poly(methylhydrosiloxane) (PMHS), or its copolymer which are non-toxic, low cost, easily fabricated, flexible and optically transparent. Coating a fibre with millions of tiny silicone filaments can result in a water-repellent clothing material. In addition, a superamphiphobic textile, which is achieved through a two-step wet-chemistry coating technique, has been shown to exhibit remarkable multi-self healing ability against physical and chemical damages and exceptional liquid-repellency to low surface-tension liquids including ethanol. However, most conventional methodologies require perfluoromaterials, poisonous chemicals, and delicate preparation procedures.

It has been shown that reduced graphene-oxide (RGO) can be applied to the surface of cotton fibres to tune the wettability of the fibres, so they become superhydrophobic to water while superoleophilic to organic materials or oils. PDMS can be further applied to the cotton fibres coated with RGO to improve its surface wettability. However, in such a process, the RGO and PDMS are not chemically bonded to each other, which means that the coating can only be used on limited types of materials under limited treatment methods. Such a coating may also have limited durability and resistance to abrasion, especially under repeated washing. Further, a high concentration of RGO is required when the textile requires to be first coated with RGO.

Another alternative that has been studied is the reduced graphene-oxide (RGO) modified organopolysiloxanes for superhydrophobic textile coating, which shows long-term acid, alkaline and hot-water resistance as well as abrasion resistance. Such RGO modified organopolysiloxanes coating materials were synthesized via aryl radical assisted addition reaction, followed by hydrosilyation to covalently bond a very small amount of RGO with organopolysiloxanes. Although the RGO-modified organopolysiloxanes showed excellent properties, there were limitations in it, including the tedious preparation process of vinyl functionalized RGO and limited Si-H groups being available for reaction with the polymer matrix.

In this regard, despite the extensive efforts that have been made to achieve superhydrophobic textile coatings, challenging issues such as the high cost of materials, mechanical properties of the coating, chemical and environmental resistance of the coating, safety and comfort of the coatings remain.

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

Summary

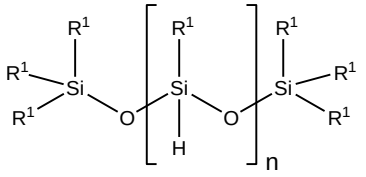
The present disclosure provides a polymeric coating material comprising a nanoadditive covalently bound to an organopolysiloxane, wherein the nanoadditive comprises

a) a nanoadditive substrate and

b) a linker covalently bound by a silyloxy moiety to the nanoadditive substrate at one end and said organopolysiloxane at the other end.

In an aspect of the present disclosure, there is provided a polymeric coating material comprising a nanoadditive covalently bound to an organopolysiloxane, wherein the nanoadditive comprises

a) a nanoadditive substrate and
b) a linker covalently bound by a silyloxy moiety to the nanoadditive substrate at one end and said organopolysiloxane at the other end;
wherein the organopolysiloxane prior to covalent bonding to the linker is a poly(methylhydrosiloxane) (PMHS) of representative formula (II)



(II)

wherein R^1 represents methyl, and n is an integer selected so that the poly(methylhydrosiloxane) has a molecular weight range of about 390 to about 10,000; and
wherein the content of nanoadditive substrate is less than about 3 % by weight.

Advantageously, the coating material may be superhydrophobic and repel water.

More advantageously, the coating material may not comprise fluorine. That is, the coating material may be fluorine-free. This means that any adverse effect associated with the use of perfluorinated materials may be circumvented by the disclosed polymeric coating material. For example, the disclosed coating material may be biocompatible, as it does not contain perfluorinated materials which may be toxic. Further, by not comprising perfluorinated materials, the disclosed coating material may be provided in a more cost-effective manner.

Further advantageously, the disclosed coating material may comprise zero- to two-dimensional nanoadditives, which may only be required in trace amounts (< 0.5% wt%). This may avoid having to use large amounts of expensive nanoadditives, resulting in the coating material being more cost-effective.

More advantageously, the disclosed coating material may have high durability in harsh conditions. The disclosed coating may have excellent long-term resistance to strong mineral acid, strong corrosive alkaline and hot water, whilst maintaining its superhydrophobic properties. Further advantageously, the disclosed coating material may retain its superhydrophobic properties even after greater than 500 (or 7 days of) washings or after strong etching.

Further advantageously, only a small amount of the disclosed coating material may be necessary to confer the superhydrophobic properties to the textile substrate, to confer resistance to strong corrosive acid, strong corrosive alkaline, hot water or chemical abrasion.

Advantageously, the nanoadditive substrate and the organopolysiloxane of the disclosed coating material may by covalently bonded. Without being bound to theory, the advantageous properties of the disclosed coating material may be due to the strong covalent linkage present between the nanoadditive substrate and the organopolysiloxane.

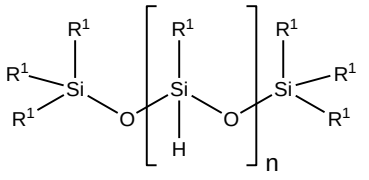
The present disclosure also provides a method for making a coating material, comprising the steps of

a) reacting a silane reagent, preferably a vinyl trialkoxy silane, with a nanoadditive substrate, which is optionally surface functionalized with hydroxyl groups,

b) covalently bonding the reaction product to an organopolysiloxane or its precursors optionally in the presence of a catalyst.

In another aspect of the present disclosure, there is provided a method for making a coating material, comprising the steps of

a) reacting a silane reagent, preferably a vinyl trialkoxy silane, with a nanoadditive substrate, which is optionally surface functionalized with hydroxyl groups,
b) covalently bonding the reaction product to an organopolysiloxane or its precursors optionally in the presence of a catalyst,
wherein the organopolysiloxane is a poly(methylhydrosiloxane) (PMHS) of representative formula (II)



(II)

wherein R^1 represents methyl, and n is an integer selected so that the poly(methylhydrosiloxane) has a molecular weight range of about 390 to about 10,000; and
wherein the content of nanoadditive substrate in the resultant coating material is less than about 3 % by weight.

Advantageously, the disclosed method provides a facile method for the synthesis of hybrid composites of nanoadditives and polysiloxanes. Further advantageously, the method facilitates

mass production of the coating material as it is suitable for scaling up compared to conventional methods.

In another aspect of the present disclosure, there is provided the use of the coating material as defined above for coating a substrate, preferably natural or man-made fibers.

In another aspect of the present disclosure, there is provided a method of coating a substrate, preferably a fiber, comprising the steps of:

a) dissolving a coating material as defined above in a solvent to form a coating solution;

b) immersing said substrate in the coating solution; and

c) removing said substrate from the coating solution.

Advantageously, the disclosed method facilitates easy coating of a substrate with the coating material as defined above. Further advantageously, the method allows the coating material to be applied to various natural or man-made fibers to achieve similar superhydrophobicity. Further advantageously, no further processing is required of the substrate after the coating process, making the application of the coating material straight forward and efficient.

In another aspect of the present disclosure, there is provided a coated substrate obtainable by any of the methods as defined above having superhydrophobic properties.

Advantageously, the physicochemical properties, the colour or the hand feel of the substrate coated with the disclosed coating material may not change. More advantageously, the coating material may be stain resistant which means that any substrate coated with the disclosed coating material may be easily washed. Further advantageously, the coating material may be applied across a wide range of substrates, including cotton, polyester, nylon and nomex, while maintaining the superhydrophobic properties. Even further advantageously, similar superhydrophobic properties may be conferred to the substrate, even if the properties of the substrates themselves are different. More advantageously, the permeability of the original substrate may be maintained even after coating the substrate with the disclosed coating material.

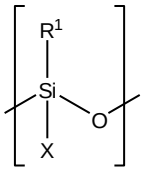
The present disclosure also provides a polymer nanoadditive composite comprising a nanoadditive covalently bound to an organopolysiloxane,

wherein the nanoadditive comprises

a) a nanoadditive substrate and

b) a linker covalently bound by a silyloxy moiety to the nanoadditive substrate at one end and said organopolysiloxane at the other end;

and wherein the organopolysiloxane comprises one or more non-terminal units of formula (III) in the polymer chains



(III)

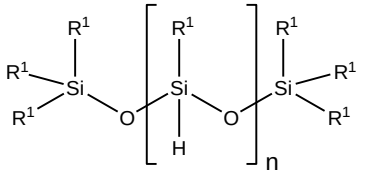
wherein

R^1, is independently selected from hydrogen, C_1 to C_{10}-alkyl, C_1 to C_{10}-alkenyl, C_1 to C_{10}-alkyl- C_6 to C_{10}-aryl or C_6 to C_{10}-aryl; and R^1 is preferably methyl;

and X is the bond to the linker.

In another aspect of the present disclosure, there is provided a polymer nanoadditive composite comprising a nanoadditive covalently bound to an organopolysiloxane,

wherein the nanoadditive comprises
a) a nanoadditive substrate and
b) a linker covalently bound by a silyloxy moiety to the nanoadditive substrate at one end and said organopolysiloxane at the other end;
and wherein the organopolysiloxane prior to covalent bonding to the linker, is a poly(methylhydrosiloxane) of representative formula (II)



(II)

wherein R^1 represents methyl, and n is an integer selected to represent an integer so that the poly(methylhydrosiloxane) has a molecular weight range of about 390 to about 10,000; and
wherein the content of nanoadditive substrate is less than about 3 % by weight.

Brief Description of Drawings

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

Fig.1

[Fig. 1] is a schematic representation of silane hydrolysis followed by condensation on a hydrated surface.

Fig.2

[Fig. 2] is a schematic representation of the silylation-polymerization procedure of PMHS with various vinyl-functionalized nanoadditives.

Fig. 3

[Fig. 3] refers to a photograph of (a) original clay and (b) vinylsilane-functionalized clay in (A) water and (B) THF.

Fig. 4

[Fig. 4] refers to FTIR spectra of (a) octavinyl POSS and (b) PMHS@POSS.

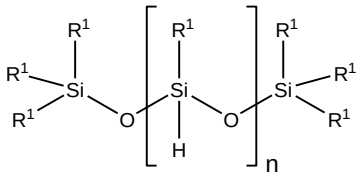
Claims

1. A polymeric coating material comprising a nanoadditive covalently bound to an organopolysiloxane, wherein the nanoadditive comprises

a) a nanoadditive substrate and

b) a linker covalently bound by a silyloxy moiety to the nanoadditive substrate at one end and said organopolysiloxane at the other end;

wherein the organopolysiloxane prior to covalent bonding to the linker is a poly(methylhydrosiloxane) (PMHS) of representative formula (II)



(II)

wherein R^1 represents methyl, and n is an integer selected so that the poly(methylhydrosiloxane) has a molecular weight range of about 390 to about 10,000; and

wherein the content of nanoadditive substrate is less than about 3 % by weight.

2. The coating material of claim 1, wherein the content of nanoadditive substrate is less than about 0.5 % by weight, and preferably between about 0.005 and 0.5 % by weight, of the organopolysiloxane.

3. The coating material of claim 1, wherein the nanoadditive substrate, prior to being linked to the organopolysiloxane, is surface-functionalized with vinyl groups, preferably by using trimethoxy(vinyl)silane as a silane reagent.

4. The coating material of claim 1, wherein the nanoadditive substrate is a particle of 10 nm to 10 μm size.

5. The coating material of claim 3 or 4, wherein the nanoadditive substrate is selected from the group consisting of carbon nanotubes, graphene oxides and reduced graphene oxides, clay , silica-dioxide nanoparticles or a polyhedral oligomeric silsesquioxane.

6. The coating material of claim 1, wherein the silyloxy linker, before forming the covalent bonds, comprises a nonhydrolyzable moiety, preferably a vinyl group, and a silyloxy moiety.

7. The coating material of claim 6, wherein the silyloxy moiety is covalently bound to the nanoadditive substrate via a silyl-ether bridge.

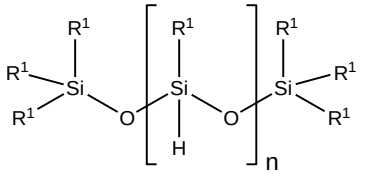
8. The coating material of claim 7, wherein the nonhydrolyzable moiety, preferably a vinyl group, is covalently bound to the polymeric organopolysiloxane.

9. A method for making a coating material, comprising the steps of

a) reacting a silane reagent, preferably a vinyl trialkoxy silane, with a nanoadditive substrate, which is optionally surface functionalized with hydroxyl groups,

b) covalently bonding the reaction product to an organopolysiloxane or its precursors optionally in the presence of a catalyst,

wherein the organopolysiloxane is a poly(methylhydrosiloxane) (PMHS) of representative formula (II)



(II)

wherein R^1 represents methyl, and n is an integer selected so that the poly(methylhydrosiloxane) has a molecular weight range of about 390 to about 10,000; and

wherein the content of nanoadditive substrate in the resultant coating material is less than about 3 % by weight.

10. The method of claim 9, wherein the catalyst is selected from group 10 elements.

11. The method of claim 10, wherein the catalyst comprises platinum.

12. Use of the coating material of any of claims 1 to 8 for coating a substrate, preferably natural or man-made fibers.

13. A method of coating a substrate, preferably a fiber, comprising the steps of:

a) dissolving a coating material according to any of claims 1 to 8 in a solvent to form a coating solution;

b) immersing said substrate in the coating solution; and

c) removing said substrate from the coating solution.

14. The method of claim 13, further comprising the step of (d) drying the substrate from step (c) to remove the solvent.

15. The method of claim 14, wherein the solvent used is selected from the group consisting of toluene, dichloromethane and chloroform.

16. A coated substrate obtainable by any of the methods of claims 13 to 15 having superhydrophobic properties.

17. The coated substrate of claim 16 for use in textile processing, packaging materials, paper industry, antifouling clothing, sportswear and boat sails.

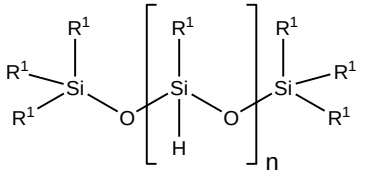
18. A polymer nanoadditive composite comprising a nanoadditive covalently bound to an organopolysiloxane,

wherein the nanoadditive comprises

a) a nanoadditive substrate and

b) a linker covalently bound by a silyloxy moiety to the nanoadditive substrate at one end and said organopolysiloxane at the other end;

and wherein the organopolysiloxane prior to covalent bonding to the linker, is a poly(methylhydrosiloxane) of representative formula (II)



(II)

wherein R^1 represents methyl, and n is an integer selected to represent an integer so that the poly(methylhydrosiloxane) has a molecular weight range of about 390 to about 10,000; and

wherein the content of nanoadditive substrate is less than about 3 % by weight**.**

19. The polymer nanoadditive composite according to claim 18, wherein the nanoadditive is selected from the group consisting of carbon nanotubes, graphene oxides and reduced graphene oxides, clay, silica-dioxide nanoparticles or a polyhedral oligomeric silsesquioxane.