

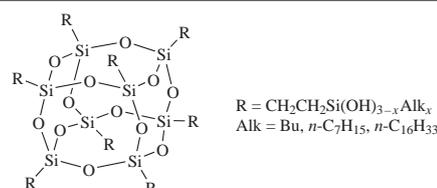
## Hydroxyl-functionalized alkyl-terminated silsesquioxanes as surface modifiers of friction geomodifiers

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Starting from octavinylsilsesquioxane, new derivatives with  $\text{CH}_2\text{CH}_2\text{SiAlk}_x(\text{OH})_{3-x}$  groups were obtained. Free hydroxyl groups at silicon atoms were employed for modifying activated vermiculite surface to study tribological properties of chromium steel friction pairs.



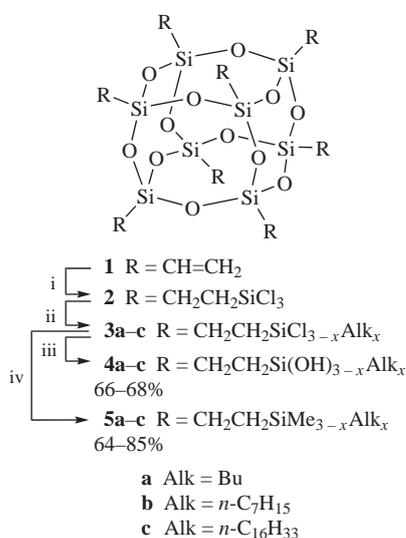
Natural geomodifiers with layered structure such as serpentinite and vermiculite as well as polymeric-silicate nanocomposites with polytetrafluoroethylene linkers find use as antifriction thin film coatings.<sup>1–4</sup> Currently, more attention is paid to the synthesis, study of physicochemical properties and application of hyperbranched polymers and compounds with dendrimeric structure suitable for practical purpose.<sup>5–8</sup> Polyamidoamine dendrimers were used to create wear-resistant antifriction coatings on the silicon surface.<sup>9,10</sup> In addition, silicon-organic dendrimers based on polyhedral oligosilsesquioxanes, in particular octaorganosilsesquioxanes, are characterized by high functionality, thermal stability, and allow hydrophobic and oleophobic coatings to be formed.<sup>11–14</sup> In this study, octavinylsilsesquioxane **1** was derivatized to access compounds with improved tribological characteristics of modified vermiculite.

The preparation of octasubstituted hydroxyl-functionalized alkyl-terminated silsesquioxanes was carried out in three stages (Scheme 1). The first stage included hydrosilylation of **1** with trichlorosilane in the presence of hexachloroplatinic acid<sup>15</sup> (the Karstedt's catalyst can also be used) to afford trichlorosilyl

derivatives **2**. The second stage was the reaction of the latter with Grignard reagents (butyl-, heptyl- and cetylmagnesium bromides). Typically, such reactions are performed upon boiling in diethyl ether. However, in our case, due to high density of functional groups, such conditions provided the replacement of less than half of chlorine atoms by alkyl fragments, moreover, with the higher homologues the substitution degree dropped. At the third stage (hydrolysis of **3**), compounds with a large number of hydroxyl groups were formed. They turned to be unstable and converted into crosslinked polymers even on storage in solutions. Therefore, to raise the degree of functionalization, the treatment of compound **2** with Grignard reagents was carried out in diethyl ether in an autoclave at 120 °C for 6 h. Thus obtained silanols **4** were viscous transparent (butyl and heptyl derivatives) or white paraffinic (cetyl derivative) substances, stable in organic solvents (more than 6 months), but in pure form capable of polycondensation and formation of crosslinked polymers within 1–14 days.

To determine the degree of functionalization of synthesized compounds **3**, after interaction of **2** with Grignard reagents, an excess of methylmagnesium iodide was added to the reaction mixture to replace the remaining chlorine atoms with methyl groups. The obtained stable alkyl-terminated silsesquioxanes **5** were suitable for studying by IR, <sup>1</sup>H, <sup>13</sup>C, <sup>29</sup>Si NMR spectroscopy and elemental analysis. According to NMR spectra of compounds **5a–c**, 19 of 24 original chlorine atoms in molecule of **2** were replaced by corresponding alkyl groups (butyl, heptyl or cetyl), while five of them were finally displaced by methyl ones. Therefore, one may state that silanol derivatives **4** contain five hydroxyl groups per molecule. Such amount of hydroxyl groups should not cause quick intermolecular condensation and provides long-term stability of obtained compounds in solutions.

Previously, it was shown that the use of polyphenylsiloxane (PPS) as a modifier of the vermiculite surface for tribotechnical tests reduces the friction coefficient at the maximum load from 0.022 to 0.014, what is several times lower than those for polytetrafluoroethylene (PTFE) (0.054) and vermiculite modified with polytetrafluoroethylene (0.050). In this work, obtained hydroxyl-functionalized alkyl-terminated octasilsesquioxanes **4a–c** were used to modify the surface of the vermiculite.<sup>†</sup> The results of tribotechnical tests are given in Table 1. The reducing of shaft wear rates after application of the compositions can be explained



**Scheme 1** Reagents and conditions: i, HSiCl<sub>3</sub>, H<sub>2</sub>PtCl<sub>6</sub>(cat.); ii, AlkMgBr, Et<sub>2</sub>O, 120 °C, 6 h (autoclave); iii, H<sub>2</sub>O/NH<sub>4</sub>Cl; iv, MeMgI, Et<sub>2</sub>O, 120 °C, 3 h.

**Table 1** Wear rate of AISI 5140 steel at various coating formation stages and with different modifying materials.

Sample	Composition	Wear rate/mg h <sup>-1</sup>			Friction coefficient in tribotests under the maximum load
		Deposition of modifier (3 min)	Coating formation (1 h)	Tribotest (3 h)	
1	PTFE <sup>4</sup>	0	0.3	1.0	0.054
2	Vermiculite + 10% PTFE <sup>4</sup>	14	2.8	0.4	0.050
3	Vermiculite <sup>4</sup>	29	1.7	0.1	0.022
4	Vermiculite + 9% PPS <sup>4</sup>	16	1.4	0.5	0.014
5	Vermiculite + 10% <b>4a</b>	9.3	4.1	0.1	0.036
6	Vermiculite + 10% <b>4b</b>	2.8	3.9	0.1	0.007
7	Vermiculite + 10% <b>4c</b>	1.2	3.3	0.8	0.007

by a more complete screening of vermiculite microcrystals, which cause wear of the shaft during the tests. The values were several times lower as compared to the reference samples 2, 3, and 4 (see Table 1). Decrease in shaft wear rate with an elongation of alkyl group was observed at the coating formation stage. During tribological tests, vermiculite modified with compounds **4a** and **4c**, as well as activated unmodified vermiculite, provided a minimum wear rate of 0.1 mg h<sup>-1</sup>; for vermiculite modified with **4c**, the wear rate was much higher, indicating the formation of weak coating that breaks down under maximum load. The friction coefficient, however, remained minimal (0.007) for heptyl (**4b**) and cetyl (**4c**) derivatives, due to the large linear dimensions of the corresponding **4b** and **4c** molecules, which provide lower

† Activated vermiculite was prepared according to described procedure.<sup>4</sup> Briefly, 0.300 g of the test substance in a toluene solution was added to 2.000 g of activated vermiculite with particle size of 1–20 μm, thoroughly mixed and dried under heating to constant weight. Then the material was washed with toluene and dried again to constant weight to give 2.214, 2.203 and 2.183 g of vermiculite modified with **4a**, **4b** and **4c**, respectively. Thus, the degree of modification with dendrimers was 71% for **4a**, 67% for **4b** and 61% for **4c**. Modified vermiculite was used for tribotechnical tests in the form of suspension in motor oil.

Tribotechnical tests were performed according to the following roll-pad scheme at a sliding velocity of 0.628 m s<sup>-1</sup>. The steel roll was mounted on the shaft of the friction machine; the pad was fixed with screws in the holder in contact with the roll. The roll-pad friction pair was located in the reservoir with the lubricant. Pads, cut from the bearing liner (Miba 33) with regular microprofile in the form of a helical groove with a depth of 16–40 μm and pitch of about 0.15 mm over the entire friction surface, what provides high fatigue strength and wear resistance and ability to sustain high specific loads, were used as an immobile sample. The roll was fabricated from AISI 5140 steel with hardness of 217 HB.

friction coefficient as compared to homologue **4a**. The use of alkyl substituents greater than C<sub>7</sub> does not cause decrease in friction coefficient and worsens the wear resistance of the coating.

In conclusion, new octavinylsilsesquioxane-derived hydroxyl-functionalized butyl-, heptyl- and cetyl-terminated silsesquioxanes were synthesized. These compounds contain five terminal hydroxyl groups providing the possibility to modify the surface of activated vermiculite. The tribological properties of friction pairs of chromium steel treated with an oil suspension of modified vermiculite were estimated. The obtained coatings have a low friction coefficient.

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#### Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2018.03.008.

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