

**FLUORINATED POSS AS ALLOYING AGENTS
IN NONFLUORINATED POLYMERS**

Cross-Reference to Related Applications

This application is a continuation-in-part of U.S. Patent Application Serial No. 11/725,994 filed on March 19, 2007.

Field of the Invention

This invention relates generally to methods for enhancing the properties of nonfluorinated thermoplastic and thermoset polymers and particulate and filler surfaces through the addition of fluorine containing POSS nanostructured chemicals. The fluorinated component may be contained inside the POSS cage, external to the POSS cage or copolymerized with POSS cages. Additionally fluorinated POSS cages may contain metal atoms to improve their compatibility with polymers and surfaces and to impart catalytic activity.

This invention also relates to processes and applications of polymeric materials and composites with improved physical properties and function that resemble those of conventional fluorinated materials. These properties and applications include improved surface properties, non-wetting, anti-icing, and low friction surfaces, biological activity, permeation control, fire retardancy, improve time-dependent mechanical properties which include (heat distortion, high temperature stability, compression set, creep, color retention, biological compatibility).

1 BACKGROUND OF THE INVENTION

2 As disclosed in U.S. Patent No. 7,193,015, the incorporation of externally
3 fluorinated POSS into fluorinated polymers further reduces their surface energy and
4 contact angle rendering them super hydrophobic. It is the objective of this
5 application to convey the ability of fluorinated POSS to impart "fluoropolymer type"
6 characteristics to nonfluorinated polymers, metal surfaces, particulates, composites
7 and biological systems.

8 It has long been recognized that the properties of polymers can be tailored to
9 a high degree through variables such as polymer sequence, structure, additive and
10 filler incorporation, composition, morphology, thermodynamic and kinetic processing
11 control. It is similarly known that various sizes and shapes of fillers, and particulates
12 (e.g. Teflon[®], calcium carbonate, silica, carbon black, etc.) can be incorporated into
13 polymers, monomer mixtures, and composites to enhance physical properties.

14 In their solid state all polymers (including amorphous, semi-crystalline,
15 crystalline, and rubber, etc.) possess considerable amounts of internal and external
16 free volume and this free volume has a tremendous impact on physical properties,
17 since it is within this volume that the dynamic properties (e.g. reptation, translation,
18 rotation, crystallization, interaction with surfaces and fillers) of polymer chains
19 primarily operate and in turn influence fundamental physical properties.

20 The accessibility of free volume in a polymer system depends greatly on
21 morphology and on the size of the agent desired to occupy the free volume.
22 Thermodynamic and kinetic properties, polymer morphology and free volume
23 dimension are major factors, which limit the ability of conventional fillers from
24 accessing the free volume in a polymer system. Significant

1 processing/compounding effort is normally required to force compatibilization
2 between fillers and polymers since conventional fillers are physically larger than
3 most polymer dimensions, chemically dissimilar, and viscometrically different than
4 most polymers.

5 Prior art in nonfluoropolymers has utilize fluorinated additives and fluorinated
6 filler particulates to impart characteristics of the fluorinated entity to the
7 nonfluorinated polymer. Unfortunately, the prior art suffers from process complexity,
8 inappropriate length scale of the reinforcement to access polymer free volume, or
9 the reinforcement lacks sufficient geometrical definition to provide structural
10 regularity and reinforcement at the molecular (10^{-10} m) and nanoscopic (10^{-9} m)
11 length scales. Consequently many desirable properties of the nonfluorinated
12 polymer are lost upon incorporation of conventional fluorinated components.

13 Furthermore, it has been calculated that as filler sizes decrease below 50 nm,
14 they become more resistant to sedimentation and more effective at providing
15 reinforcement to polymer systems. The full application of this knowledge, however,
16 has been thwarted by the lack of a practical source of fluorinate particulates or
17 fluorinated additives less than 50 nm and preferably with a rigid 1 nm to 5 nm size
18 range. Particularly desirable are monodisperse, nanoscopic chemicals with precise
19 chemical compositions, rigid and well defined geometrical shapes, and which are
20 dimensionally large enough to provide reinforcement of polymer chains. Such
21 nanoscopic chemicals are desirable as they form stable dispersions within polymer
22 systems, well below the length scale necessary to scatter light and hence are
23 visually nondetectable when incorporated. Further fluorinated nanoscopic chemicals
24 would be chemically compatible with nonfluoropolymers and dissolve into and

1 among the polymer chains, thus eliminating the need for the complex processing
2 requirements of the prior art.

3 The fundamental premise behind this invention is underpinned
4 mathematically through computation of the surface area and volume contribution
5 provided at various loadings of 1 nm diameter fluorine containing nanostructured
6 chemical entities into or onto a nonfluorinated polymeric material. Computation
7 reveals that a fluorinated nanostructured chemical contributes more surface area
8 and more volume as a wt% of its incorporation into a material than is possible for
9 larger particles (see Figure 1, Figure 2, and Figure 3). The net effect is that even
10 small loadings of nanostructured chemicals can dominate the surface characteristics
11 of a material. This is an important economic consideration since fluorinated
12 materials are traditionally expensive and desired to be used in minimal quantities.

13 Further, the incorporation of fluorinated nanostructured chemicals onto the
14 surface of a secondary material (such as TiO_2 , CaCO_3 , glass or mineral fillers, and
15 fibers) can be utilized to creating more surface area on such particle and improve
16 their compatibility with fluorinated and nonfluorinated polymers.

17 Recent developments in nanoscience have enabled the cost effective
18 manufacture of commercial quantities of materials that are best described as
19 nanostructured chemicals due to their specific chemical formula, hybrid (inorganic-
20 organic) chemical composition, geometrically precise and rigid shape, large physical
21 size relative to traditional chemicals (0.3-0.5 nm), and small physical size relative to
22 larger sized traditional fillers (>50 nm).

23 Nanostructured chemicals are best exemplified by those based on low-cost
24 Polyhedral Oligomeric Silsesquioxanes (POSS) and Polyhedral Oligomeric Silicates

Figures 4, 5, 6 illustrate some representative examples of fluorinated nanostructured chemicals, which are also referred to as fluorinated POSS in this application. It is recognized that oligomeric, polymeric, and metal containing versions of fluorinated POSS may also be utilized. Nanostructured chemicals based on polyhedral oligomeric silsesquioxanes and polyhedral metallosesquioxanes are discussed in detail in U.S. Patent Nos. 5,412,053; 5,484,867; 6,329,490; and 6,716,919, which are expressly incorporated herein by reference in their entirety.

SUMMARY OF THE INVENTION

9 As disclosed in U.S. Patent No. 7,193,015, the incorporation of externally
10 fluorinated POSS into fluorinated polymers further reduces surface energy and
11 contact angles rendering them super hydrophobic. It is the objective of this
12 application to attain control over the contact angle, coefficient of friction, and
13 hydrophobicity of nonfluorinated polymers and filler additives and metal surfaces
14 through the use of fluorinated POSS.

The present invention describes methods of preparing new compositions by incorporating fluorinated-nanostructured chemicals into nonfluorinated polymers. The resulting nano-alloyed polymers are wholly useful by themselves or in combination with other polymers or in combination with macroscopic reinforcements such as fiber, clay, glass, mineral and other fillers and fibers. The nano-alloyed polymers are particularly useful for producing polymeric compositions with desirable physical properties such processing aids, surface lubricity, adhesion to polymeric surfaces, composite and metal surfaces, water repellency, reduced melt viscosity, reduced surface energy, low dielectric constant, resistance to abrasion and fire, biological compatibility, optical quality plastics, cosmetic applications.

1 The preferred compositions presented herein contain three primary material
2 combinations: (1) fluorinated nanostructured chemicals, fluorinated-nanostructured
3 oligomers, or fluorinated-nanostructured polymers from the chemical classes of
4 fluorine containing polyhedral oligomeric silsesquioxanes, polysilsesquioxanes,
5 polyhedral oligomeric silicates, polysilicates, polyoxometallates, carboranes,
6 boranes, and fluorinated polymorphs of carbon; (2) nonfluorinated polymer systems
7 such as aromatic and aliphatics, semicrystalline, crystalline, glassy, elastomeric, oils,
8 and lubricants thereof as derived from hydrocarbons, or silicones and copolymers
9 thereof; and (3) inorganics metals, and particulate minerals and silicacious powders,
10 and all forms of carbon including diamond powder, graphite, carbon black, tubes,
11 spheres, mesophase, pitch, and fiber.

12 Preferably, the method of incorporating nanostructured chemicals into
13 nonfluoropolymers is accomplished via blending of the fluorinated nanostructured
14 chemicals with the nonfluorinated materials. All types and techniques of coating,
15 blending, including melt blending, dry blending, solution blending, reactive and
16 nonreactive blending are effective.

17 In addition, selective incorporation of a nanostructured chemical into a
18 specific region of a polymer can be accomplished by compounding into the polymer
19 a nanostructured chemical with a chemical potential (miscibility) compatible with the
20 chemical potential of the region desired within the material. This is most preferably
21 accomplished using POSS chemicals with partially externally fluorinated cage such
22 as $[(\text{RSiO}_{1.5})_{8-x}(\text{R}_f\text{SiO}_{1.5})_x]\sum_8$ or cages containing fluorine inside of the cage cavity
23 such as $\text{Cation}[(\text{RSiO}_{1.5})_8@F]\sum_8$. The internally fluorinate cages

1 Cation $[(\text{RSiO}_{1.5})_8\text{@F}]_{\Sigma 8}$ are particularly useful for incorporation into polar polymers
2 (such as hydrogels because they are also polar and hence exhibit compatibility.

3 The physical size of POSS cages in combination with tailorable compatibility
4 enables fluorinated POSS to be selectively incorporated into polymers, composites,
5 metals, ceramics and biological materials to control the surface topology, surface
6 properties, and chain dynamics and subsequently favorably impact a multitude of
7 physical properties. Properties most favorably improved are surface properties,
8 including contact angle, coefficient of friction, anti-icing, surface tension,
9 hydrophobicity, and lubricity. Other properties improved include time dependent
10 mechanical and thermal properties such as heat distortion, heat stability, creep,
11 compression set, shrinkage, modulus, hardness, and abrasion resistance. In
12 addition to mechanical properties, other physical properties are favorably improved,
13 including thermal conductivity, refractive index, fire resistance, oxygen permeability,
14 oxidative stability, electrical properties, printability and biological compatibility and
15 activity.

16 BRIEF DESCRIPTION OF THE DRAWINGS

17 FIG 1 illustrates diameter and volume contributions for $[(\text{c-C}_6\text{H}_{11}\text{SiO}_{1.5})_8]_{\Sigma 8}$
18 POSS cage.

19 FIG 2 illustrates the surface area contribution for $[(\text{c-C}_6\text{H}_{11}\text{SiO}_{1.5})_8]_{\Sigma 8}$ POSS
20 cage relative to wt % loading.

21 FIG. 3 illustrates the volume contribution for $[(\text{c-C}_6\text{H}_{11}\text{SiO}_{1.5})_8]_{\Sigma 8}$ POSS cage
22 relative to wt % loading.

1 FIG. 4 illustrates representative examples of externally fluorinated POSS
2 nanostructured chemicals.

3 FIG. 5 illustrates representative examples of internally fluorinated POSS
4 nanostructured chemical which also contain a counter cation to balance charge and
5 assert additional compatibility.

6 FIG. 6 illustrates a representative example of partially externally fluorinated
7 POSS nanostructured chemical.

8 FIG. 7 illustrates the contact angles for polystyrene showing increasing
9 contact angle with $[(CF_3(CF_2)_7(CH_2)_2SiO_{1.5})_8]_{\Sigma 8}$ POSS incorporation.

10 FIG. 8 illustrates the contact angles for LDPE showing increasing contact
11 angle with $[(CF_3(CF_2)_7(CH_2)_2SiO_{1.5})_8]_{\Sigma 8}$ POSS incorporation.

12 FIG. 9 illustrates the contact angles for styrene acrylonitrile showing
13 increasing contact angle with $[(CF_3(CF_2)_7(CH_2)_2SiO_{1.5})_8]_{\Sigma 8}$ POSS incorporation.

14 FIG. 10 illustrates the contact angles for polymethylmethacrylate showing
15 increasing contact angle with $[(CF_3(CF_2)_7(CH_2)_2SiO_{1.5})_8]_{\Sigma 8}$ and
16 $(CH_3)_4N[(CF_3(CF_2)_7(CH_2)_2SiO_{1.5})_8@F]_{\Sigma 8}$ POSS incorporation.

17 **DEFINITION OF FORMULA REPRESENTATIONS FOR NANOSTRUCTURES**

18 For the purposes of understanding this invention's chemical compositions the
19 following definitions for formula representations of Polyhedral Oligomeric
20 Silsesquioxane (POSS) and Polyhedral Oligomeric Silicate (POS) nanostructures
21 are made.

1 Polysilsesquioxanes are materials represented by the formula $[\text{RSiO}_{1.5}]_x$
 2 where x represents molar degree of polymerization and R = represents organic
 3 substituent (H, siloxy, cyclic or linear aliphatic or aromatic groups that may
 4 additionally contain reactive functionalities such as alcohols, esters, amines,
 5 ketones, olefins, ethers and R_f = represents halogenated organic groups which
 6 includes fluorinated groups). Polysilsesquioxanes may be either homoleptic or
 7 heteroleptic. Homoleptic systems contain only one type of R group while
 8 heteroleptic systems contain more than one type of R group.

9 POSS and POS nanostructure compositions are represented by the formula:

10 $[(\text{RSiO}_{1.5})_n]_{\Sigma\#}$ for homoleptic compositions

11 $[(\text{RSiO}_{1.5})_n(\text{R}'\text{SiO}_{1.5})_m]_{\Sigma\#}$ for heteroleptic compositions (where $\text{R} \neq \text{R}'$)

12 $[(\text{RSiO}_{1.5})_n(\text{RXSiO}_{1.0})_m]_{\Sigma\#}$ for functionalized heteroleptic compositions (where R
 13 groups can be equivalent or inequivalent)

14 In all of the above R is the same as defined above and X includes but is not
 15 limited to OH, Cl, Br, I, F, alkoxide (OR), acetate (OOCR), peroxide (OOR), amine
 16 (NR_2) isocyanate (NCO), and R. The symbols m and n refer to the stoichiometry of
 17 the composition. The symbol Σ indicates that the composition forms a
 18 nanostructure and the symbol # refers to the number of silicon atoms contained
 19 within the nanostructure. The value for # is usually the sum of m+n, where n ranges
 20 typically from 1 to 24 and m ranges typically from 1 to 12. It should be noted that $\Sigma\#$
 21 is not to be confused as a multiplier for determining stoichiometry, as it merely
 22 describes the overall nanostructural characteristics of the system (aka cage size).

1 The symbol @ is also used in association with the POSS formula representations
2 and indicates the presence of an F anion inside of the cage cavity.

3 DETAILED DESCRIPTION OF THE INVENTION

4 The present invention teaches the use of fluorinated POSS nanostructured
5 chemicals as agents for imparting the characteristics of a fluorinated material (such
6 as polymers) to nonfluorinated polymers, composites, additives, metals, and all
7 types of particles.

8 The keys that enable POSS nanostructured chemicals to impart fluorinated
9 characteristics to such a diverse number of materials are: (1) their unique size with
10 respect to polymer chain dimensions, and (2) their ability to be compatibilized with
11 polymer systems to overcome forces that promote incompatibility and expulsion of
12 the nanoreinforcing agent by polymer chains and surfaces and (3) their ability to bind
13 to dissimilar surfaces.

14 Additionally advantageous are the fundamental aspects of high surface area,
15 low density, and controlled volume contributions imparted by the nanoscopic size of
16 the POSS cage. The nanoscopic cage size imparts these properties to materials at
17 very small loading amounts and affords POSS to dominate the surface and volume
18 characteristics of materials.

19 The chemical nature of POSS cages renders their dispersion characteristics
20 to be governed by the Gibbs free energy of mixing equation ($\Delta G = \Delta H - T\Delta S$) rather
21 than kinetic dispersive mixing as for insoluble particulates. Thus the ability of POSS
22 to interact with a surface or with polymers through Van der Waals interactions,
23 covalent, ionic, or hydrogen bonding that can be utilized to chemically,

1 thermodynamically, and kinetically drive their dispersion and surface modification.
2 Furthermore since POSS cages are monoscopic in size, entropic dispersion (ΔS) is
3 favored.

4 While fluoropolymers are known for their hydrophobicity, low surface energy,
5 and low coefficients of friction, the incorporation of fluorinated POSS has been
6 shown in US Patent No. 7,193,015 to further improve these properties in fluorinated
7 polymers. Therefore extension of fluorinated POSS into nonfluorinated systems is a
8 logical means for cost-effectively attaining such properties in nonfluorinated
9 polymers.

10 **EXAMPLES**

11 **General Process Variables Applicable To All Processes**

12 As is typical with chemical processes there are a number of variables that can
13 be used to control the purity, selectivity, rate and mechanism of any process.
14 Variables influencing the process for the incorporation of nanostructured chemicals
15 (e.g. POSS/POS etc.) into plastics include the size and polydispersity, and
16 composition of the nanostructured chemical. Similarly the molecular weight,
17 polydispersity and composition of the polymer system must also be matched with
18 that of the nanostructured chemical. Finally, the kinetics, thermodynamics, and
19 processing aids used during the compounding process are also tools of the trade
20 that can impact the loading level and degree of enhancement resulting from
21 incorporation of nanostructured chemicals into polymers. Blending processes such
22 as melt blending, dry blending and solution mixing blending are all effective at mixing
23 and alloying nanostructured chemical into plastics.

1 Water contact angles are a measure of surface hydrophobicity and provide
2 insight into the free energy of the surface. Critical surface tension of the POSS,
3 POSS polymers, and POSS blends were determined. The surface tension of the
4 fluid is graphed in relation to its contact angle on the surface. It should be noted that
5 a surface with a contact angle of 90° or higher is considered a "non-wetting" surface,
6 while a surface with a contact angle below 90° is considered "wetting."

7 **Synthesis of Internally Fluorinated CationPOSS@F cages**

8 **(Bu₄N)[(PhSiO_{1.5})₈@F]_{Σ8}** (via literature Bassindale, et al Angew. Chem. Int. Ed.
9 (2003), vol 42, 3488) Tetrabutylammonium octaphenyl octasilsesquioxane fluoride
10 **(Bu₄N)[(PhSiO_{1.5})₈@F]_{Σ8}**: Tetrabutylammonium fluoride (1m solution in THF, 2.5 ml ,
11 with 5% water) was added to phenyl triethoxysilane (1.02 g, 4.2 mmol) dissolved in
12 dry THF (20 ml). The mixture was stirred at room temperature for 24 h and a yellow
13 viscous liquid obtained after removal of the solvent. Dry chloroform (10 ml) was
14 added, and a white powder was obtained after filtration. Recrystallization from
15 acetone afforded colorless crystals (1.25 g, 46%). ²⁹Si NMR (79.30 MHz, CDCl₃,
16 TMS): d= 80.6 ppm.

17 **(Me)₄N[(PhSiO_{1.5})₈@F]_{Σ8}** To a 1 gram anhydrous THF (50 mL) suspension of
18 **[(PhSiO_{1.5})₈]_{Σ8}** (0.968 mmole) was added a slight excess of anhydrous
19 tetramethylammonium fluoride (91 mg, 0.98 mmole). After stirring under a nitrogen
20 atmosphere for several hours the solution clarified as the product dissolves in THF.
21 The solution was filtered through diatomaceous earth and the solvent removed
22 under vacuum to give a quantitative yield of the salt with fluoride inside the
23 silsesquioxane cage. ¹⁹F NMR (in THF) -26.5 (s) ppm. ²⁹Si NMR (in THF) -80.7 (s)
24 ppm.

- 1 **(Me)₄N[(VISiO_{1.5})₈@F]_{Σ8}** To a 0.5 gram anhydrous THF (50 mL) suspension of
2 [(VISiO_{1.5})₈]_{Σ8} (0.790 mmole) was added a slight excess of anhydrous
3 tetramethylammonium fluoride (75 mg, 0.80 mmole). After stirring under a nitrogen
4 atmosphere for several hours the solution clarified as the product dissolves in THF.
5 The solution was filtered through diatomaceous earth and the solvent removed
6 under vacuum to give a quantitative yield of the salt with fluoride inside the
7 silsesquioxane cage. ¹⁹F NMR (in THF) -25.5 (s) ppm. ²⁹Si NMR (in THF) -83.0 (s)
8 ppm.
- 9 **(Me)₄N[(CF₃(CH₂)₃SiO_{1.5})₈@F]_{Σ8}** To a 1 gram anhydrous THF (50 mL) suspension of
10 [(CF₃(CH₂)₃SiO_{1.5})₈]_{Σ8} (0.816 mmole) was added a slight excess of anhydrous
11 tetramethylammonium fluoride (76 mg, 0.82 mmole). After stirring under a nitrogen
12 atmosphere for several hours the solution clarified as the product dissolves in THF.
13 The solution was filtered through diatomaceous earth and the solvent removed
14 under vacuum to give a quantitative yield of the salt with fluoride inside the
15 silsesquioxane cage. ¹⁹F NMR (in THF) -28.8 (s, 1F), -69.9 (s, 24F) ppm. ²⁹Si NMR
16 (in THF) -70.4 (s) ppm.
- 17 **(Me)₄N[(CF₃CF₂CF₂CF₂CH₂CH₂SiO_{1.5})₈@F]_{Σ8}** To a 1 gram anhydrous THF (50 mL)
18 suspension of [(CF₃CF₂CF₂CF₂CH₂CH₂SiO_{1.5})₈]_{Σ8} (0.396 mmole) was added a slight
19 excess of anhydrous tetramethylammonium fluoride (37 mg, 0.40 mmole). After
20 stirring under a nitrogen atmosphere for several hours the solution clarified as the
21 product dissolves in THF. The solution was filtered through diatomaceous earth and
22 the solvent removed under vacuum to give a quantitative yield of the salt with
23 fluoride inside the silsesquioxane cage. ¹⁹F NMR (in THF) -28.8 (s, 1F), -82.4 (t,
24 24F), -117.2 (m, 16F), -125.4 (m, 16F), -127.1 (m, 16F) ppm. ²⁹Si NMR (in THF) -

1 70.1 (s) ppm.

2 **(Me)₄N[(CF₃CF₂CF₂CF₂CF₂CF₂CH₂CH₂SiO_{1.5})₈@F]_{Σ8}** To a 1 gram anhydrous THF
 3 (50 mL) suspension of [(CF₃CF₂CF₂CF₂CF₂CF₂CH₂CH₂SiO_{1.5})₈]_{Σ8} (0.295 mmole)
 4 was added a slight excess of anhydrous tetramethylammonium fluoride (28 mg,
 5 0.30 mmole). After stirring under a nitrogen atmosphere for several hours the
 6 solution clarified as the product dissolves in THF. The solution was filtered through
 7 diatomaceous earth and the solvent removed under vacuum to give a quantitative
 8 yield of the salt with fluoride inside the silsesquioxane cage. ¹⁹F NMR (in THF) -30.6
 9 (s, 1F), -84.1 (t, 24F), -119.0 (m, 16F), -124.7 (m, 16F), -125.7 (m, 16F), -126.3 (m,
 10 16F) ppm. ²⁹Si NMR (in THF) -70.6 (s) ppm.

11 **(Me)₄N[(CF₃CF₂CF₂CF₂CF₂CF₂CF₂CH₂CH₂SiO_{1.5})₈@F]_{Σ8}** To a 1 gram
 12 anhydrous THF (10 mL) suspension of
 13 [(CF₃CF₂CF₂CF₂CF₂CF₂CF₂CH₂CH₂SiO_{1.5})₈]_{Σ8} (0.279 mmole) was added a slight
 14 excess of anhydrous tetramethylammonium fluoride (27 mg, 0.29 mmole). After
 15 stirring under a nitrogen atmosphere for several hours the solution clarified as the
 16 product dissolves in THF. The solution was filtered through diatomaceous earth and
 17 the solvent removed under vacuum to give a quantitative yield of the salt with
 18 fluoride inside the silsesquioxane cage. ¹⁹F NMR (in THF) -28.7 (s, 1F), -82.2 (t,
 19 24F), -117.2 (m, 16F), -122.6 (m, 16F), -122.8 (m, 32F), -123.7 (m, 16F), -124.5 (m,
 20 16F), -127.2 (m, 16F) ppm. ²⁹Si NMR (in THF) -70.7 (s) ppm.

21 Cation Exchange for CationPOSS@F Cages

22 The utility of F@POSS cages can be controlled through variation of the R
 23 group on the cage and through variation of the counter cation associated with the

1 cage. Numerous advantages can be realized by exchanging nonreactive onium
2 cations such as tetramethyl ammonium, and tetrabutyl ammonium with onium
3 cations containing reactive groups capable of polymerization, catalytic activity,
4 wetability, color and pigmentation properties, radiation absorbance, biological
5 activity, or therapeutic properties. Such functional activity is highly desired for the
6 practical utility of F@POSS.

7 Onium exchange can be carried out by dissolving tetramethylammonium
8 octaphenyl octasilsesquioxane fluoride $(\text{Me})_4\text{N}[(\text{PhSiO}_{1.5})_8\text{@F}]_{\Sigma 8}$ into THF followed
9 by addition of a stoichiometrically equivalent amount of cetyltrimethyl ammonium
10 chloride and stirring for 10 minutes at 25°C. Then 50ml of hexane was added to the
11 mixture to form a second layer into which the resulting Cetyl $(\text{Me})_3\text{N}[(\text{PhSiO}_{1.5})_8\text{@F}]_{\Sigma 8}$
12 was extracted. Upon removal of volatiles and drying a quantitative amount of
13 product was obtained. The Cetyl $(\text{Me})_3\text{N}[(\text{PhSiO}_{1.5})_8\text{@F}]_{\Sigma 8}$ was observed to be
14 significantly more effective as a biocidal agent than the tetramethylammonium cation.

15 $\text{K}[(\text{PhSiO}_{1.5})_8\text{@F}]_{\Sigma 8}$ Similarly, cation exchange of the onium groups on
16 F@POSS with an inorganic cation such as K^+ , Na^+ , Li^+ , Ag^+ is desirable as they
17 afford higher temperature stability and do not produce a noticeable smell when
18 heated. Onium exchange for inorganic cations was successfully accomplished for
19 example, by addition of KPF₆ to a THF solution of tetramethylammonium octaphenyl
20 octasilsesquioxane fluoride $(\text{Me})_4\text{N}[(\text{PhSiO}_{1.5})_8\text{@F}]_{\Sigma 8}$. This mixture was allowed to
21 stir for about 15 minutes, at which time the solution was filtered and the POSS
22 product was isolated by filtration and the $[(\text{Me})_4\text{N}]^+\text{PF}_6^-$ salt was retained in solution.
23 The POSS product was collected in near quantitative yield upon removal of volatiles
24 and evaluated with TGA and FTIR relative to the starting materials. Similar cation

exchange can be carried out using other inorganic salts (e.g. AgNO₃, CuSO₄) in which one of the products is water soluble.

Polymerization of Fluorinated POSS Cages to

[CF₃(CH₂)₃SiO_{1.5})₇(propylmethacrylate)₁SiO_{1.5})₇]₈/methylmethacrylate copolymers

Copolymers of hepta(trifluoropropyl)propylmethylmethacrylate octamer POSS ([CF₃(CH₂)₃SiO_{1.5})₇(propylmethacrylate)SiO_{1.5})₁]₈) and methylmethacrylate were prepared using the following general procedure. Under a nitrogen atmosphere, a dry, oxygen free solution of toluene (2.72 mL, 2.35 g), [CF₃(CH₂)₃SiO_{1.5})₇(propylmethacrylate)SiO_{1.5})₁]₈ (300 mg, 0.245 mmol), methylmethacrylate (2702 mg, 26.99 mmol) and AIBN (11.0 mg, 0.068 mmol) was prepared and heated to 63 °C for 16 hours. This solution was then diluted with 15 mL of CHCl₃ and precipitated into 75 mL of methanol. After stirring overnight a white solid formed, and was collected by vacuum filtration in 85% yield and ¹H NMR spectroscopy showed no unreacted monomers. In general it was observed that glass transition of the copolymers decreases with increasing [CF₃(CH₂)₃SiO_{1.5})₇(propylmethacrylate)SiO_{1.5})₁]₈ content relative to that of methylmethacrylate and ranges from 120°C to 130°C, while the heat capacity and thermal gravimetric performance increases with higher POSS loadings. The contact angle for a series of these copolymers is listed in Table 1.

Table 1. Contact angles of [CF₃(CH₂)₃SiO_{1.5})₇(propylmethacrylate)₁SiO_{1.5})₇]₈/methylmethacrylate copolymers.

Composition	Average Contact Angle	Standard Deviation
PMMA	78.5	8.5
3/97 [CF ₃ (CH ₂) ₃ SiO _{1.5}) ₁₂] ₁₂ /PMMA	89.7	5.8
5/95 [CF ₃ (CH ₂) ₃ SiO _{1.5}) ₁₂] ₁₂ /PMMA	80.5	11.2

10/90 $[\text{CF}_3(\text{CH}_2)_3\text{SiO}_{1.5}]_{12}/\text{PMMA}$	84.3	10.9
20/80 $[\text{CF}_3(\text{CH}_2)_3\text{SiO}_{1.5}]_{12}/\text{PMMA}$	88.4	7.0

1

2 Synthesis of Externally Fluorinated POSS

3 In a 1L volumetric flask, combine one mole of

4 $[(\text{CF}_3\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OEt})_3 \text{ or}$

5 $[(\text{CF}_3\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OEt})_3$, 27.20 g was made from 100 mL of DI

6 water and 0.774 g of 85% KOH and absolute ethanol. Transfer to a 2L flask and stir

7 under nitrogen for 5 days. A white precipitate forms, which is removed by vacuum

8 filtration. The precipitate is dissolved in dichloromethane and washed three times

9 with DI water. The solvent is removed *in vacuo* just until precipitate starts to form.

10 This cloudy solution is dripped into rapidly stirring methanol yielding a fluffy white

11 precipitate. The solid is removed by vacuum filtration. ^{29}Si NMR (CD_2Cl_2) δ :

12 $[(\text{CF}_3\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{SiO}_{1.5})_8 @ \text{F}]_{\Sigma 8} / [(\text{CF}_3\text{CF}_2\text{CF}_2 \text{ CF}_2$

13 $\text{CF}_2\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{SiO}_{1.5})_8 @ \text{F}]_{\Sigma 8}$, -66.7 ppm. Melting point

14 $[(\text{CF}_3\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{SiO}_{1.5})_8 @ \text{F}]_{\Sigma 8}$ 124 °C, $[(\text{CF}_3\text{CF}_2\text{CF}_2 \text{ CF}_2$

15 $\text{CF}_2\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{SiO}_{1.5})_8 @ \text{F}]_{\Sigma 8}$ 138 °C. Typical yields of product range from

16 98-99% can be obtained at reaction concentrations of 0.1M. More concentrated

17 preparations can also be carried out with mechanical stirring of the reaction.

18 Additionally fluorinated POSS cages also bearing reactive groups are

19 desirable for surface modification of metals, fillers, and composites can be prepared.

20 Preferred reactive groups include but are not limited to silanols, siloxides,

21 methacrylates, thiols, amines, acids, esters, alcohols, isocyanates, epoxides, and

22 Lewis acidic metals.

signage, utensils and optical applications. PMMA is widely utilized in dental and prosthetic application, paints, adhesives, and coatings in which the uptake of moisture causes degradation of mechanical properties. The contact angles for a series of these blends were measured after annealing for 2 hours at 140°C (Table 3) and after annealing for 2 hours at 175°C (Table 4).

Table 3 . Contact angles of $[\text{CF}_3(\text{CH}_2)_3\text{SiO}_{1.5}]_{12}\Sigma_{12}$ and PMMA blends annealed at 140°C.

Composition	Average Contact Angle	Standard Deviation
PMMA	74.6	14.3
3% $[\text{CF}_3(\text{CH}_2)_3\text{SiO}_{1.5}]_{12}\Sigma_{12}$ blend	78.2	4.6
5% $[\text{CF}_3(\text{CH}_2)_3\text{SiO}_{1.5}]_{12}\Sigma_{12}$ blend	87.6	2.1
10% $[\text{CF}_3(\text{CH}_2)_3\text{SiO}_{1.5}]_{12}\Sigma_{12}$ blend	97.4	3.5
20% $[\text{CF}_3(\text{CH}_2)_3\text{SiO}_{1.5}]_{12}\Sigma_{12}$ blend	100.5	2.6

Table 4 . Contact angles of $[\text{CF}_3(\text{CH}_2)_3\text{SiO}_{1.5}]_{12}\Sigma_{12}$ and PMMA blends annealed at 175°C.

Composition	Average Contact Angle	Standard Deviation
PMMA	82.1	12.1
3% $[\text{CF}_3(\text{CH}_2)_3\text{SiO}_{1.5}]_{12}\Sigma_{12}$ blend	82.6	5.25
5% $[\text{CF}_3(\text{CH}_2)_3\text{SiO}_{1.5}]_{12}\Sigma_{12}$ blend	83.3	2.0
10% $[\text{CF}_3(\text{CH}_2)_3\text{SiO}_{1.5}]_{12}\Sigma_{12}$ blend	90.0	1.3
20% $[\text{CF}_3(\text{CH}_2)_3\text{SiO}_{1.5}]_{12}\Sigma_{12}$ blend	96.5	3.9

Properties of Nonfluorinated Polymers Containing Externally Fluorinated POSS and Internally Fluorinated POSS

Nonfluorinated thermoplastics were obtained from a variety of commercial suppliers. The melting and processing temperature for each polymer was determined by differential scanning calorimetry (DSC). Externally and internally fluorinated POSS were prepared as described. A general method for incorporation of the POSS into the thermoplastic polymer utilized a twin screw extruder

1 (MicroCompounder, DACA Instruments) and compounding of the polymer and
2 POSS thoroughly until a steady-state of mixer torque was observed.

3 Thermosetting polymers can similarly be utilized in which the POSS is
4 incorporated via both high and low shear mixing and copolymerization. The
5 preferred method is dependent upon the visual homogenization of the system and
6 the viscosity of the initial resin mixture.

7 In general the incorporation of externally fluorinated and internally fluorinated
8 POSS was effective at increasing the hydrophobicity of the polymers into which it
9 was incorporated.

10 Examples provided in Figures 7-10 illustrate trends for the enhancement and
11 are not intended to represent limitations on the scope, range or utility, or
12 effectiveness of the method. It is realized that differing degrees of hydrophobicity
13 are required for specific applications along with other desirable properties such as
14 mechanical, thermal, biological, optical, processing, and finish properties.

15 While certain representative embodiments and details have been shown for
16 purposes of illustrating the invention, it will be apparent to those skilled in the art that
17 various changes in the methods and apparatus disclosed herein may be made
18 without departing from the scope of the invention which is defined in the appended
19 claims.

20 What is claimed is:

CLAIMS

1. A method of alloying an internally fluorinated nanostructured chemical selected from the group consisting of POSS cages containing a fluorine ion inside the cage and POS cages containing a fluorine ion inside the cage into a nonfluoropolymer, comprising the step of compounding the internally fluorinated nanostructured chemical into the polymer.
2. A method according to claim 1, wherein a mix of different nanostructured chemicals is blended into the polymer.
3. A method according to claim 1, wherein the nonfluorinated polymer is in a physical state selected from the group consisting of oils, amorphous, semicrystalline, crystalline, elastomeric, rubber, and crosslinked materials.
4. A method according to claim 1, wherein the nonfluorinated polymer contains a chemical sequence and related polymer microstructure.
5. A method according to claim 1, wherein the polymer is a polymer coil, a polymer domain, a polymer chain, a polymer segment, or mixtures thereof.
6. A method according to claim 1, wherein the nanostructured chemical reinforces the nonfluorinated polymer at a molecular level.
7. A method according to claim 1, wherein the nanostructured chemical contributes to volume of the polymer.
8. A method according to claim 1, wherein the nanostructured chemical contributes to surface area of the polymer.
9. A method according to claim 1, wherein the compounding is nonreactive.
10. A method according to claim 1, wherein the compounding is reactive.
11. A method according to claim 1, wherein a physical property of the nonfluorinated polymer is improved as a result of incorporating the nanostructured chemical into the polymer.

12. A method according to claim 11, wherein the physical property comprises a member selected from the group consisting of lubricity, contact angle, water repellency, adhesion to a polymeric surface, adhesion to a composite surface, adhesion to a metal surface, water repellency, density, low dielectric constant, thermal conductivity, glass transition, viscosity, melt transition, storage modulus, relaxation, stress transfer, abrasion resistance, fire resistance, biological compatibility, gas permeability, and porosity.
13. A method according to claim 1, wherein the compounding step is accomplished by blending the nanostructured chemical into the polymer.
14. A method according to claim 1, wherein the compounding step is accomplished by a blending process selected from the group consisting of melt blending, dry blending, and solution blending.
15. A method according to claim 1, wherein the nanostructured chemical functions as a plasticizer.
16. A method according to claim 1, wherein the nanostructured chemical functions as a filler.
17. A method according to claim 1, wherein the nanostructured chemical functions as both a plasticizer and a filler.
18. A method according to claim 1, wherein the nanostructured chemical is selectively compounded into the polymer such that the nanostructured chemical is incorporated into a predetermined region within the polymer.
19. A polymer composition produced by a method according to claim 1.
20. The method of claim 1, wherein the compounding allows control of the molecular motion of the polymer.
21. A method according to claim 20, wherein a time dependent property is enhanced as a result of compounding the nanostructured chemical into the polymer.

22. A method according to claim 21, wherein the time dependent property is selected from the group consisting of T_g , HDT, modulus, creep, set, permeability, erosion resistance, abrasion resistance.
23. The method of claim 1, wherein the nanostructured chemical is selected to have chemical properties compatible with a selected region of the polymer, and thereby reinforces a selected region of the polymer.
24. The method of claim 1, further comprising the step of blending the nanostructured chemical with a particulate material.
25. The method of claim 24, wherein the particulate material is selected from the group consisting of metals, minerals, silicacious powders, and carbon.