removes excess modifiers.

5 The method of preparing a modified clay material may further comprise drying the modified clay material, for example under vacuum. In various embodiments, the method may further comprise pulverizing or grinding the dried modified clay material into fine powders for future use or storage.

10 In various embodiments, the method of preparing a modified clay material disclosed herein is different from conventional silanization methods. Modified nanoclay obtained using conventional silanization techniques tends to form aggregates due to the crosslinking nature of silane molecules. Furthermore, it is believed that the interplanar distance of such modified nanoclay is short due to
15 the small molecular size of the silane modifier, which is thus unfavorable for the exfoliation of nanoclay. Accordingly, in various embodiments, the method is devoid of a step of reacting the clay material with amine- or epoxide-functionalized silane. In various embodiments, the method is also devoid of a solvent exchange process, for example where an aqueous solvent (e.g. water) is
20 exchanged with an organic solvent (e.g. acetone). Advantageously, this means that embodiments of the methods disclosed herein are easily industrially scalable.

 There is also provided a method of preparing a composite such as an
25 epoxy composite disclosed herein. The method may comprise mixing an epoxy resin or matrix disclosed herein with a filler comprising a modified clay material disclosed herein. The mixing step may be carried out in the presence of a hardener. Thus, in various embodiments, the mixing step comprises mixing an epoxy resin/matrix, modified clay material and a hardener/curing agent together.
30 The filler may be added in an amount that is no more than 3 wt% of the final composite product. The epoxy resin and hardener may be mixed in a weight ratio in a range of from 5:1 to 2:1. Advantageously, the mixing of the expanded and

modified clay materials, epoxy and hardener/curing agent may serve to exfoliate clay materials to form the composite. The exfoliation of clay materials such as nanoclay in polymer composites into single platelets is desired to fully exert its excellent mechanical and thermal properties.

5

The mixing step may also be carried out in the presence of an organic solvent is selected from the group consisting of tetrahydrofuran (THF), dichloromethane (DCM), acetonitrile (ACN), dimethyl sulfoxide (DMSO), γ -valerolactone (GVL), propylene carbonate (PC), dimethylcarbonate (DMC),
10 dioxane, dioxolane, diglyme, acetone, methyl ethyl ketone (MEK) and the like and combinations thereof. The weight ratio of the epoxy resin/matrix to hardener may be in the range of from about 5:1 to about 2:1, or from about 4.5:1 to about 3.5:1, or from about 4:1 to about 3:1. The mixing step may be comprise a step of stirring or agitation of the mixture such as using magnetic stirring or sonication
15 so as to obtain a substantially homogenous suspension.

There is also provided a compound comprising a functionalized silsesquioxane having one or more epoxide group(s) and one or more organocation group(s). The compound may be a compound that is adapted to
20 used as a precursor, an intermediate or an actual reactant to eventually produce an epoxy composite (having an epoxy matrix and a filler) that has a tensile strength and/or tensile modulus that is higher than the epoxy matrix alone. In various embodiments, the compound is at least one of a clay modifier or a modified clay. Accordingly, in various embodiments, the modifier or modified clay
25 is suitable for use with epoxy to improve composites toughness and strength. The silsesquioxane, epoxide group(s) and/or organocation group(s) of the compound may have one or more of the properties/characteristics described herein. Similarly, the method of preparing the compound may comprise one or more steps described herein.

30

BRIEF DESCRIPTION OF FIGURES

FIG. 1 is a schematic diagram 100 for illustrating a cation exchange mechanism involved in a method of preparing a modified clay material in accordance with various embodiments disclosed herein.

FIG. 2 is a graph showing the fourier-transform infrared (FTIR) spectra of a modified nanoclay in an exemplary embodiment shown in Example 4 ("POSS-MMT") and a pristine nanoclay ("MMT").

FIG. 3 is a graph showing the thermal gravimetric profiles of a modified nanoclay in an exemplary embodiment shown in Example 4 ("POSS-MMT"), a commercial nanoclay modified by octadecyl ammonium ("I.30E") and a pristine nanoclay ("MMT"). The thermal gravimetric analysis (TGA) was performed in N₂ atmosphere and the temperature ramp rate was 20°C/min.

FIG. 4 is a graph showing the X-ray diffraction (XRD) patterns of a modified nanoclay in an exemplary embodiment shown in Example 4 ("POSS-MMT"), a commercial nanoclay modified by octadecyl ammonium ("I.30E") and a pristine nanoclay ("MMT").

FIGS. 5A-5B are transmission electron micrography (TEM) images of nanoclay/epoxy composites, with the scale bar representing 50 nm. FIG. 5A is the TEM image obtained for Comparative Example 2 (i.e. a nanoclay/epoxy composite fabricated with epoxy and a commercial nanoclay "I.30E"; loading ratio is 0.8 wt% of "I.30E" to resin mixture). FIG. 5B is the TEM image obtained for Composite 2 (i.e. a nanoclay/epoxy composite fabricated with epoxy and a modified nanoclay in an exemplary embodiment shown in Example 6 "POSS-modified MMT"; loading ratio is 0.8 wt% of "POSS-modified MMT" to resin mixture).

FIG. 6A is a graph showing changes in the Young's modulus (GPa) of nanoclay/epoxy composites with varying filler loading (wt%). FIG. 6B is a graph showing changes in the tensile strength (MPa) of nanoclay/epoxy composites with varying filler loading (wt%). The nanoclay/epoxy composites tested are Composites 1 to 3 (■) and Comparative Examples 1 to 4 (●).

FIG. 7 is a graph showing the tangent of the phase angle of nanoclay/epoxy composites as a function of temperature. The nanoclay/epoxy composites tested are Composites 1 to 3 (■) and Comparative Examples 1 to 4 (●). Comparative Example 1 is an epoxy matrix without any filler (i.e. "0% POSS-MMT").

FIG. 8 is a graph showing changes in the fracture toughness measured in terms of critical stress intensity factor (K_{Ic}) with varying filler loading (wt%). The nanoclay/epoxy composites tested are Composites 1 to 3 (■) and Comparative Examples 1 to 4 (●). Comparative Example 1 is an epoxy matrix without any filler (i.e. "0% POSS-MMT").

FIGS. 9A-9B are scanning electron microscopy (SEM) images of the fracture surface of nanoclay/epoxy composites, with the scale bar representing 10 μm . FIG. 9A is the SEM image obtained for Comparative Example 2 (i.e. a nanoclay/epoxy composite fabricated with epoxy and a commercial nanoclay "I.30E"; loading ratio is 0.8 wt% of "I.30E" to resin mixture). FIG. 9B is the SEM image obtained for Composite 2 (i.e. a nanoclay/epoxy composite fabricated with epoxy and a modified nanoclay in an exemplary embodiment shown in Example 4 "POSS-modified MMT"; loading ratio is 0.8 wt% of "POSS-modified MMT" to resin mixture).

EXAMPLES

Example embodiments of the disclosure will be better understood and readily apparent to one of ordinary skill in the art from the following examples,

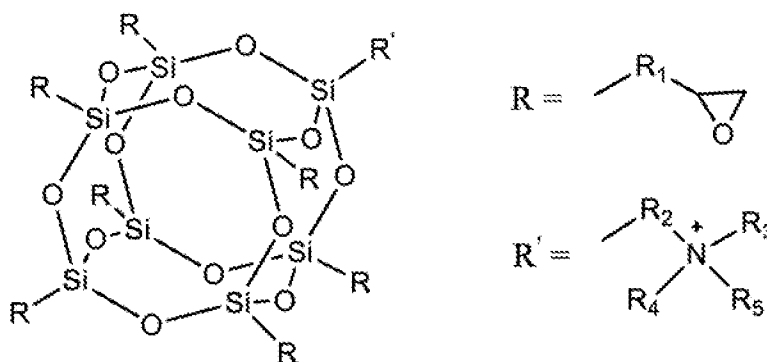
tables and if applicable, in conjunction with the figures. It should be appreciated that other modifications related to structural, and chemical changes may be made without deviating from the scope of the invention. Example embodiments are not necessarily mutually exclusive as some may be combined with one or more
 5 embodiments to form new example embodiments. The example embodiments should not be construed as limiting the scope of the disclosure.

Example 1: Design of Nanoclay Modifier

10 A chemical structure of an example of a nanoclay modifier designed in accordance with various embodiments disclosed herein is shown in Scheme 1. The modifier comprises a silsesquioxane core ($\text{SiO}_{3/2}$) and corners made up of epoxide groups and cations. The silsesquioxane core is based on a polyhedral oligomeric silsesquioxane (POSS) with a nanocage structure in the size of 1-3
 15 nm. The cations and epoxide groups co-exist at the corners of the cage. The molar ratio between cation and epoxide may vary from 1/7 to 1/1.

The silsesquioxane may be an octahedral oligomeric silsesquioxane with R groups containing epoxide and R' group containing cation, as shown in Scheme

20 1. The cation at R' may be a quaternary ammonium cation ($-\text{N}^+$).



Scheme 1. Chemical structure of an exemplary nanoclay modifier

The chemical structure of the nanoclay modifier comprises a POSS core. The function of the POSS core is to enlarge/lengthen the interplanar distance of a nanoclay and thereby promoting the intercalation of the POSS polymer chains into the nanoclay. Meanwhile, the cation group is designed to anchor the modifier
5 onto the nanoclay surface *via* an ion exchange process. Furthermore, the co-existing epoxide group is employed to enhance the compatibility and form covalent bonds between the modified nanoclay and an epoxy matrix.

Advantageously, the POSS-based modifier possesses unique features
10 which include: (1) high thermal stability offered by the inorganic/organic hybrid nature of POSS; and (2) high rigidity so that it has no plasticization effect in polymer composites, which is unlike most conventional surfactant-based modifiers.

15 **Example 2: Preparation of Nanoclay Modifier**

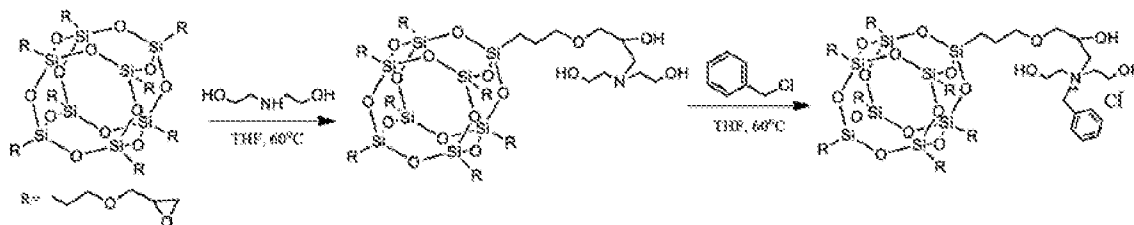
The synthetic route for preparing a nanoclay modifier in accordance with various embodiments disclosed herein is based on the chemical reactions illustrated in Scheme 2.

In this example, the steps involved in the synthesis of a POSS-based nanoclay modifier containing quaternary ammonium cation and glycidyl groups, i.e. a quaternary ammonium cation/glycidyl functionalized POSS-based nanoclay
20 modifier are described as follows.

The silsesquioxane used as a starting material is an octahedral oligometric silsesquioxane with R = glycidyl, i.e. glycidyl-functionalized POSS.

Firstly, 20.0 g glycidyl-functionalized POSS (15.0 mmol, Hybrid Plastics)
30 and 1.58 g diethanolamine (15.0 mmol, Sigma) were mixed with 100 mL tetrahydrofuran (THF), forming a mixture. The mixture was stirred magnetically at 60°C for 12 hours to allow the reaction between glycidyl and amine groups to

be completed. Subsequently, 2.09 g benzyl chloride (16.5 mmol, Sigma) was added to the mixture. The quaternization reaction was kept at 60°C for 12 hours to yield the POSS-based modifier containing quaternary ammonium cation.



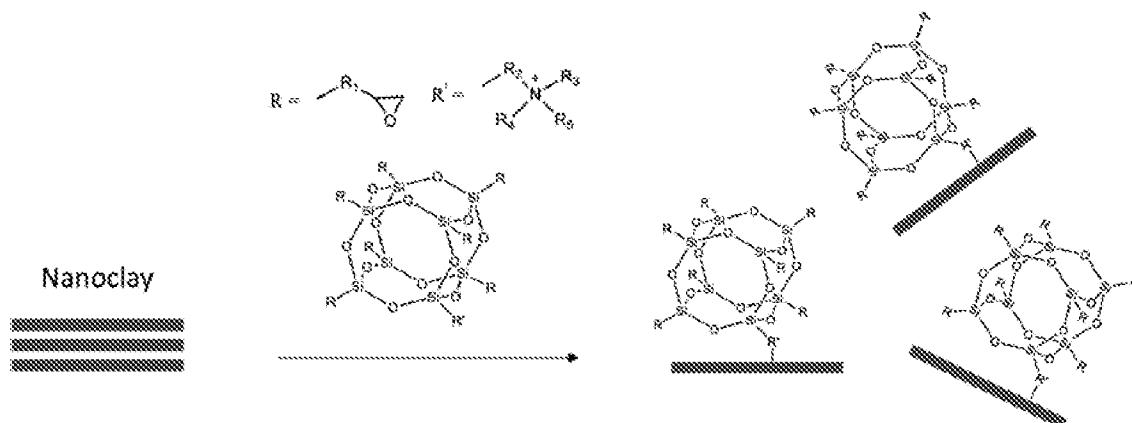
Scheme 2. Chemical reactions involved in the synthesis of an exemplary nanoclay modifier

Example 3: Modified Nanoclay (Nanoclay Modified with Nanoclay Modifier)

The nanoclay modifier prepared according to embodiments of the method disclosed herein can be used to modify nanoclay.

Scheme 3 is a schematic diagram illustrating the modification of a nanoclay with a nanoclay modifier to obtain a modified nanoclay. Nanoclay exists as stacked layers held together by van der Waals interactions. As shown in the scheme, upon introduction of a POSS-based nanoclay modifier to the nanoclay, the nanoclay modifier enters and intercalates into the nanoclay. With the intercalation of the POSS molecules into the nanoclay, the van der Waals interaction between the platelets of nanoclay is greatly weakened, leading to an expansion and/or eventual separation of the stacked layers, which is schematically illustrated in Scheme 3.

An example of the chemical structure of a modified nanoclay prepared in accordance with various embodiments disclosed herein is also shown in Scheme 3. Such a modified nanoclay exists in the form of separated layers containing epoxide groups, thus making said modified nanoclay a highly compatible and reactive 2-dimensional nanofiller for epoxy.



Scheme 3. Modification of nanoclay with an exemplary nanoclay modifier to obtain a modified nanoclay

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Without being bound by theory, it is believed that the nanoclay undergoes modification with the nanoclay modifier *via* an ion exchange process, in particular, in a cation exchange mechanism, as shown in FIG. 1.

10

In FIG. 1, nanoclay which is shown in the figure as a single clay layer/sheet 102 comprises a plurality of negative surface charges 104a, 104b and 104c. These negative surface charges are balanced by a plurality of positive charges (for e.g. inorganic cations such as Na^+) 106a, 106b and 106c that exist naturally between each layer/sheet of the nanoclay 102, i.e. in the interspacing layers of the nanoclay structure.

15

When an nanoclay modifier molecule carrying a net positive charge (i.e. organocation) 108a is added to and comes into contact with nanoclay 102, a cation exchange process occurs between nanoclay modifier 108a and nanoclay 102, whereby the positive charges (for e.g. inorganic cations such as Na^+) 106a, 106b and 106c are replaced/displaced synthetically with/by positively charged nanoclay modifier molecules 108b, 108c and 108d respectively to obtain a modified nanoclay. The resulting modified nanoclay shows the plurality of negative surface charges 104a, 104b and 104c on nanoclay 102 balanced by a

20

plurality of positive charges carried by the nanoclay modifier molecules 108b, 108c and 108d.

As shown, the resulting modified nanoclay comprises ionic interactions
5 110a, 110b and 110c coupling the nanoclay 102 and nanoclay modifier 108.

Example 4: Preparation of Modified Nanoclay

This example describes the steps involved in the modification of a
10 nanoclay with a POSS-based nanoclay modifier containing quaternary ammonium cation and glycidyl groups prepared in accordance with Example 2.

In this example, the nanoclay used is sodium montmorillonite (Na-MMT).

15 Firstly, sodium montmorillonite (Na-MMT, Nanocor) was dispersed in deionized water to obtain a 2 wt% suspension. Next, 250 mL THF solution containing 10 g of the POSS-based modifier from Example 2 was added dropwise to 500 mL of the clay (MMT) suspension. The resulting mixture was kept stirring at a rotation speed of 500 rpm for 6 hours to allow the ion exchange between Na⁺
20 and the POSS-based modifier to be completed. Subsequently, the mixture was centrifuged at 6000 rpm for 10 min to remove the excessive POSS-based modifier, followed by washing with THF. The process of washing with THF followed by centrifugation was repeated for 3 times to purify the product. Finally, the modified MMT was either dried under vacuum and grounded to fine powders
25 for material characterizations, or re-dispersed in THF at 2 wt% for the fabrication of epoxy nanocomposites.

Example 5: Characterization Studies of Modified Nanoclay

30 The following experimental results demonstrate that the method of preparing the modified nanoclay as disclosed herein is effective and the nanoclay modifier was successfully intercalated into the nanoclay. As will be shown in the

following figures, the results indicated that the modified nanoclay possesses enhanced thermal stability. The results also indicated that the modified nanoclay possesses enhanced intercalation of polymer chains attributed to the presence of the POSS group which increased the interplanar distance in the nanoclay.

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The properties of the modified nanoclay prepared in accordance with Example 4 (i.e. quaternary ammonium cation/glycidyl functionalized POSS-modified nanoclay, herein referred to as "POSS-modified MMT" or "POSS-MMT") were analysed and compared with those of a pristine nanoclay (i.e. pristine MMT, or herein referred to as "MMT"), and also those of a commercial nanoclay product (i.e. commercial name Nanomer® I.30E, or herein referred to as "I.30E"). The commercial nanoclay product used for comparison purposes was modified by octadecyl ammonium and obtained from Nanocor Inc.

15 Fourier-Transform Infrared (FTIR) Spectroscopy of Modified Nanoclay

The POSS-modified MMT prepared in accordance with Example 4 was grounded to powder form and characterized by fourier-transform infrared (FTIR) spectroscopy. The FTIR spectrum obtained was compared with that of a pristine MMT, as shown in FIG. 2.

20

A comparison between the FTIR spectra of modified MMT ("POSS-MMT") and pristine MMT ("MMT") reveals that three new peaks were observed upon MMT modification. The peaks at 2936 cm^{-1} and 2880 cm^{-1} are attributed to the stretching of C–H bonds while the peak at 697 cm^{-1} corresponds to the bend of the benzyl ring existing on the POSS modifier. Accordingly, the results clearly indicated that the POSS-based nanoclay modifier was successfully attached onto MMT.

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Thermogravimetric Analysis (TGA) of Modified Nanoclay

Thermogravimetric analysis (TGA) was performed to evaluate the thermal stability as well as measure the content of the POSS-based nanoclay modifier in the nanoclay.

The TGA curves obtained for pristine MMT ("MMT"), POSS-modified MMT ("POSS-MMT") and I.30E modified by octadecyl ammonium ("I.30E") are shown respectively in FIG. 3.

A comparison between the TGA curves in FIG. 3 reveals that the POSS-modified MMT has a higher thermal stability than I.30E that was modified by octadecyl ammonium.

Data on thermal degradation temperatures (i.e. the critical temperature T_d at which a material experienced a 2% weight loss) and the content of the modifier present in the modified nanoclays are also derived from the TGA curves and provided in Table 1.

It is further shown that in comparison to the commercial nanoclay modified by octadecyl ammonium ("I.30E"), the POSS-modified MMT not only requires a lesser amount of modifier, it also have a higher thermal degradation temperature, therefore showing its immense potential for use in applications that require high processing temperatures.

Table 1. Thermal degradation temperature and content of modifier in nanoclay

Modified MMT	T _d * (°C)	Content of modifier (wt %)
POSS-modified MMT	306	24.3
I.30E	255	28.7

*denoted as the critical temperature at which 2 wt% weight loss was experienced.

X-Ray Diffraction (XRD) Analysis

The structure of the modified nanoclays was characterized using X-ray diffraction (XRD). The XRD patterns obtained for pristine MMT ("MMT"), POSS-
5 modified MMT ("POSS-MMT") and I.30E modified by octadecyl ammonium ("I.30E") are shown respectively in FIG. 4.

As shown in FIG. 4, the XRD pattern of pristine MMT observed a sharp peak at $2\theta = 7.1^\circ$, which corresponds to an interplanar distance, $d = 1.2$ nm. As
10 for the XRD pattern of I.30E, it is shown that the treatment of MMT with octadecyl ammonium elongated the distance to 2.7 nm as indicated by the emerging peak at $2\theta = 3.2^\circ$.

Meanwhile, the XRD pattern of POSS-modified MMT observed a broad
15 and weak peak around 6.5° . This peak corresponding to $d = 1.4$ nm is attributed to the ordered POSS molecules being absorbed on the 2-dimensional nanoclay platelets. In addition, no peaks for the layered structure of nanoclay was observed in the 2θ range between 3° to 7° , therefore suggesting that POSS-modified MMT is amorphous or has a high d spacing of above 3.0 nm.

Example 6: Preparation of Nanoclay/Epoxy Composite

This example describes the steps involved in the fabrication of a composite from a modified nanoclay (i.e. quaternary ammonium cation/glycidyl
25 functionalized POSS-modified nanoclay, herein referred to as "POSS-modified MMT" or "POSS-MMT") prepared in accordance with Example 4 and an epoxy matrix.

A slurry compounding method was used to fabricate the nanoclay/epoxy
30 composite.

POSS-modified MMT from Example 4 was mixed with diglycidyl ether of bisphenol A epoxy (D.E.R. 332, Dow Chemicals), diethyltoluenediamine hardener (Ethacure 100-LC, Albemarle) and THF *via* magnetic stirring and sonication to obtain a homogeneous suspension. The weight ratio between epoxy and hardener used was fixed at 3.8:1. Three different composites were fabricated by varying the loading ratio of POSS-modified MMT to the whole/entire resin mixture at 0.4 wt% (herein termed "Composite 1"), 0.8 wt% (herein termed "Composite 2") and 1.2 wt% (herein termed "Composite 3") respectively. The loading ratio was capped at 1.2 wt% due to the fact that a high loading of POSS-modified MMT may lead to a significant increase in the mixture's viscosity. After complete solvent removal and degassing under vacuum at 90°C for 1 hour, the mixture was poured into a glass mold coated with releasing agent. Finally, the mixture was cured at 100°C for 2 h and post-cured at 200°C for 5 h.

For comparative purposes, the reaction was repeated by replacing the POSS-modified MMT with a commercial nanoclay product (i.e. commercial name Nanomer® I.30E, or herein referred to as "I.30E"). The commercial nanoclay product used for comparison purposes was modified by octadecyl ammonium and obtained from Nanocor Inc. Three different composites were fabricated by varying the loading ratio of I.30E to the whole/entire resin mixture at 0.8 wt% (herein termed "Comparative Example 2"), 1.5 wt% (herein termed "Comparative Example 3") and 3.0 wt% (herein termed "Comparative Example 4") respectively. Comparative Example 1 is an epoxy matrix without any filler, i.e. 0% nanoclay.

Example 7: Characterization Studies of Nanoclay/Epoxy Composite

The following experimental results demonstrate that composites fabricated from epoxy matrix and modified nanoclay in accordance with various embodiments disclosed herein are mechanically and thermally strong and stable, therefore making them attractive for use in a wide variety of applications such as aerospace, construction and electronics industry.

Dispersibility of Nanoclay in Epoxy

Transmission electron microscopy (TEM) was performed to study the dispersibility of nanoclay in epoxy.

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FIG. 5A shows the TEM image obtained for Comparative Example 2 (i.e. nanoclay/epoxy composite fabricated with the incorporation of I.30E). FIG. 5B shows the TEM image obtained for Composite 2 (i.e. nanoclay/epoxy composite fabricated with the incorporation of POSS-modified MMT). The loading ratio of nanoclay for both composites are 0.8 wt% of the resin mixture.

10

As shown in FIG. 5A, I.30E in epoxy stayed in the form of aggregates comprising tens of layered flakes, manifesting the poor dispersibility of such a composite. In contrast, as shown in FIG. 5B, the POSS-modified MMT was exfoliated into single or very few layers and dispersed uniformly in the matrix. This result confirms that the POSS-modified MMT exhibited excellent dispersibility in epoxy.

15

Young's Modulus and Tensile Strength

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The Young's modulus and tensile strength of the epoxy nanocomposites were determined using an Instron 5569 Table Tester at a speed of 1 mm/min in accordance with ASTM D638.

25

FIG. 6A shows the Young's modulus data (in GPa) obtained for Composites 1 to 3 and Comparative Examples 1 to 4 fabricated with varied loadings of clay. FIG. 6B shows the tensile strength data (MPa) obtained for Composites 1 to 3 and Comparative Examples 1 to 4 fabricated with varied loadings of clay.

30

Although incorporation of POSS-modified MMT or I.30E could enhance the stiffness of epoxy, it is clearly shown in FIGS. 6A and 6B that the use of

POSS-modified MMT have higher effectiveness in stiffening epoxy as compared to the use of I.30E.

In terms of mechanical strength of the nanocomposites (FIG. 6B), increasing the content of I.30E resulted in a substantial decrease in the tensile strength of the epoxy. In contrast, the filling of POSS-modified MMT resulted in an increase in the tensile strength of epoxy, although increase is slight.

Glass Transition Temperature (T_g)

The glass transition temperature (T_g) of the nanocomposites was measured with a dynamic mechanical analyzer (DMA Q800, TA Instruments) by using the single cantilever mode. The dimension of the specimen was 40 mm (length) $\times$ 13 mm (width) $\times$ 3 mm (thickness). Scans were conducted in a temperature range of 30°C to 250°C at a heating rate of 3°C/min and a frequency of 1 Hz.

FIG. 7 shows the $\tan \delta$ of nanoclay/epoxy Composites 1 to 3 and Comparative Examples 1 to 4 obtained at varied temperatures.

As shown, there is a substantial decrease in the glass transition temperature (T_g) of epoxy derived from the peak position of the curves when I.30E was used in the composite. In contrast, the incorporation of POSS-modified MMT did not affect the T_g of epoxy.

Critical Stress Intensity Factor (K_{Ic})

The critical stress intensity factor (K_{Ic}) was measured according to ASTM D5045 using single-edge-notch 3-point-bend (SEN-3PB) testing with a span of 24 mm and the specimen dimensions are 30 mm (length) $\times$ 6 mm (width) $\times$ 3 mm (thickness). A sharp notch was introduced by pressing a fresh razor blade at the

bottom of a saw-slot in the middle of the test bar. The measurements were conducted on an Instron 5569 Table Tester at a compression speed of 1 mm/min.

FIG. 8 shows the fracture toughness measured in terms of critical stress intensity factor (K_{IC}) of nanoclay/epoxy Composites 1 to 3 and Comparative Examples 1 to 4 that were fabricated with varied filler contents.

The POSS-modified MMT is a very effective toughening agent for epoxy as the K_{IC} of epoxy experienced a 58% increase at only 0.8 wt% loading of nanoclay (see Composite 2). In comparison, the use of I.30E was much less effective as the toughness enhancement was observed only when the clay loading exceeded 1.5 wt% and K_{IC} increment was only 21% even at 3.0 wt% loading (see Comparative Example 4).

Morphology of Fracture Surface of Nanoclay/Epoxy Composite

The morphology of the fracture surface of specimen was observed by scanning electron microscopy (SEM) to expose the toughening mechanism.

FIG. 9A shows the SEM image of representative fracture surfaces of Comparative Example 2 (i.e. nanoclay/epoxy composite fabricated with the incorporation of I.30E). FIG. 9B shows the SEM image of representative fracture surfaces of Composite 2 (i.e. nanoclay/epoxy composite fabricated with the incorporation of POSS-modified MMT). The loading ratio of nanoclay for both composites are 0.8 wt% of the resin mixture.

The SEM image in FIG. 9A shows formation of microcracks, which indicated that the composite has a much weaker toughening effect. This is expected since I.30E existed as aggregates in the compositions (as shown in FIG. 5A). In contrast, the SEM image in FIG. 9B shows that the formed microcracks are much lesser due to the presence of the POSS-modified nanoclay

inhibiting the crack propagation, which is therefore indicative of a significant enhancement of the toughness of epoxy.

Table 2 provides a summary of the mechanical and thermal properties of the epoxy composites filled with POSS-modified MMT (i.e. Composites 1, 2 and 3) in comparison with those filled with I.30E (i.e. Comparative Examples 2, 3 and 4), and that of epoxy without any filler (i.e. Comparative Example 1).

It is clearly shown that with the incorporation of modified nanoclay using the modifier in accordance with various embodiments disclosed herein, epoxy nanocomposites with greatly enhanced toughness can be fabricated at a low filler content of less than 1 wt%. Owing to the fully exfoliation of nanoclay and the formation of covalent bonding between the nanoclay and epoxy matrix, the developed nanoclay/epoxy composites exhibit high toughness, high strength and also high T_g , which have great applications in many industries such as aerospace, construction and electronics.

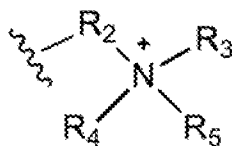
Table 2. Material properties of the nanoclay/epoxy composites

Composite formulation	Composite 1	Composite 2	Composite 3	Comparative Example 1	Comparative Example 2	Comparative Example 3	Comparative Example 4
Type of modified nanoclay	POSS-modified MMT	POSS-modified MMT	POSS-modified MMT	n.a.	I.30E	I.30E	I.30E
Content of nanoclay (wt%)	0.4	0.8	1.2	0	0.8	1.5	3.0
Properties							
Tensile modulus (GPa)	2.0 ± 0.2	2.1 ± 0.3	2.2 ± 0.2	1.9 ± 0.1	2.0 ± 0.2	2.2 ± 0.2	2.3 ± 0.3
Tensile strength (MPa)	62.4 ± 6.2	62.8 ± 5.5	61.9 ± 4.3	61.3 ± 3.2	54.6 ± 3.3	51.5 ± 4.8	48.3 ± 4.2
T_g (°C)	214	213	212	214	210	205	191
K_{IC} (MPa/m ^{1/2})	1.9 ± 0.1	2.4 ± 0.2	2.6 ± 0.2	1.5 ± 0.2	1.6 ± 0.2	1.7 ± 0.3	1.8 ± 0.2

It will be appreciated by a person skilled in the art that other variations and/or modifications may be made to the embodiments disclosed herein without departing from the spirit or scope of the disclosure as broadly described. For example, in the description herein, features of different exemplary embodiments
5 may be mixed, combined, interchanged, incorporated, adopted, modified, included etc. or the like across different exemplary embodiments. The present embodiments are, therefore, to be considered in all respects to be illustrative and not restrictive.

CLAIMS

1. A modifier for modifying clay material, the modifier comprising a functionalized silsesquioxane having one or more epoxide group(s) and one or more organocation group(s).
2. The modifier according to claim 1, wherein the organocation group comprises a quaternary ammonium group.
3. The modifier according to claim 2, wherein the quaternary ammonium group is represented by general Formula (I):



Formula (I)

wherein

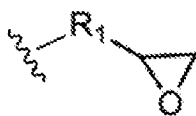
R₂ is selected from the group consisting of a single bond, alkyl, alkylphenyl, cycloalkyl, alkenyl, cycloalkenyl, alkynyl, alkoxy, ether (or alkyloxyalkyl), alkoxyalkyl, alkylcarbonyl, alkoxy carbonyl, alkylphenyloxyalkyl, aryl, aryloxy, arylalkenyl and heteroaryl;

R₃, R₄ and R₅ are each independently selected from the group consisting of hydroxy, hydroxyalkyl, halogen, haloalkyl, cyano, cyanoalkyl, nitro, nitroalkyl, carboxyl, alkyl, alkylphenyl, cycloalkyl, alkenyl, cycloalkenyl, alkynyl, alkoxy, ether (or alkyloxyalkyl), alkoxyalkyl, alkylcarbonyl, alkoxy carbonyl, alkylphenyloxyalkyl, aryl, aryloxy, arylalkenyl and heteroaryl;

wherein one or more hydrogen atom(s) is/are optionally replaced by hydroxy, hydroxyalkyl, halogen, haloalkyl, cyano, cyanoalkyl and nitro, and

wherein one or more carbon atom(s) is/are optionally replaced by heteroatom(s) selected from the group consisting of O, S, S=O and C=O.

- 5 4. The modifier according to claim 2, wherein the quaternary ammonium group comprises a hydroxyl group.
5. The modifier according to any one of the preceding claims, wherein the epoxide group is represented by general Formula (II):



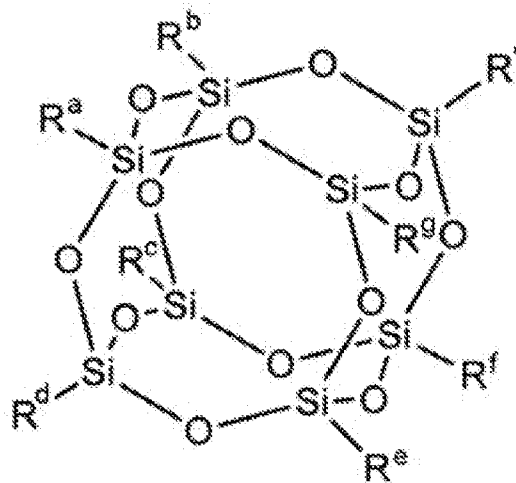
Formula (II)

wherein R₁ is selected from the group consisting of a single bond, alkyl, alkylphenyl, cycloalkyl, alkenyl, cycloalkenyl, alkynyl, alkoxy, ether (or alkyloxyalkyl), alkoxylalkyl, alkylcarbonyl, alkoxycarbonyl, alkylphenyloxyalkyl, aryl, aryloxy, arylalkenyl and heteroaryl;

wherein one or more hydrogen atom(s) is/are optionally replaced by hydroxy, hydroxyalkyl, halogen, haloalkyl, cyano, cyanoalkyl and nitro, and

wherein one or more carbon atom(s) is/are optionally replaced by heteroatom(s) selected from the group consisting of O, S, S=O and C=O.

6. The modifier according to any one of the preceding claims, wherein the epoxide group comprises a glycidyl group.
7. The modifier according to any one of claims 3 to 6, wherein the functionalized silsesquioxane is represented by general Formula (III):



Formula (III)

wherein R^a , R^b , R^c , R^d , R^e , R^f , R^g and R' are each independently selected from the group consisting of hydrogen, general Formula (I) and general Formula (II), with at least one of R^a , R^b , R^c , R^d , R^e , R^f , R^g and R' having general Formula (I) and at least one of R^a , R^b , R^c , R^d , R^e , R^f , R^g and R' having general Formula (II).

8. The modifier of any one of the preceding claims, wherein the molar ratio of the one or more organocation group(s) to the one or more epoxide group(s) ranges from 1:7 to 1:1.

9. A modified clay material comprising a clay material that is modified by or that comprises a modifier as claimed in any one of claims 1 to 8.

10. The modified clay material of claim 9, wherein the clay material comprises a layered clay material.

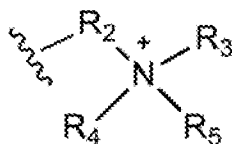
11. The modified clay material of claim 10, wherein the modified clay material comprises said modifier intercalated between layers of said layered clay material.

12. The modified clay material of claim 10 or 11, wherein the d-spacing of modified clay material is no less than 3 nm.
13. The modified clay material of any one of claims 9 to 12, wherein the clay material is coupled to the modifier through at least ionic interactions.
14. The modified clay material of any one of claims 9 to 13, wherein the clay material comprises a nanoclay.
15. A composite comprising:
(i) an epoxy matrix; and
(ii) a filler comprising a modified clay material according to any one of claims 9 to 14.
16. The composite of claim 15, wherein the filler is no more than 3 wt% of the composite.
17. The composite of claim 15 or 16, wherein the composite has a tensile strength and/or tensile modulus that is higher than the epoxy matrix alone.
18. A method of preparing a modifier of any one of claims 1 to 8, the method comprising:
a) reacting a silsesquioxane having one or more epoxide group(s) with an organocation precursor having an organic functional group to obtain a silsesquioxane having one or more epoxide group(s) and one or more of the organic functional group(s); and
b) converting one or more of the organic functional group(s) obtained in a) to the corresponding organocation group(s) to obtain a functionalized silsesquioxane having one or more epoxide group(s) and one or more organocation group(s).

19. The method of claim 18, wherein the organocation precursor in a) comprises a secondary amine precursor and the silsesquioxane obtained in a) has one or more epoxide group(s) and one or more tertiary amine group(s).

20. The method of claim 19, wherein b) comprises converting one or more tertiary amine group(s) obtained in a) to the corresponding quaternary ammonium cation(s) to obtain a functionalized silsesquioxane having one or more epoxide group(s) and one or more quaternary ammonium group(s).

21. The method of any one of claims 18 to 20, wherein the quaternary ammonium group is represented by general Formula (I):



Formula (I)

wherein

R₂ is selected from the group consisting of a single bond, alkyl, alkylphenyl, cycloalkyl, alkenyl, cycloalkenyl, alkynyl, alkoxy, ether (or alkyloxyalkyl), alkoxylalkyl, alkylcarbonyl, alkoxycarbonyl, alkylphenyloxyalkyl, aryl, aryloxy, arylalkenyl and heteroaryl;

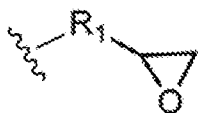
R₃, R₄ and R₅ are each independently selected from the group consisting of hydroxy, hydroxyalkyl, halogen, haloalkyl, cyano, cyanoalkyl, nitro, nitroalkyl, carboxyl, alkyl, alkylphenyl, cycloalkyl, alkenyl, cycloalkenyl, alkynyl, alkoxy, ether (or alkyloxyalkyl), alkoxyalkyl, alkylcarbonyl, alkoxycarbonyl, alkylphenyloxyalkyl, aryl, aryloxy, arylalkenyl and heteroaryl;

wherein one or more hydrogen atom(s) originally present is/are replaced by hydroxy, hydroxyalkyl, halogen, haloalkyl, cyano, cyanoalkyl and nitro, and

wherein one or more carbon atom(s) is/are optionally replaced by heteroatom(s) selected from the group consisting of O, S, S=O and C=O.

22. The method of any one of claims 18 to 21, wherein the quaternary ammonium group comprises a hydroxyl group.

23. The method of any one of claims 18 to 22, wherein the epoxide group is represented by general Formula (II):



Formula (II)

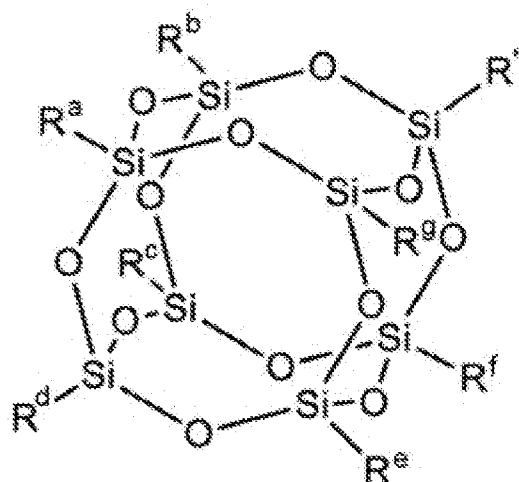
wherein R₁ is selected from the group consisting of a single bond, alkyl, alkylphenyl, cycloalkyl, alkenyl, cycloalkenyl, alkynyl, alkoxy, ether (or alkyloxyalkyl), alkoxyalkyl, alkylcarbonyl, alkoxy carbonyl, alkylphenyloxyalkyl, aryl, aryloxy, arylalkenyl and heteroaryl;

wherein one or more hydrogen atom(s) originally present is/are replaced by hydroxy, hydroxyalkyl, halogen, haloalkyl, cyano, cyanoalkyl and nitro, and

wherein one or more carbon atom(s) is/are optionally replaced by heteroatom(s) selected from the group consisting of O, S, S=O and C=O.

24. The method of any one of claims 18 to 23, wherein the epoxide group comprises a glycidyl group.

25. The method of any one of claims 21 to 24 wherein the functionalized silsesquioxane is represented by general Formula (III):



Formula (III)

wherein R^a , R^b , R^c , R^d , R^e , R^f , R^g and R^h are each independently selected from the group consisting of hydrogen, general Formula (I) and general Formula (II), with at least one of R^a , R^b , R^c , R^d , R^e , R^f , R^g and R^h having general Formula (I) and at least one of R^a , R^b , R^c , R^d , R^e , R^f , R^g and R^h having general Formula (II).

26. A method of preparing a modified clay material of any one of claims 9 to 14, the method comprising:

mixing a clay material with a modifier as claimed in any one of claims 1 to 8 to obtain a modified clay material.

27. The method of claim 26, wherein the method comprises intercalating the modifier into the clay material.

28. The method of claim 27, wherein the step of intercalating the modifier into the clay material comprises exchanging a cation in the clay material with an organocation of the modifier.

29. A method of preparing a composite of any one of claims 15 to 17, the method comprising:

mixing an epoxy matrix with a filler comprising a modified clay material according to any one of claims 9 to 14.

5

30. The method according to claim 29, wherein the mixing step is carried out in the presence of a hardener.

31. The method according to any one of claims 29 to 30, wherein the filler is added in an amount that is no more than 3 wt% of the final composite product.

10

32. The method according to any one of claims 30 to 31, wherein the epoxy resin and hardener are mixed in a weight ratio in a range of from 5:1 to 2:1.

15

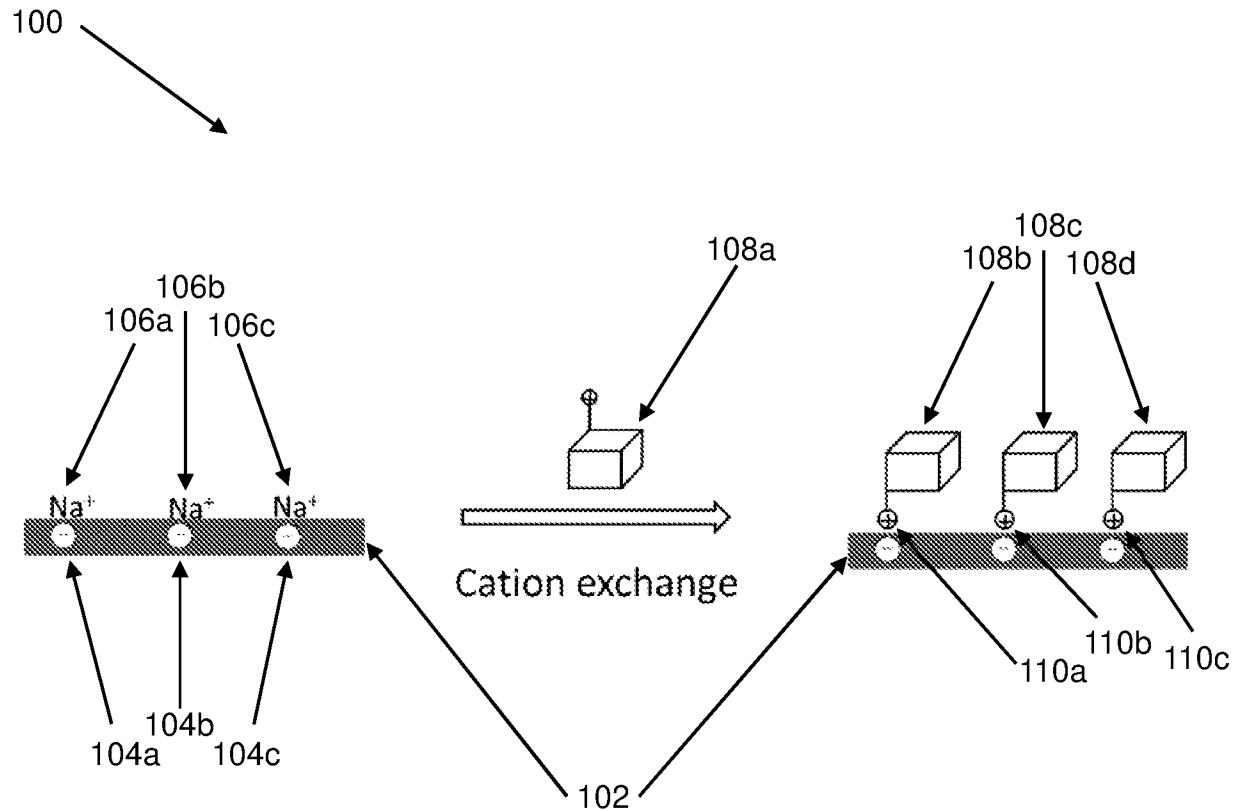


FIG. 1

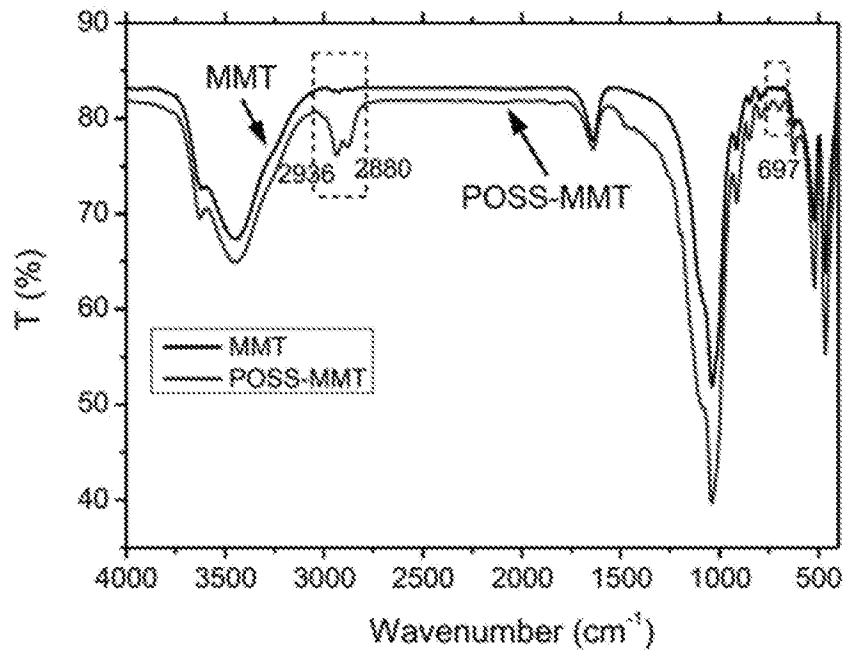


FIG. 2

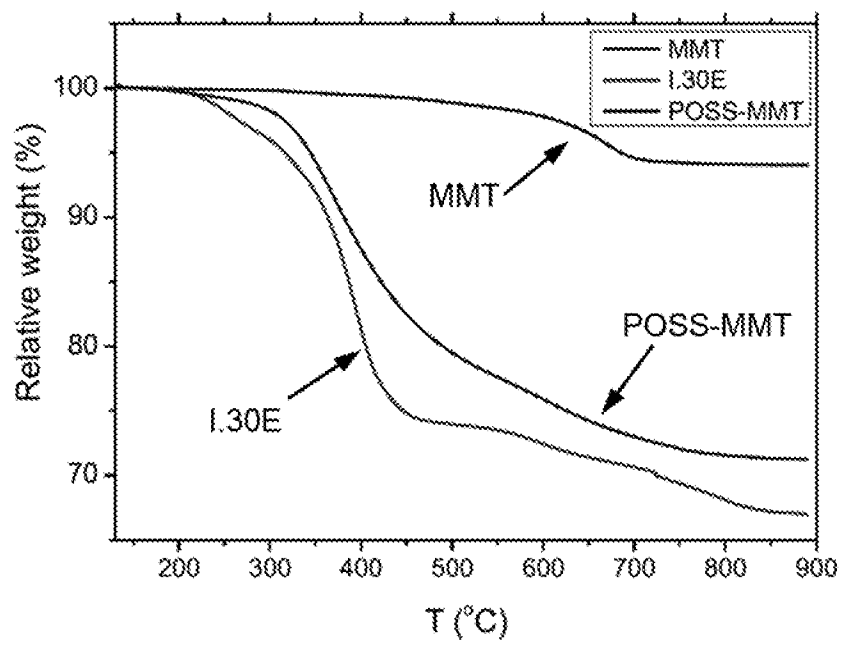


FIG. 3

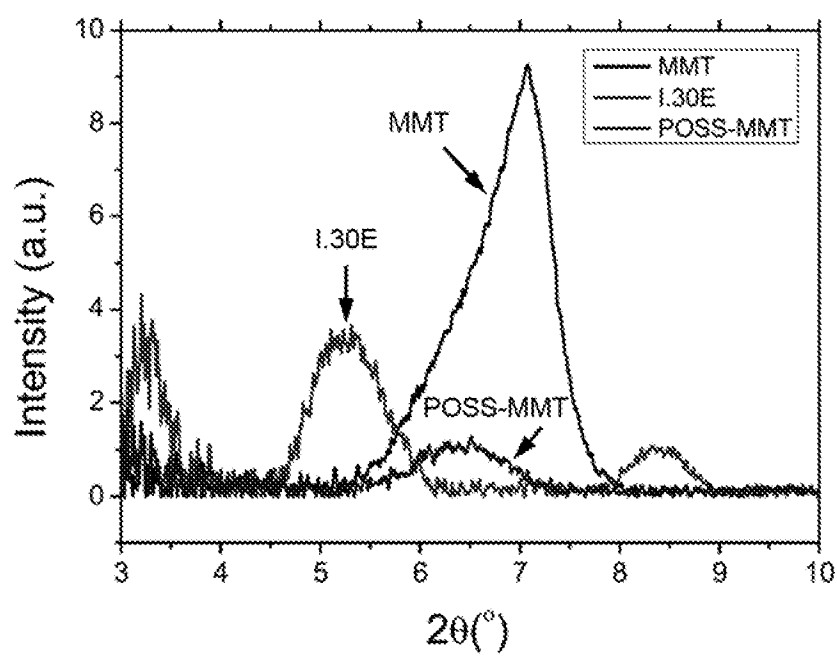


FIG. 4

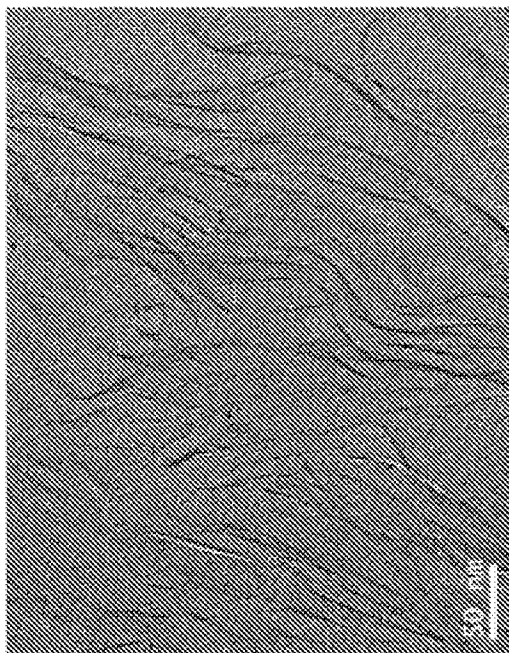


FIG. 5B

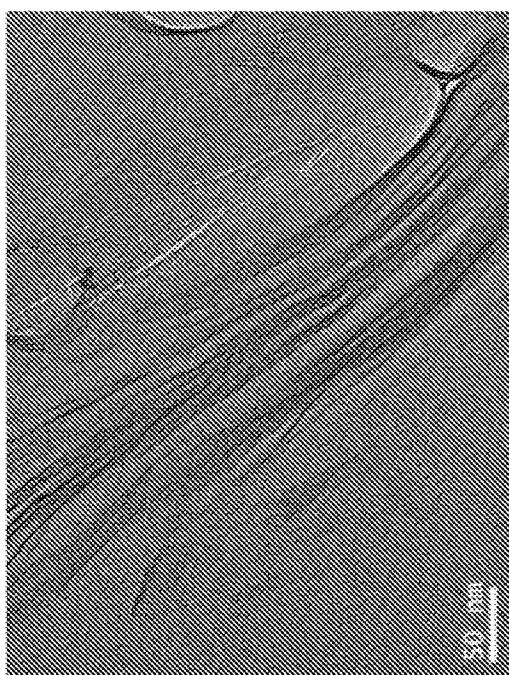


FIG. 5A

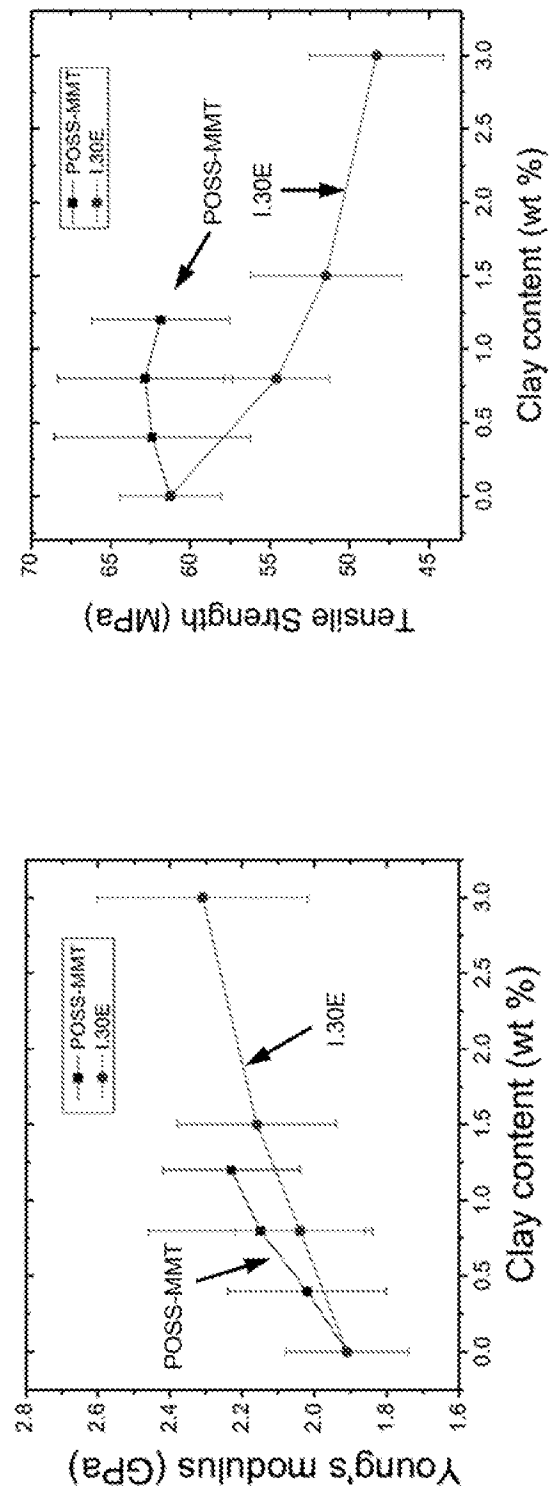


FIG. 6B

FIG. 6A

7/9

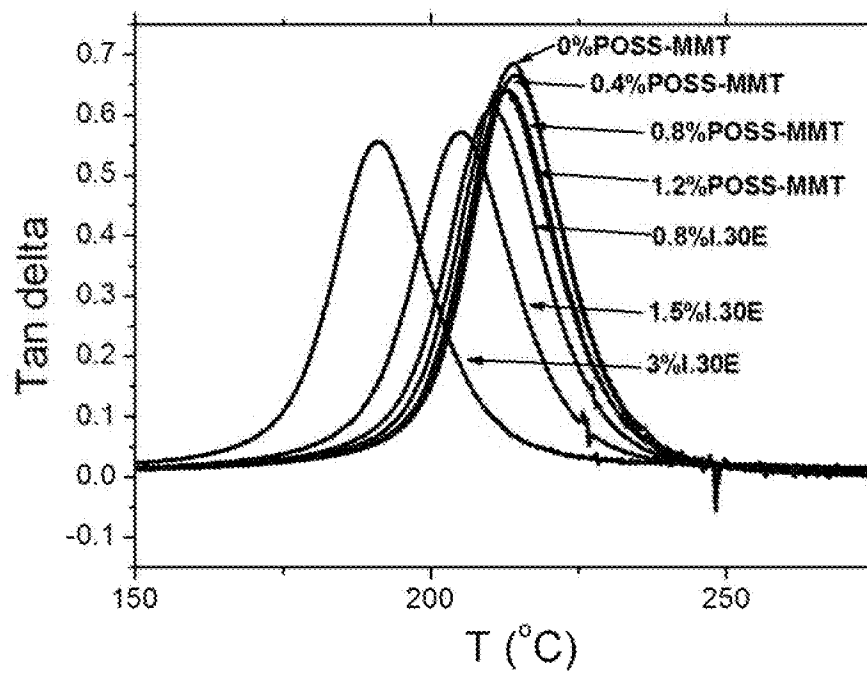


FIG. 7

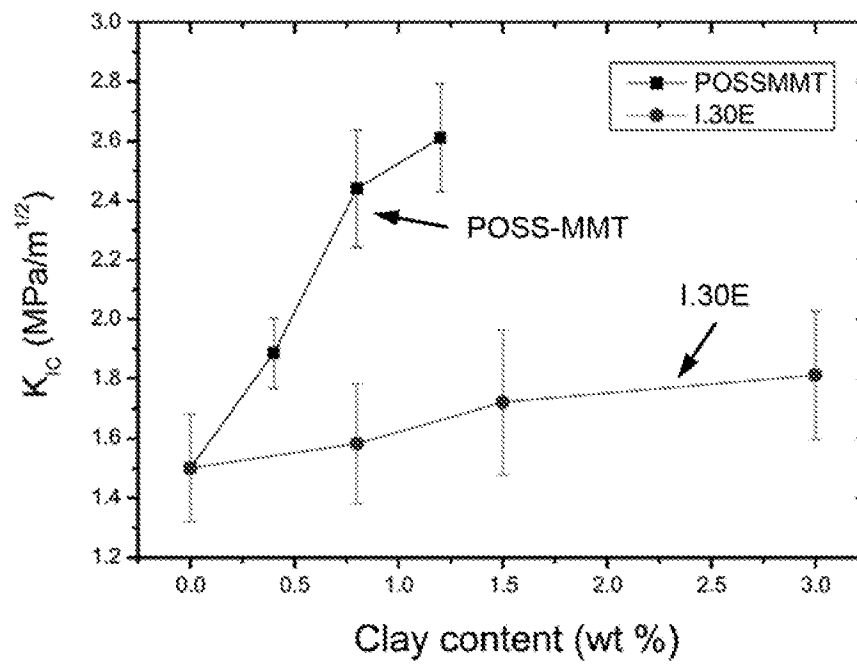


FIG. 8

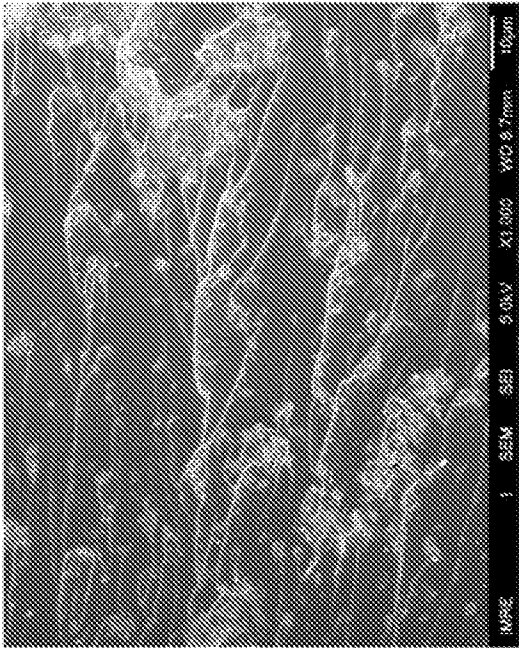


FIG. 9B

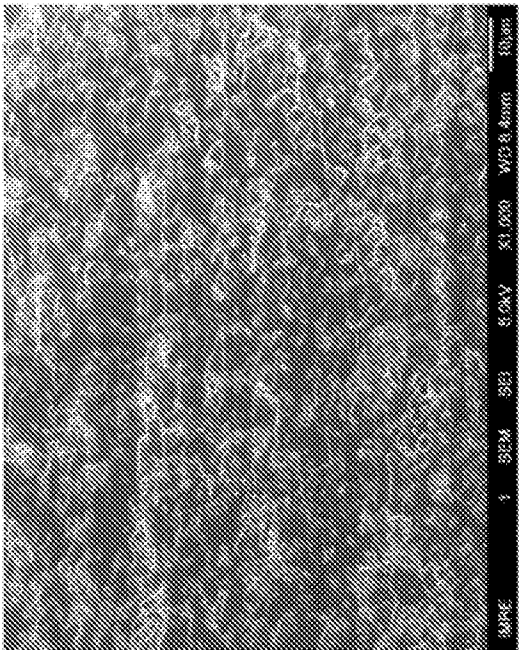


FIG. 9A

INTERNATIONAL SEARCH REPORT

International application No.

PCT/SG2019/050622

A. CLASSIFICATION OF SUBJECT MATTER

See Supplemental Box

According to International Patent Classification (IPC)

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C07F, C08K, C01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

Databases: FAMPAT, CAPLUS, COMPENDEX and INSPEC

Keywords: silsesquioxane, epoxy, glycidyl, oxirane, organocation, ammonium, clay, montmorillonite and related terms.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CN 107501560 A (INST APPLIED CHEMISTRY JIANGXI ACADEMY SCIENCES) 22 December 2017 see paragraphs [0006] and [0020]-[0026] of the original non-English language document (a machine translation is enclosed only for your reference)	1-8 and 18-25
X	LIU, H. ET AL., Montmorillonite intercalated by ammonium of octaaminopropyl polyhedral oligomeric silsesquioxane and its nanocomposites with epoxy resin. <i>Polymer</i> , 16 November 2004, Vol. 46, No. 1, pages 157-165 [Retrieved on 2020-02-24] <DOI: 10.1016/J.POLYMER.2004.10.078> see Sections 2.4, 3.1, 3.2 and Schemes 2 and 3	9-17 and 26-32
A	WO 2006/125708 A1 (DEGUSSA AG) 30 November 2006 see pages 13 and 14 of the machine translation	-
A	EP 2155761 B1 (MAYATERIALS, INC.) 14 August 2013 see paragraphs [0008], [0009], [0083] and [0104]	-

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

*Special categories of cited documents:

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"D" document cited by the applicant in the international application

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

24/02/2020

(day/month/year)

Date of mailing of the international search report

02/03/2020

(day/month/year)

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/SG2019/050622

Supplemental Box (Classification of Subject Matter)

Int. Cl.

C07F 7/21 (2006.01)

C08K 3/34 (2006.01)

C08K 9/06 (2006.01)

C01B 33/44 (2006.01)

B82Y 30/00 (2011.01)

B82Y 40/00 (2011.01)

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/SG2019/050622

Note: This Annex lists known patent family members relating to the patent documents cited in this International Search Report. This Authority is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
CN 107501560 A	22/12/2017	NONE	
WO 2006/125708 A1	30/11/2006	NONE	
EP 2155761 B1	14/08/2013	WO 2009/002660 A2 EP 2155761 A2 JP 20105-30911 A ES 2435200 T3	31/12/2008 24/02/2010 16/09/2010 16/12/2013