SYNTHESIS OF HEPTA(ISOBUTYL)ETHYLTRIETHOXYSILYL-OCTASILSESQUIOXANE AND ITS APPLICATION AS A MODIFIER OF BOTH HYDRATED AND EMULSION SILICAS

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Abstract. Hepta(isobuthyl)ethyltriethoxysilyloctasilsequioxane was synthesized by hydro-silylation of hepta(isobuthyl)vinyloctasilsequioxane with triethoxysilane, over Karstedt catalyst and tetrahydrofuran. Hybrid systems of silica and monofunctional silsesquioxane (SiO₂ POSS) were obtained by solvent evaporation, using emulsion silica (ES) and hydrated silica (HS), obtained by precipitation in emulsion or water media. For their surface modification hepta(isobuthyl)ethyltriethoxysilyloctasilsequioxane was used. The hybrids were characterized by dispersion analysis (NIBS method and laser diffraction technique) and morphological analysis (transmission electron microscopy) as well as wettability profiles in an aqueous system. The adsorptive properties of the hybrids were evaluated on the basis of surface area BET, pore volume and size. The effectiveness of modification of the hybrid fillers was tested by FTIR and ²⁹Si CP MAS NMR.

keywords: silica, surface modification, silsesquioxanes cage, hybrid nanofillers

1. Introduction

Polyhedral Oligomeric Silsesquioxanes or POSS make an important group of organic-inorganic hybrid materials. They occur in many varieties differing in the size of cages, the number and type of side groups (Iyer, 2007). Particularly stable is T₈ silsesquioxane in which the organic groups R are attached to the inorganic fragments of each vertex of a silsesquioxane cage containing Si–O–Si group (Wallace, 2000).

The chemistry of silsesquioxanes is dominated by the chemistry of T₈ and its derivatives, which is related to its easy synthesis, easy isolation from the reaction mixture and high yields of the processes in which it is involved when compared to those of the other POSS (Janowski, 2008). POSS show many interesting properties
such as thermal stability, easy chemical modification and tendency to formation of nanometric size particles (Madhavan, 2009).

POSS containing 8 silicon atoms in its molecule (T₈) is most often used in synthesis of polymers (Tang, 2009; Lin, 2009), in dentistry (Wu, 2009), microelectronics and optics (Matisons, 2010). Silicas modified with cage POSS have been so far used only for determination of catalytic properties of metallocenes (Bianchini, 2005).

The main aim of this work was the synthesis of hepta(isobuthyl)-ethyltriethoxysilyloctasilsesquioxane and its application as a modifier of hydrated and emulsion silicas. Moreover, the influence of such modification process on the physicochemical properties of hybrid fillers obtained was evaluated.

2. Experimental

2.1. Synthesis of hepta(isobuthyl)ethyltriethoxysilyloctasilsesquioxane

Hepta(isobuthyl)ethyltriethoxysilyloctasilsesquioxane (K-POSS) was synthesized in the hydrosilylation reaction of previously synthesized hepta(isobuthyl)-vinylloctasilsesquioxane (Żak, 2009) with triethoxysilane (Fig. 1). The process was carried out in the presence of a Karstedt catalyst and THF as a solvent. Hepta(isobuthyl)vinyloctasilsesquioxane (5 g, 5.9 mmol), triethoxysilane with 10% excess (1.1 g, 6.7 mmol) together with 100 cm³ of THF as a solvent were placed in a three necked, round bottom flask equipped with a thermometer, condenser and magnetic bar. The Karstedt catalyst (3.7 mg, 4.07·10⁻⁷ mol Pt) was added at room temperature and the solution was heated to 60°C and kept at this temperature overnight. Then, the solvent and the excess of triethoxysilane were evaporated under vacuum to give the product as white powder (5.8 g, 98% of theoretical yield).

To control the course of synthesis and to verify the products structure the spectra: ¹H NMR (300 MHz), ¹³C NMR (75 MHz) and ²⁹Si NNR (59 MHz) were recorded on a Varian XL 300 spectrometer at room temperature using C₆D₆ as solvent. All chemicals were used as received from suppliers without any further purification.
2.2. SiO$_2$/POSS hybryd synthesis

The process was begun with production of silicas on a large laboratory scale. Two types of silica were prepared, obtained in the emulsion (ES) or in the aqueous (HS) system. The idea of production of silica fillers was presented in detail by Jesionowski (2003, 2009). The SiO$_2$/POSS hybrids were obtained by solvent evaporation. At first a fraction of ES or HS silica was introduced into the reactor and then on the silica surface a mixture made of a monosubstituted silsesquixane cage and 30 cm$^3$ toluene was introduced in doses by the atomization method. The modifying substance was introduced in the amounts of 3, 5 or 10 weight parts by mass of SiO$_2$. After introduction of the whole portion of the mixture, the contents were moved into a flask of 500 cm$^3$ in capacity and placed in a vacuum evaporator Rotavapor RII made by Büchi Labortechnik AG to perform the modification and to evaporate the solvent. Finally the product was subjected to convection drying at 120°C for 48h (chamber drier SEL–I3, made by Memmert). The idea of synthesis of hybrid fillers is schematically presented in Fig. 2.

![Fig. 2. A scheme of synthesis of SiO$_2$/POSS hybrids](image)

The final product was characterized by a number of methods. The particle size distributions of the samples were measured using Zetasizer Nano ZS and Mastersizer 2000, both made by Malvern Instruments Ltd., enabling measurements in the range 0.6–6000 nm (NIBS method) and 0.2–2000 μm (laser diffraction technique). Microstructure of the samples was analyzed by using the transmission electron microscopy images (Joel 1200 EX II). The wettability with water was measured by a tensiometer K100 made by Krüss equipped with necessary attachments. For selected hybrid systems the nitrogen adsorption/desorption isotherms were recorded using an ASAP 2020 analyzer, made by Micromeritics Instrument Co. On the basis of the isotherms the specific surface area BET ($S_{BET}$) was calculated and the pore size ($S_p$) and volume ($V_p$) were found from BJH equation. The effectiveness and degree of
modification of SiO$_2$ with POSS were estimated using the FTIR IFS 66v/S spectrophotometer made by Bruker. The $^{29}$Si CP MAS NMR spectra analysis of unmodified and modified silicas was conducted with a DSX spectrometer (Bruker).

3. Results and discussion

Results of NMR analysis of the silsesquioxane product confirmed its structure:

$^1$H NMR (C$_6$D$_6$, 298K, 300 MHz) ppm: 0.78–0.92 (CH$_2$), 1.02–1.09, 1.23–1.38 (CH$_3$), 1.93–2.14 (CH), 4.32–4.54 (–OCH$_2$),

$^{13}$C NMR (C$_6$D$_6$, 298K, 75.5 MHz) ppm: 6.3 (CH$_3$Si), 13.4 (SiCH$_2$), 18.8 (CH$_3$), 22.5, (CH$_2$), 23.9 (CH), 26.2 (CH$_3$), 53.3 (OCH$_2$),

$^{29}$Si NMR (C$_6$D$_6$, 298K, 59.6 MHz) ppm: -64.6, -66.9, -67.7, -68.2.

Functionalization of silica was performed with monosubstituted hepta-(isobuthyl)ethyltriethoxysilyloctasilsesquioxane (K-POSS). Table 1 presents the data characterizing dispersive and physicochemical properties of the hybrids obtained.

Table 1. Dispersion characterization and physicochemical properties of the hybrid systems made of hydrated silica (HS) and hepta(isobuthyl)ethyltriethoxysilyloctasilsesquioxane

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Amount of POSS modifiers (wt./wt.)</th>
<th>Polydispersity index (PdI)</th>
<th>Diameters from Zetasizer Nano ZS (nm)</th>
<th>Diameters from Mastersizer 2000 (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>–</td>
<td>0.514</td>
<td>91–220</td>
<td>3090–6440</td>
</tr>
<tr>
<td>2</td>
<td>3</td>
<td>0.663</td>
<td>122–342</td>
<td>5.91 15.40 30.64 17.18</td>
</tr>
<tr>
<td>3</td>
<td>5</td>
<td>0.543</td>
<td>122–342</td>
<td>5.72 28.48 91.58 76.00</td>
</tr>
<tr>
<td>4</td>
<td>10</td>
<td>0.749</td>
<td>91–220 1110–3580</td>
<td>6.03 31.93 96.57 79.00</td>
</tr>
</tbody>
</table>

The hybrids obtained were subjected to particle size determination to check a possible relation between the degree of agglomeration and the amount of the modifier used. Moreover, for the unmodified silicas and the hybrids, the TEM images were recorded.

Analysis of Table 1 data for the hybrid made with HS has revealed that sample 3, obtained with 5 weight parts by mass of K-POSS shows the lowest degree of agglomeration. Moreover, the polydispersity index for this sample is 0.543. The particle size distribution measured for sample 3 shows only one band covering the particle diameters from the range 122–342 nm. The same range of particle diameters was also found for sample 2, although the maximum volume contributions of particles were different for these two samples. The greatest tendency towards agglomeration was noted for sample 4, which is related to the use of the greatest amount of the modifier for its preparation.

The sizes of particles in samples 2–4, measured by Mastersizer 2000 (Table 1), varied in practically the same ranges of diameters. In sample 3 obtained with 5 weight
parts by mass of K-POSS (sample 3) 10% of particles had diameters not greater than 5.72 μm and 50% of particles had diameters not greater than 28.48 μm and 90% not greater than 91.58 μm. The mean diameter of particles in this sample D[4.3] corresponded to agglomerations of the maximum diameter of 76.00 μm. TEM images of samples 2, 3 and 4 obtained with 3, 5 and 10 weight parts by mass of K-POSS (Fig. 3) inform about their inhomogeneous structure and the presence of primary particles and secondary agglomerates. Particles of irregular shapes making larger clusters are observed for samples 2 and 3, (Figs. 3b, c). Despite the worse dispersion parameters, sample 4 (Fig. 3d) has particles of the greatest refinement, they are much smaller and the clusters they make are also small.

The hybrid systems obtained by functionalization of emulsion silica (ES) with K-POSS show much different dispersive and morphological character. The relevant data are presented in Table 2. As follows from these data, sample 7 (ES grafted with 5 weight parts by mass K-POSS) is characterised by the greatest degree of homogeneity, which is confirmed by the particle size distribution measured by Zetasizer Nano ZS. The polydispersity index of this sample is 0.219. Sample 7 also shows the lowest tendency towards agglomeration (Fig. 4b). Its particles have spherical shape and their adhesion to irregular K-POSS particles is rather strong.

Samples 6 and 8 obtained with 3 and 10 weight parts by mass of K-POSS have definitely inhomogeneous character, their particles are greater and their polydispersity indices are higher. The differences in dispersion characteristics are illustrated by TEM images (Fig. 4b,d). These samples have spherical shape particles, making primary and secondary agglomerations. Because of significant hydrophobicity of these samples, no measurements of particle size distribution by the laser diffraction method were made. The SiO₂/POSS hybrid systems obtained by mechanical method were characterized by much different dispersive and morphological properties (Szwarc 2012). The final products obtained by the mechanical method with the use of mortar mill, were made of particles with diameters of the order of 200 nm, despite the use of micrometric hydrated silica as the matrix for functionalization.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Amount of POSS modifiers (wt./wt.)</th>
<th>Polydispersity index (PdI)</th>
<th>Diameters from Zetasizer Nano ZS (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>–</td>
<td>0.252</td>
<td>255–712</td>
</tr>
<tr>
<td>6</td>
<td>3</td>
<td>0.268</td>
<td>531–1480</td>
</tr>
<tr>
<td>7</td>
<td>5</td>
<td>0.219</td>
<td>255–1280</td>
</tr>
<tr>
<td>8</td>
<td>10</td>
<td>0.447</td>
<td>825–2300</td>
</tr>
</tbody>
</table>

At the next step of hybrids characterization they were subjected to a water wettability analysis. Figure 5 presents the wettability profiles of the initial hydrated...
silica and the hybrids based on HS obtained with the use of 3, 5 and 10 weight parts by mass of K-POSS (samples 1–4), while Fig. 6 shows the wettability profiles of ES and the hybrids made of ES and K-POSS (samples 5–8). The greatest tendency to water absorption was found for sample 1, while the lowest amount of water was absorbed by sample 4, modified with 10 wt./wt. of K-POSS. The character of the wettability profiles indicates that with increasing amount of the modifying monofunctional POSS, the hydrophobic character of the product increases.

Fig. 3. TEM microphotographs of (a) pure hydrated silica and hybrid modified with (b) 3, (b) 5, and (d) 10 weight parts by mass of hepta(isobuthyl)ethyltriethoxysilyloctasilsesquioxane (K-POSS)
Fig. 4. TEM microphotographs of (a) pure emulsion silica and hybrid modified with (b) 3, (b) 5, and (d) 10 weight parts by mass of hepta(isobutyl)ethyltriethoxysilyloctasilsesquioxane (K-POSS)

The hybrids with K-POSS based on silica precipitated from the emulsion system show similar tendencies to water absorption, although sample 5 has the highest sorption capacity expressed by a mass increase of 0.32 g. The smallest mass increase was noted for sample 8, obtained with the use of 10 wt./wt. of K-POSS. It should be emphasised that the initial silicas differed significantly in hydrophilic character. Hydrated silica absorbed about 50% more water than emulsion silica.
Fig. 5. Wettability profiles obtained for hydrated silica (HS) and selected SiO$_2$/POSS hybrids

Fig. 6. Wettability profiles obtained for emulsion silica (ES) and selected SiO$_2$/POSS hybrids

Fig. 7. Nitrogen adsorption/desorption isotherms and adsorptive properties for: (a) unmodified HS (sample 1), (b) unmodified ES (sample 5) and silicas modified with 3, 5 or 10 weight parts by mass of hepta(isobuthyl)ethyltriethoxysilyloctasilsesquioxane (K-POSS)

To evaluate the adsorptive properties of the samples studied, they were subjected to determination of nitrogen adsorption/desorption isotherms. Analysis of the isotherms permitted determination of the surface area as well as pore volume and diameters (see Fig. 7). Figure 7 presents the nitrogen adsorption/desorption isotherms for the unmodified hydrated silica (HS) and emulsion silica (ES) samples and for the hybrids modified with 3, 5 or 10 wt./wt. of K-POSS. The isotherms show a systematic increase in the volume of adsorbed nitrogen with increasing relative pressure till reaching a maximum value of 240 cm$^3$/g for sample 1 at p/p$_0$=1 (Fig. 7a). For hybrids the
increase in the volume of adsorbed nitrogen after the threshold value \( (p/p_0 = 0.7) \) is not so steep and the maximum values for \( p/p_0 = 1 \) are much lower. Also the specific surface area, pore volume and pore size were drastically lower than those for unmodified samples, e.g. \( A_{\text{BET}} = 30 \text{ m}^2/\text{g} \) for sample 4 modified with 10 wt./wt. of K-POSS. A similar effect is observed for the hybrids based on ES; for the unmodified silica the specific surface area \( (A_{\text{BET}}) \) was 40 \text{ m}^2/\text{g} and for sample 8 it has decreased to 14 \text{ m}^2/\text{g} (Fig. 7b). These changes are consequences of blocking the active centres on the SiO\textsubscript{2} surface by the molecules of silsesquioxane. The pore size determined proves the mesoporous character of the hybrids obtained.

Figure 8 presents the FT-IR spectra of the unmodified silicas (HS and ES) and the hybrids obtained after the silicas modifications with 10 wt./wt. of K-POSS.

![FT-IR spectra of unmodified silicas (samples 1 and 5) and the hybrids obtained by their modification with 10 wt./wt. of K-POSS (samples 4 and 8)](image)

The FT-IR spectra (Fig. 8) revealed signals typical of K-POSS used for silica surface modification. In the range 3700–3200 cm\(^{-1}\) the spectra show the signals corresponding to the stretching vibrations of hydroxyl groups from the adsorbed water molecules. In each spectrum there was a signal assigned to \( \delta(\text{C–H}) \) in the range 2900–2850 cm\(^{-1}\). At 1350 cm\(^{-1}\) there is a band assigned to the bending vibrations of \( \gamma(\text{C–H}) \) groups. The bands appearing in the range 1500–1450 cm\(^{-1}\) and 860–700 cm\(^{-1}\) are characteristic of the vibrations of Si–C bond. Strong bands at 1100 cm\(^{-1}\) and 500 cm\(^{-1}\) correspond to the stretching vibrations of Si–O–Si. At about 850 cm\(^{-1}\) there is a band assigned to \( \delta(\text{C–C}) \) from isobutyl groups of K-POSS. Comparing the spectra presented in Fig. 8a and 8b, no significant differences were found in the content of characteristic functional groups in the filler structure, irrespective of the type of silica used.

The effectiveness of silica modification with K-POSS was verified by the \(^{29}\text{Si CP MAS NMR spectra}, which are presented in Figs. 9 and 10.

The \(^{29}\text{Si CP MAS NMR spectrum of unmodified HS (Fig. 9) shows two signals at } -110 \text{ and } -100 \text{ ppm. The main signal at } -110 \text{ ppm is assigned to three siloxane groups}
and one silanol group (Q³), while the signal at −100 ppm corresponds to four siloxane bridges (Q⁴, =Si–O–Si≡). The spectra of samples modified with K-POSS besides the Q³ and Q⁴ signals also have a band assigned to T³ group at −67 ppm. Although the presence of T² and T³ structures testifies to the chemical modification of SiO₂ surface, we cannot draw such conclusions as no changes in the intensities of Q³ and Q⁴ signals were observed as a result of functionalization with K-POSS.

![Fig. 9. $^{29}\text{Si CP MAS NMR}$ spectra of unmodified HS (Sample 1) and silica functionalized with 5 wt./wt. K-POSS (Sample 3)](image)

![Fig. 10. $^{29}\text{Si CP MAS NMR}$ spectra of unmodified ES (sample 5) and silica functionalized with 5 wt./wt. of K-POSS (sample 7)](image)

The spectrum of unmodified ES (sample 5) reveals three characteristic signals at −110, −100 and −99 ppm. The latter small signal is assigned to the double silanol groups, to the so-called silicon site Q². The spectrum of sample 7 shows additionally the T³ structure (−67 ppm), characteristic of condensation of the modifier (K-POSS) with the silica support. As a result of silica functionalization, a change in the intensity
of signals corresponding to the silanol ($Q^3$ –100 ppm) and siloxane ($Q^4$, –110 ppm) groups, which could indicate that chemical adsorption have taken place. However, because of the lack of $T^2$ structure, we can conclude only about the adhesion of cage POSS to the silica surface.

Recently, the interest in the hybrid systems has been increasing. A combination of inorganic matrix with organic–inorganic cage POSS gave products showing a number of interesting physicochemical and dispersive-morphological properties.

Modification of silica supports gives changes in the dispersive and morphological properties and enhances the hydrophobic character of the products. The process of silica modification with K-POSS proved effective as evidenced by the results of FTIR, NMR analysis and adsorption parameters. Functionalization of silica with selected POSS compounds permits controlling of the physicochemical properties of the products to meet specific target demands.

4. Conclusions

The proposed method of silica modification involving solvent evaporation has brought products of homogeneity lower than that of the initial silicas. Functionalization of the silica surface with hepta(isobuthyl)ethyltriethoxysilyloctasilsesquioxane (K-POSS) gave products containing greater size particles, showing a tendency to formation of primary and secondary agglomerates. Much better dispersive properties were obtained for the products based on the amorphous hydrated silica.

With increasing amount of the monosubstituted POSS used for functionalization, the products obtained showed increasingly higher hydrophobic character.

The functionalization with K-POSS also resulted in a significant reduction of the surface area BET, e.g. from 110 $m^2/g$ for the unmodified hydrated silica to 30 $m^2/g$ for the hybrid filler (sample 4). The same tendency was noted for the emulsion silica. The other parameters characterizing adsorptive properties such as the pore diameters and pore volume as well as the amount of nitrogen adsorbed, were also much decreased.

The proposed method of silica modification with K-POSS had advantageous effect on the physicochemical parameters as evidenced by the FT-IR results.

Analysis of $^{29}$Si CP MAS NMR spectra confirmed no chemical interactions between the silica support and the K-POSS modifier. The results indicated the condensation phenomenon and strong adhesion of the modifier to the support.

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