essential both with respect to fire retardancy and the other physical properties of the polymer POSS-composite.

Incorporation of POSS in a monomer mixture to obtain a polymer POSS composite is not trivial since the properties of the POSS must allow it to be intimately blended with the monomer before polymerization occurs.

The aim of present invention is to provide novel POSS compounds having excellent properties as fire retardants, while offering improved solubility properties in plasticizers allowing them to be homogenously dispersed in various polymer blends.

Summary

The present disclosure is defined by the appended claims and in the following:

In one aspect, the present disclosure provides a silsesquioxane of formula:

$(R_1SiO_{1,5})_x\ (R_2SiO_{1,5})_y\ (R_3SiO_{1,5})_z$, wherein

$x \geq 1$, $y \geq 1$, $z \geq 1$, and $x + y + z = 6,8,10$ or 12;

R_1 is L_1-phthalimide, wherein L_1 is a residue selected from the group consisting of saturated or unsaturated C_1-C_8 hydrocarbon radicals which may be straight, branched or cyclic; and substituted or non-substituted arylene; wherein the carbon chains of said residues optionally include one or more of the elements oxygen and nitrogen; and the phthalimide is optionally substituted by one or more halogen, C_1-C_6 alkyl, -COOH,-OH or -NO_2;

R_2 is a residue selected from the group consisting of saturated or unsaturated C_1-C_{18} hydrocarbon radicals which may be straight, branched or cyclic; wherein the carbon chains of said residues optionally include one or more oxygens and are optionally substituted by one or more halogens;

and

R_3 is L_2-NH-CO-R_4, wherein L_2 is a residue selected from the group consisting of saturated or unsaturated C_1-C_8 hydrocarbon radicals which may be straight, branched or cyclic; and substituted or non-substituted arylene; wherein the carbon chains of said residues optionally include one or more of the elements oxygen and nitrogen; and wherein R_4 is a C_1-C_{34} alkyl or a C_8-C_{34} alkene.

The term “the carbon chains of said residues optionally include one or more of the elements oxygen and nitrogen” is intended to mean that the carbon chains may include an ether moiety R-O-R or a secondary amine moiety R-NH-R.

In an example of the silsesquioxane according to the first aspect, L_1 may be C_1-C_6 alkyl, phenyl or vinyl.

In an example of the silsesquioxane according to the first aspect, R_2 may be a C_1-C_{18} alkyl, a C_2-C_7 alkene or a phenyl group, optionally substituted by one or more halogens.

In an example of the silsesquioxane according to the first aspect, R_2 may be a C_1-C_8 alkyl, a C_2-C_5 alkene or a phenyl group, optionally substituted by one or more halogens.

In an example of the silsesquioxane according to the first aspect, L_2 may be a C_1-C_6 alkyl, phenyl or vinyl.

In an example of the silsesquioxane according to the first aspect, R_4 may be a C_8-C_{34} alkyl or a C_{12}-C_{24} alkene.

In an example of the silsesquioxane according to the first aspect, R_4 may be a C_{12}-C_{24} alkyl or a C_{12}-C_{24} alkene.

In an example of the silsesquioxane according to the first aspect, R_4 may be a C_{18}-C_{22} alkyl or a C_{18}-C_{22} alkene.

In an example of the silsesquioxane according to the first aspect L_1 and L_2 may be identical. In other words, L_1 is equal to L_2.

In an example of the silsesquioxane according to the first aspect, L_1 and L_2 may both be a C_1-C_6 alkyl, and R_2 is a C_1-C_8 alkyl, a C_1-C_7 alkene or a phenyl group.

In an example of the silsesquioxane according to the first aspect, R_4 may be derived from a suitable fatty acid, such as stearic acid, lauric acid, behenic acid or soya acid.

The present disclosure provides a silsesquioxane of formula:

$$(H_2N\text{-}L_1\text{-}SiO_{1,5})_x\ (R_2SiO_{1,5})_y, \text{ wherein}$$

$x \geq 2$, $y \geq 2$, and $x + y = 6,8,10$ or 12;

L_1 is a residue selected from the group consisting of saturated or unsaturated C_1-C_8 hydrocarbon radicals which may be straight, branched or cyclic; and substituted or non-substituted arylene; wherein the carbon chains of said residues optionally include one or more of the elements oxygen and nitrogen; and

R_2 is is a residue selected from the group consisting of saturated or unsaturated C_1-C_{18} hydrocarbon radicals which may be straight, branched or cyclic; wherein the carbon chains of said residues optionally include one or more oxygens and are optionally substituted by one or more halogens.

In another aspect, the present disclosure provides a silsesquioxane of formula:

$$(H_2N\text{-}L_1\text{-}SiO_{1,5})_x\ (R_2SiO_{1,5})_y,$$ wherein

$x \geq 2$, $y \geq 2$, and $x + y = 6,8,10$ or 12;

L_1 is a residue selected from the group consisting of saturated or unsaturated C_1-C_8 hydrocarbon radicals which may be straight, branched or cyclic; and substituted or non-substituted arylene; wherein the carbon chains of said residues optionally include one or more of the elements oxygen and nitrogen; and

R_2 is a C_1-C_{18} alkyl or a C_1-C_7 alkene.

In an example of the silsesquioxane as described above, L_1 and R_2 may be as defined above.

In another aspect, the present disclosure provides for the use of a silsesquioxane as described herein as a flame retardant additive.

The flame retardant additive may be added to any suitable material in need thereof, such as any suitable polymeric material, including thermoplastic, thermoset or elastomeric polymeric materials, for instance selected from the group comprising polyvinyl chloride (PVC), polyethylene (PE), polyurethane (PU), polyamides (PA), polypropylene (PP), epoxides, various polyesters and polystyrene (PS). The flame retardant additive may advantageously be used in combination with an inorganic flame retardant additive, such as aluminium trihydrate (ATH) or antimony trioxide.

In another aspect, the present disclosure provides a plasticizer composition comprising:

a) 50-99 wt% of a plasticizer; and
b) 1-50 wt% of a silsesquioxane according to the first or second aspect;

wherein

the plasticizer is selected from a dicarboxylic/tricarboxylic ester-based plasticizers selected from the group of phthalates, 1,2-cyclohexane dicarboxylates, trimellitates, adipates, sebacates, maleates, terephthalates or any combination thereof, and

wherein the combined wt% of the plasticizer and the silsesquioxane is within the range of 90-100 wt% of the total weight of the plasticizer composition.

Where mentioned above, the plasticizer composition comprises 1-10 or 1-5 wt% of the silsesquioxane as described above.

In another aspect, the present disclosure provides a polymeric material comprising a silsesquioxane as described above or a plasticizer composition as described above. The polymeric material may be a thermoplastic, thermoset or elastomer, for instance selected from the group comprising polyvinyl chloride (PVC), polyethylene (PE), polyurethane (PU), polyamides (PA), polypropylene (PP), epoxides, various polyesters and polystyrene (PS). The polymeric material may advantageously comprise an inorganic flame retardant additive, such as aluminium trihydrate (ATH) or antimony trioxide.

In another aspect, the present disclosure provides a method of manufacturing a silsesquioxane as described above or a composition as described above comprising the steps of:

- condensing a compound of formula $H_2N\text{-}L_1\text{-}Si(OR_5)_3$ and a compound of formula $R_2Si(OR_6)_3$ in a mole ratio of 0.25 to 4, wherein

  L_1 is a residue selected from the group consisting of saturated or unsaturated C_1-C_8 hydrocarbon radicals which may be straight, branched or cyclic; and substituted or non-substituted arylene; wherein the carbon chains of said residues optionally include one or more of the elements oxygen and nitrogen;

  R_2 is a residue selected from the group consisting of saturated or unsaturated C_1-C_{18} hydrocarbon radicals which may be straight, branched or cyclic; wherein the carbon chains of said residues optionally include one or more oxygens and are optionally substituted by one or more halogens; and

  each of R_5 and R_6 are any of $-CH_3$ and $-CH_2CH_3$;

- obtaining an intermediate silsesquioxane of formula $(H_2N\text{-}L_1\text{-}SiO_{1,5})_x(R_2SiO_{1,5})_y$, wherein

  $x \geq 2$, $y \geq 2$, and $x + y = 6,8,10$ or 12;

- reacting the intermediate silsesquioxane with a first compound of formula LG-CO-R_4, wherein LG is a suitable leaving group and R_4 is a C_1-C_{34} alkyl or a C_8-C_{34} alkene, and a second compound being phthalic

anhydride optionally substituted by one or more halogen, C_1-C_5 alkyl, -COOH, -OH or -NO_2; and

- obtaining a silsesquioxane as described above.

Where mentioned above, the mole ratio of the compound of formula H_2N-L_1-$Si(OR_5)_3$ and the compound of formula $R_2Si(OR_6)_3$ is 0.4 to 2.5.

Where mentioned above, the method comprises a step of adding the obtained silsesquioxane to a suitable plasticizer to obtain a composition according to the fourth aspect.

Where mentioned above, the first compound is added in a mole ratio of 0.2 to 0.8, 0.3 to 0.7 or 0.4 to 0.6 relative to the compound of formula H_2N-L_1-$Si(OR_5)_3$.

Where mentioned above, the first compound is added in a mole ratio of 0.1 to 0.6 relative to the intermediate silsesquioxane.

Where mentioned above, the second compound is added in a mole ratio of 0.2 to 0.8, 0.3 to 0.7 or 0.4 to 0.6 relative to the compound of formula H_2N-L_1-$Si(OR_5)_3$.

Where mentioned above, the second compound is added in a mole ratio of 0.1 to 0.6 relative to the intermediate silsesquioxane.

Where mentioned above, the first compound may be a suitable fatty acid, such as stearic acid, lauric acid, behenic acid or soya acid.

The present disclosure provides a method of manufacturing a silsesquioxane as described above, or a composition as described above, comprising the steps of:

- condensing a compound of formula H_2N-L_1-$Si(OR_5)_3$ and a compound of formula $R_2Si(OR_6)_3$ in a mole ratio of 0.25 to 4, wherein

  L_1 is a residue selected from the group consisting of saturated or unsaturated C_1-C_8 hydrocarbon radicals which may be straight, branched or cyclic; and substituted or non-substituted arylene; wherein the carbon chains of said residues optionally include one or more of the elements oxygen and nitrogen;

R_2 is a residue selected from the group consisting of saturated or unsaturated C_1-C_{18} hydrocarbon radicals which may be straight, branched or cyclic; wherein the carbon chains of said residues optionally include one or more oxygens and are optionally substituted by one or more halogens; and

each of R_5 and R_6 are any of $-CH_3$ and $-CH_2CH_3$; and

- obtaining a silsesquioxane according to the second aspect.

In another aspect, the present disclosure provides a method of manufacturing a silsesquioxane as described herein or a composition as described herein comprising the steps of:

- condensing a compound of formula H_2N-L_1-$Si(OR_5)_3$ and a compound of formula $R_2Si(OR_6)_3$ in a mole ratio of 0.25 to 4, wherein

  L_1 is a residue selected from the group consisting of saturated or unsaturated C_1-C_8 hydrocarbon radicals which may be straight, branched or cyclic; and substituted or non-substituted arylene; wherein the carbon chains of said residues optionally include one or more of the elements oxygen and nitrogen;

  R_2 is a C_1-C_{18} alkyl or a C_1-C_7 alkene; and

  each of R_5 and R_6 are any of $-CH_3$ and $-CH_2CH_3$;

- obtaining a silsesquioxane as described herein.

The present disclosure provides a silsesquioxane obtainable by the method as described above.

As used herein, the terms “alkyl” and “alkene” are intended to encompass straight chained, cyclic and branched alkyls and alkenes, respectively.

In other words, a C_1-C_{18} alkyl may for instance be a methyl ethyl, propyl, sec-propyl, n-butyl, t-butyl, sec-butyl, pentyl, cyclopentyl, hexyl, cyclohexyl, octyl or octadecyl.

Detailed description of the invention

Unless specifically defined herein, all technical and scientific terms used have the same meaning as commonly understood by a skilled artisan in the fields of organic chemistry and polymer technology.

All methods and materials similar or equivalent to those described herein can be used in the practice or testing of the present invention, with suitable methods and materials being described herein. All publications, patent applications, patents, and other references mentioned herein are incorporated by reference in their entirety. In case of conflict, the present specification, including definitions, will prevail.

Where a numerical limit or range is stated herein, the endpoints are included. Also, all values and sub ranges within a numerical limit or range are specifically included as if explicitly written out.

The background for the present invention was the desire to provide novel POSS compounds having improved fire retardancy and appropriate solubility for incorporation into polymer blends. The novel POSS should preferably not have any negative impact upon the mechanical properties of the final polymeric material.

Claims

1. A silsesquioxane of formula:

$$(R_1SiO_{1,5})_x\ (R_2SiO_{1,5})_y\ (R_3SiO_{1,5})_z,\ \text{wherein}$$

$x \geq 1$, $y \geq 1$, $z \geq 1$, and $x + y + z = 6,8,10$ or 12;

R_1 is L_1-phthalimide, wherein L_1 is a residue selected from the group consisting of saturated or unsaturated C_1-C_8 hydrocarbon radicals which may be straight, branched or cyclic; and substituted or non-substituted arylene; wherein the carbon chains of said residues optionally include one or more of the elements oxygen and nitrogen; and the phthalimide is optionally substituted by one or more halogen, C_1-C_6 alkyl, -COOH, -OH or -NO_2;

R_2 is a residue selected from the group consisting of saturated or unsaturated C_1-C_{18} hydrocarbon radicals which may be straight, branched or cyclic; wherein the carbon chains of said residues optionally include one or more oxygens and are optionally substituted by one or more halogens;

and

R_3 is L_2-NH-CO-R_4, wherein L_2 is a residue selected from the group consisting of saturated or unsaturated C_1-C_8 hydrocarbon radicals which may be straight, branched or cyclic; and substituted or non-substituted arylene; wherein the carbon chains of said residues optionally include one or more of the elements oxygen and nitrogen; and wherein R_4 is a C_1-C_{34} alkyl or a C_8-C_{34} alkene.

2. A silsesquioxane according to claim 1, wherein L_1 is C_1-C_6 alkyl, phenyl or vinyl.

3. A silsesquioxane according to claim 1 or 2, wherein R_2 is a C_1-C_{18} alkyl, a C_1-C_7 alkene or a phenyl group, optionally substituted by one or more halogens.

4. A silsesquioxane according to any of the preceding claims, wherein R_2 is a C_1-C_8 alkyl, a C_1-C_5 alkene or a phenyl group, optionally substituted by one or more halogens.

5. A silsesquioxane according to any of the preceding claims, wherein L_2 is C_1-C_6 alkyl, phenyl or vinyl.

6. A silsesquioxane according to any of the preceding claims, wherein R_4 is a C_{12}-C_{24} alkyl or a C_{12}-C_{24} alkene.

7. A silsesquioxane according to any of the preceding claims, wherein R_4 is a C_{18}-C_{22} alkyl or a C_{18}-C_{22} alkene.

8. A silsesquioxane according to any of the preceding claims, wherein L_1 and L_2 are identical.

9. A silsesquioxane according to any of the preceding claims, wherein L_1 and L_2 are both C_1-C_6 alkyl, and R_2 is a C_1-C_8 alkyl, a C_1-C_7 alkene or a phenyl group.

10. A silsesquioxane of formula:

$$(H_2N\text{-}L_1\text{-}SiO_{1,5})_x\ (R_2SiO_{1,5})_y, \text{ wherein}$$

$x \geq 2$, $y \geq 2$, and $x + y = 6,8,10$ or 12;

L_1 is a residue selected from the group consisting of saturated or unsaturated C_1-C_8 hydrocarbon radicals which may be straight, branched or cyclic; and substituted or non-substituted arylene; wherein the carbon chains of said residues optionally include one or more of the elements oxygen and nitrogen; and

R_2 is a C_1-C_{18} alkyl or a C_1-C_7 alkene.

11. Use of a silsesquioxane according to any of the preceding claims as a flame-retardant additive.

12. A plasticizer composition comprising:
    a) 50-99 wt% of a plasticizer; and
    b) 1-50 wt% of a silsesquioxane according to any of claims 1-10;

    wherein

    the plasticizer is selected from a dicarboxylic/tricarboxylic ester-based plasticizers selected from the group of phthalates, 1,2-cyclohexane

dicarboxylates, trimellitates, adipates, sebacates, maleates, terephthalates or any combination thereof, and

wherein the combined wt% of the plasticizer and the silsesquioxane is within the range of 95-100 wt% of the total weight of the plasticizer composition.

13. A polymeric material comprising a silsesquioxane according to any of claims 1-10 or a plasticizer composition according to claim 12.

14. A method of manufacturing a silsesquioxane according to any of claims 1-9 or a composition according to claim 12 comprising the steps of:

- condensing a compound of formula $H_2N\text{-}L_1\text{-}Si(OR_5)_3$ and a compound of formula $R_2Si(OR_6)_3$ in a mole ratio of 0.25 to 4, wherein

  L_1 is a residue selected from the group consisting of saturated or unsaturated C_1-C_8 hydrocarbon radicals which may be straight, branched or cyclic; and substituted or non-substituted arylene; wherein the carbon chains of said residues optionally include one or more of the elements oxygen and nitrogen;

  R_2 is a residue selected from the group consisting of saturated or unsaturated C_1-C_{18} hydrocarbon radicals which may be straight, branched or cyclic; wherein the carbon chains of said residues optionally include one or more oxygens and are optionally substituted by one or more halogens; and

  each of R_5 and R_6 are any of $-CH_3$ and $-CH_2CH_3$;

- obtaining an intermediate silsesquioxane of formula $(H_2N\text{-}L_1\text{-}SiO_{1,5})_x(R_2SiO_{1,5})_y$, wherein

  $x \geq 2$, $y \geq 2$, and $x + y = 6,8,10$ or 12;

- reacting the intermediate silsesquioxane with a first compound of formula LG-CO-R_4, wherein LG is a suitable leaving group and R_4 is a C_1-C_{34} alkyl or a C_8-C_{34} alkene, and a second compound being phthalic anhydride optionally substituted by one or more halogen, C_1-C_5 alkyl, -COOH, -OH or $-NO_2$; and

- obtaining a silsesquioxane according to any of claims 1-9.

15. A method of manufacturing a silsesquioxane according to claim 10 or a composition according to claim 12 comprising the steps of:

- condensing a compound of formula $H_2N\text{-}L_1\text{-}Si(OR_5)_3$ and a compound of formula $R_2Si(OR_6)_3$ in a mole ratio of 0.25 to 4, wherein

  L_1 is a residue selected from the group consisting of saturated or unsaturated C_1-C_8 hydrocarbon radicals which may be straight, branched or cyclic; and substituted or non-substituted arylene; wherein the carbon chains of said residues optionally include one or more of the elements oxygen and nitrogen;

  R_2 is a C_1-C_{18} alkyl or a C_1-C_7 alkene; and

  each of R_5 and R_6 are any of $-CH_3$ and $-CH_2CH_3$;

- obtaining a silsesquioxane according to claim 10.