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SYNTHESIS AND CHARACTERISATION OF SiO_2/POSS HYBRID SYSTEMS OBTAINED USING THE MECHANICAL METHOD

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Abstract. Hybrid systems of silica and polyhedral oligomeric silsesquioxanes (SiO_2/POSS) were obtained by the mechanical method with the use of spherical or hydrated silicas, precipitated in the emulsion or aqueous environment. The SiO_2 surface was modified with the following cage silsesquioxanes: hepta(isobutyl)2-triethoxysilylethyloctasilsesquioxane, octakis ({3-glycidoxy-propyl}dimethylsiloxy)octasilsesquioxane and octakis ({3-methacryloxypropyl} dimethylsiloxy)-octasilsesquioxane. The nanofillers obtained were subjected to thorough dispersive analysis (NIBS method) and morphological analysis (transmission electron microscopy). Their wettability in water systems was evaluated and their adsorption activity was characterised by determination of the specific surface area BET, pore diameters and volume. Thermal stability of the nanofillers was checked. The effect of surface modification on the degree of coverage was assessed on the basis of elemental analysis.

keywords: SiO_2, hybrid nanofillers, polyhedral oligomeric silsesquioxanes, mechanical treatment, surface morphology

1. Introduction

Nanotechnology is a new highly attractive field of science that combines the achievements in chemistry, physics, biotechnology, informatics and material science (Makles, 2005; Swiderski, 2008). It includes fundamental studies and application at either molecular or atomic levels. The size of nanoparticles varies from 1 to 100 nm (Huang, 2010). Mineral nanomaterials are commonly used as fillers of polymer composites and their addition improves certain important parameters of the composites like thermal stability (Swiderski, 2008). Extended range of application of polymer materials has stimulated the need for new and versatile materials of improved properties. The search for new nanofillers has led to development of new organicinorganic hybrid materials such as polyhedral oligomeric silsesquioxanes (POSS).

POSS are described by the chemical formula of $(RSiO_{1.5})_n$ (Carmo do Ribeiro, 2007) and are intermediates between silica SiO_2 and silicones RSiO (Iyer, 2007). The R group localised at the corners of the cage can be an arbitrary organic substituent.

Hybrid-ceramic structure of oligosilsesquioxanes ensures high thermal stability and makes it possible to maintain the original mechanical properties of these compounds while in polymer composites (DeArmitt, 2008).

Moreover, the compounds have a wide range of melting points and decomposition temperatures and very low volatility (Chiu, 2010).

Silica which is the main skeleton or matrix of silsesquioxanes is the most common component of the Earth crust. It occurs in the amorphous or crystalline (quartz, tridymite) forms (Oldenburg, 1998; Westcott, 1998). Silica has been widely applied in nanotechnology, glass production, electronic industry, construction industry and many other areas. It is highly stable, chemically inert, shows high mechanical strength and high susceptibility to modifications (Georgakilas, 2008). Functionalisation of silica particles has been proved very successful and has been most often performed with silane proadhesive compounds, polymers and single metal atoms (Oldenburg, 1998; Westcott, 1998).

The hitherto achievements in functionalisation of the surface of silica fillers have prompted the attempts at modification of silica surface with oligosilsesquioxanes by the mechanical method and production of SiO_2/POSS type hybrid systems as a new class of nanofillers. The study is aimed at an attempt of binding POSS compounds to the silica surface to get the best possible adhesion and/ or chemical interactions between the support and the modifier. So far no such attempts have been made.

2. Experimental

POSS compounds were obtained by a two-stage synthesis including the “corner capping” and hydrosilylation reactions performed in the same conditions over a Karstedt catalyst in the amount of $1 \cdot 10^{-5}$ mol Pt/mol Si–H and toluene or tetrahydrofurane (THF) as a solvent. The syntheses of monosubstituted and octasubstituted oligosilsesquioxanes are presented in Figs. 1 and 2 (Dutkiewicz, 2009; Marciniec, 2010).

The process of hybrid production was begun with obtaining silica under laboratory conditions in the quarter-technical scale.

The silica precipitation process was preceded by preparation of two emulsions, of which the alkaline one (E1) contained appropriate volume of sodium silicate solution and cyclohexane. The other was an acidic emulsion (E2) and contained hydrochloric acid and an organic solvent. The third component of both emulsion involved the same emulsifier, added to the emulsions in various amounts. Emulsion E2 was placed in a reactor and emulsion E1 was introduced in doses to the reactor while its entire content was mixed using a homogeniser. The precipitated silica was destabilised and then, the organic solvent was distilled off.

Another sample of silica was precipitated from water solution. A 5% solution of sodium silicate and a 5% solution of sulphuric acid were added in doses to aqueous solution of the hydrophobising agent (unsaturated fatty alcohol of a medium degree of oxyethylenation 7). The coagulating agent added to this reaction mixture was sodium sulphate. The product of the reaction was white silica precipitate, which was separated from the post-reaction mixture by vacuum filtration. The precipitate was washed a few times with hot water to remove the residues of the post-reaction salt and the surfactant, then the precipitate was subjected to convection drying at 105°C for 24h.

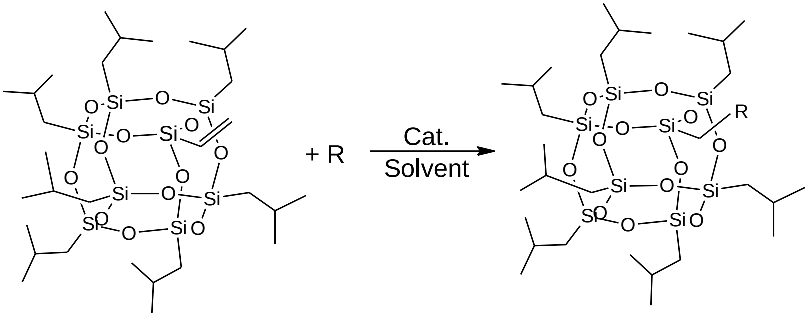


Fig. 1. Synthesis of monosubstituted polyhedral oligomeric silsesquioxanes

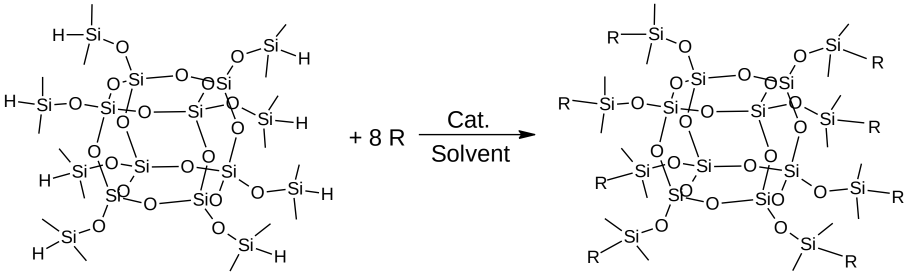


Fig. 2. Synthesis of octasubstituted polyhedral oligomeric silsesquioxanes

The hybrid nanofillers of SiO_2/POSS type were obtained by the mechanical method in an electric mortar RM 100 made by Retsch. A portion of silica precipitated in the emulsion or water system was placed in the mortar and then a mixture of POSS and 10 cm^3 of toluene was introduced by a peristaltic pump PP1B–05A made by Zalimp, at a constant rate of 0.3 cm^3/min. The modifying mixture 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 ground for 30 minutes. Then, the whole content was moved to a flask of 500 cm^3 in capacity and placed in a vacuum evaporator Rotavapor RII made by Büchi Labortechnik AG to remove the solvent. The final step was drying by convection at 120°C for 48 h (chamber drier SEL–I3, made by Memmert). The method of obtaining the hybrid nanofillers is schematically illustrated in Fig. 3.

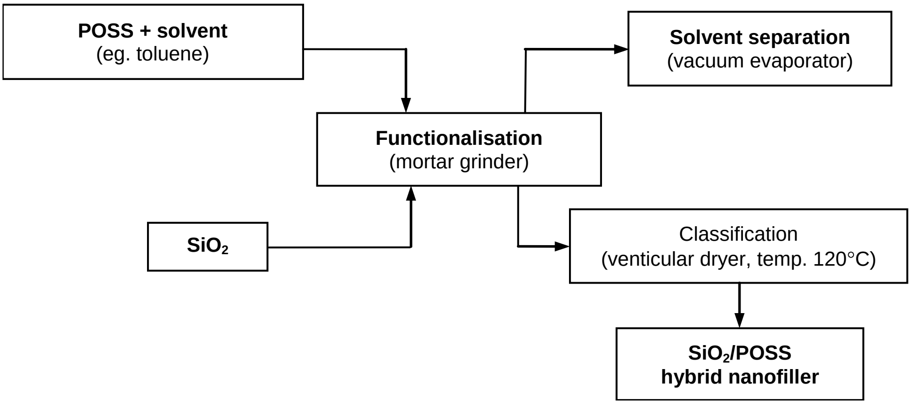


Fig. 3. Scheme of functional nanofillers mechanical preparation

The final product was accurately characterised by a number of methods. The particle size distributions of the samples were measured by a Zetasizer Nano ZS, made by Malvern Instruments Ltd., enabling measurements in the range 0.6–6000 nm (NIBS method). Microstructures of the samples were analysed in the images obtained by the transmission (TEM Joel, 1200 EX II) and scanning electron microscopy (SEM Zeiss, VO40). 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 analyser, made by Micromeritics Instrument Co., to measure the specific surface area BET (S_{BET}) and then obtain the pore diameter (*S*p) and volume (*V*p). Thermal stability of the nanomaterials obtained was assessed by thermogravimetric analysis TG/DTA (Jupiter STA 449 F3, Netzsch). The degree of coverage was evaluated on the basis of the Berendsen and de Golan formula (Berendsen, 1978), on the basis of the data from the elemental analysis (Vario EL Cube, Elementar) and specific surface area of the initial silica.

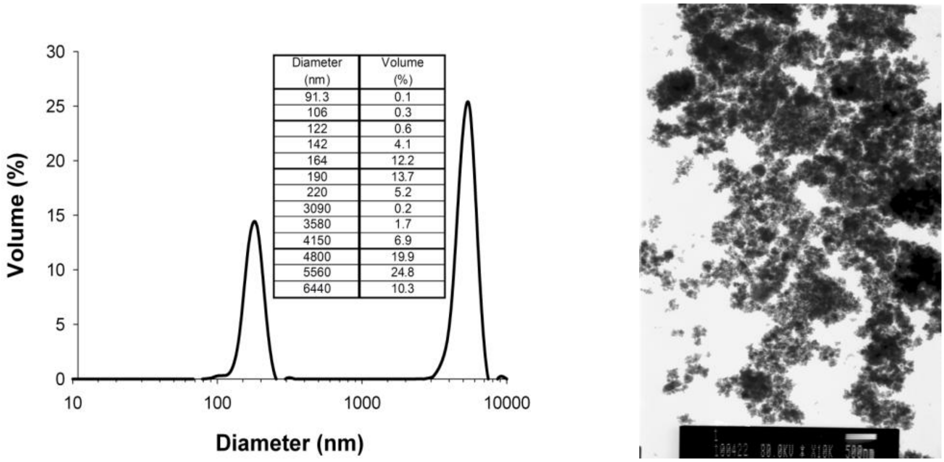
3. Results and discussion

Hybrid nanofillers were prepared on the basis of silica obtained either in the emulsion or aqueous system. The modifying substances were some monosubstituted cage silsesquioxanes hepta(isobutyl)2-triethoxysilylethyloctasilsesquioxane (K-POSS), and octasubstituted ones octakis ({3-glycidoxypropyl}dimethyl-siloxy) octasilsesquioxane (G-POSS) and octakis ({3-methacryloxypropyl }-dimethylsiloxy) octasilsesquioxane (M-POSS). The initial silicas precipitated in the emulsion or water systems were functionalised with the cage silsesquioxanes by the mechanical method. Table 1 presents results of measurements of the dispersive and physico-chemical parameters.

Table 1. Dispersive and physico-chemical properties of hybrid nanofillers made of silica precipitated in the emulsion or water systems and cage silsesquioxanes

Sample No.	Hybrid nanofillers		Dispersive properties	
	Acronym	Amount of POSS modifiers (weigh parts)	Bulk density (g/dm^3)	Particle diameter from Zetasizer Nano ZS (nm)
1	KU	–	212	91–220; 3090–6440
2	M-KU-G3	3	274	59–142; 1990–6440
3	M-KU-G5	5	260	68–164; 825–1720; 2300–6440
4	M-KU-G10	10	257	79–190; 1990–6440
5	M-KU-M3	3	275	106–190; 3580–6440
6	M-KU-M5	5	270	91–164; 2670–6440
7	M-KU-M10	10	268	79–220; 2300–6440
8	M-KU-K3	3	252	79–220; 1110–6440
9	M-KU-K5	5	248	91–142; 2670–6440
10	M-KU-K10	10	233	122–220; 4150–6440
11	KE	–	273	295–825
12	M-KE-G3	3	331	142–295
13	M-KE-G5	5	332	122–295
14	M-KE-G10	10	339	106–1480
15	M-KE-M3	3	342	142–459
16	M-KE-M5	5	345	122–396
17	M-KE-M10	10	347	164–396; 2300-4800
18	M-KE-K3	3	337	164–459
19	M-KE-K5	5	351	164–531
20	M-KE-K10	10	380	142–1110

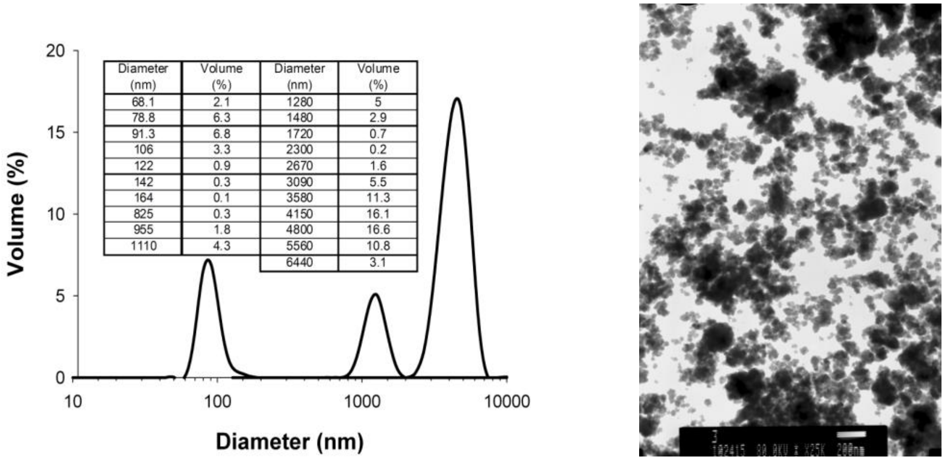
The hybrids obtained by the mechanical method have non-uniform structure. Nevertheless, the final effect is satisfactory as the hybrids show a high degree of refinement and contain particles of very small diameters (~200 nm) thanks to the use of a mortar. The unmodified silica obtained in the water system (amorphous) (Sample 1) as well as that obtained in the emulsion system (Sample 11) are characterised by the lowest bulk densities. After the surface functionalisation, the samples based on silica precipitated in the water system have bulk densities from 233 to 274 g/dm^3. For the hybrids based on silica precipitated from the emulsion system the bulk densities are even higher and vary from 331 g/dm^3 (Sample 12) to 380 g/dm^3 (Sample 20). The best dispersive features were obtained for the hybrids made of silica of either type and octakis({3-glycidoxypropyl}dimethylsiloxy)octasil- sesquioxanes. The amorphous hydrated silica shows great refinement because of its hydrophilic character. Figures 4 and 5 present the particle size distribution and TEM images of the unmodified hydrated silica and the hybrid made of this silica functionalised with 5 wt./wt. of octakis({3-glycidoxypropyl}dimethylsiloxy)- octasilsesquioxane (Samples 1 and 3). Figures 4a and 5a present bimodal particle size distribution for sample 1, with two bands covering the diameter ranges 91–220 and 3090–6440 nm. The TEM image shows particles of irregular surface having a high tendency to formation of secondary agglomerates.



Diameter (nm)	Volume (%)
91.3	0.1
106	0.3
122	0.6
142	4.1
164	12.2
190	13.7
220	5.2
3090	0.2
3580	1.7
4150	6.9
4800	19.9
5560	24.8
6440	10.3

(a) (b)

Fig. 4. (a) Particle size distribution (Zetasizer Nano ZS) and (b) TEM microphotograph of unmodified hydrated silica



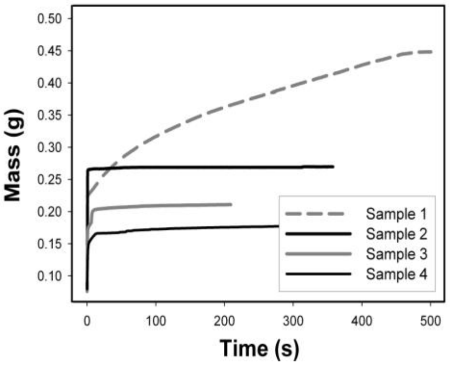
Diameter (nm)	Volume (%)	Diameter (nm)	Volume (%)
68.1	2.1	1280	5
78.8	6.3	1480	2.9
91.3	6.8	1720	0.7
106	3.3	2300	0.2
122	0.9	2670	1.6
142	0.3	3090	5.5
164	0.1	3580	11.3
825	0.3	4150	16.1
955	1.8	4800	16.6
1110	4.3	5560	10.8
		6440	3.1

(a) (b)

Fig. 5. (a) Particle size distribution (Zetasizer Nano ZS) and (b) TEM microphotograph of hydrated silica modified with 5 wt./wt. of octakis({3-glycidoxypropyl}dimethylsiloxy)octasilsesquioxane

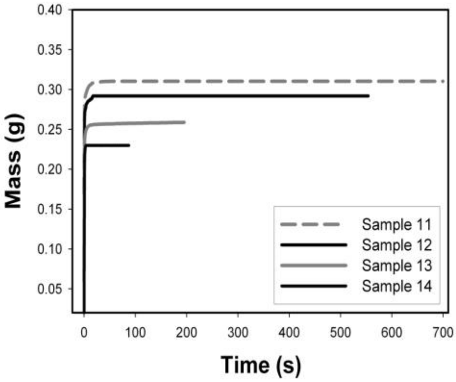
Sample 3 has much different dispersive and morphological features. The particle size distribution in Fig. 5a displays three bands covering the diameter ranges 68–164, 825–1720 and 2300–6440 nm. The TEM (Fig. 5b) image reveals highly refined particles with a low tendency to agglomeration.

The hybrid systems functionalised with octakis({3-glycidoxypropyl}-dimethylsiloxy)octasilsesquioxane was also subjected to determination of wettability. Figure 6 presents the wettability profiles of the initial hydrated silica and the hybrids obtained with 3, 5 or 10 wt./wt. of POSS (Samples 1–4). Figure 7 shows the wettability profiles of the silica obtained by precipitation in the emulsion system and the hybrids obtained on its basis (Samples 11–14). The highest tendency to water absorption was noted for Sample 1 (0.45 g), while the lowest for Sample 4 functionalised with 10 wt./wt. G-POSS (0.17 g). As follows from the character of the wettability curves, increase in the amount of the modifying substances enhances the hydrophobicity of the product which should have beneficial effect for its application as polymer filler.



(a)

Fig. 6. Profiles of wettability with water recorded for the initial hydrated silica and selected SiO_2/POSS hybrid systems



(b)

Fig. 7. Profiles of wettability with water recorded for the initial silica precipitated in the emulsion system and selected SiO_2/POSS hybrid systems

The tendency to water absorption was also observed for the hybrid systems based on the silica precipitated from the emulsion system. From among these samples the greatest sorption of 0.32 g was noted for Sample 11, while the lowest for Sample 14 obtained after modification with 10 wt./wt. of octakis({3-glycidoxypropyl}dimethylsiloxy)octasilsesquioxanes. To verify the right course of modification the adsorption activity was evaluated on the basis of nitrogen adsorption/desorption. Analysis of the isotherms recorded for SiO_2/POSS fillers permitted determination of specific surface area, pore diameter and pore volume (see Table 2). The specific surface area of the initial amorphous silica is 110 m^2/g. Functionalisation of the silica surface with POSS led to a significant decrease in the surface activity as the specific surface area decreased to 24–41 m^2/g. This effect is a consequence of blocking the active centres on the SiO_2 surface by the molecules of oligosilsesquioxanes. According to pore size, the materials were classified as mesoporous.

Figure 8 presents the adsorption/desorption isotherms obtained for the unmodified silicas of both types and the hybrids functionalised with 10 wt./wt. G-POSS. A systematic increase in the relative pressure and in the volume of adsorbed nitrogen was noted with a maximum value of 240 cm^3/g for Sample 1 at $p/p_0=1$. For the hybrids, the increase in the volume of adsorbed nitrogen after the threshold value was much smoother and the maximum values reached at $p/p_0 = 1$ were much lower.

Table 2. Adsorptive properties of unmodified hydrated and emulsion silicas and hydrid nanofillers modified with octakis({3-glycidoxypropyl}dimethylsiloxy)octasilsesquioxane in different amounts

Sample No.	BET surface area, S_{BET} (m^2/g)	Total volume of pores, Vp (cm^3/g)	Mean size of pores, Sp (nm)
1	110	0.37	13
2	41	0.02	3
3	34	0.02	3
4	24	0.02	3
11	40	0.17	16
12	24	0.01	2
13	17	0.01	2
14	8	0.01	2

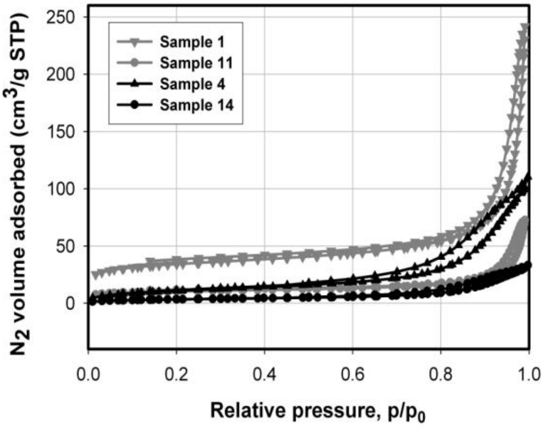


Fig. 8. Nitrogen adsorption/desorption isotherms for the unmodified silica of two types (Samples 1 and 11), and for the samples functionalised with 10 wt./wt. of octakis({3-glycidoxypropyl}dimethylsiloxy)octasilsesquioxanes (Samples 4 and 14)

Thermal stability of the unmodified silica and selected hybrids functionalised with octakis({3-glycidoxypropyl}dimethylsiloxy)octasilsesquioxanes was evaluated on the basis of thermogravimetric analysis. Measurements were made in the nitrogen atmosphere at temperature changed from 25 to 1000°C at a step of 10°C/min. The thermogravimetric (TGA) curves obtained are presented in Figs. 9 and 10.

Decomposition of hydrated silica (Sample 1) begins already at 25°C and occurs in a single step (Fig. 9). The mass loss observed in the range 25–150°C is rather abrupt. Above 700°C the sample gets stabilised and its mass almost does not change. In the temperature range 25–1000°C, pure hydrated silica loses only 10% of the total mass. The process of degradation of the hybrids takes place in two steps, the first is related to the loss of water and the second to the decomposition of the functional groups in the corners of the silsesquioxane cage. Figure 10 shows the TGA curve for the unmodified silica precipitated in the emulsion system and based on it hybrids modified with 3 wt./wt. and 10 wt./wt. of G-POSS, recorded on heating. Decomposition of Sample 11 run at two steps, in contrast to that of Sample 1. The first mass loss noted in the range from about 25 to about 300°C is most probably related to the loss of water. In this range the mass loss reaches a little more than 8%. For the hybrids obtained as a result of modification with 3 or 10 wt./wt. G-POSS the TGA curves display two inflection points: the first at about 300°C and the second at about 325°C.

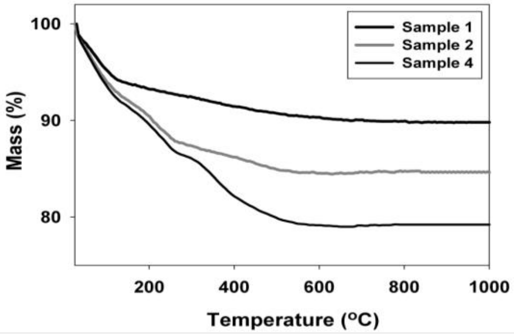


Fig. 9. TGA curves for the unmodified hydrated silica (Sample 1) and hybrids functionalised with octakis ({3-glycidoxypropyl) dimethylsiloxy)octasilsesquioxanes (Samples 2 and 4)

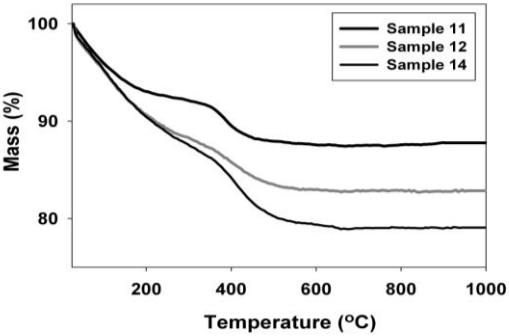


Fig. 10. TGA curves recorded for the unmodified silica precipitated in the emulsion system (Sample 11) and for the samples functionalised with octakis ({3-glycidoxypropyl} dimethylsiloxy) octasilsesquioxanes (Samples 12 and 14)

It is presumed that the first temperature corresponds to the beginning of degradation of the organic substituents at the silica atoms in POSS skeleton. Until reaching 600°C a considerable mass loss is observed, above this temperature the mass loss is slight. In the range from 25 to 1000°C Sample 14 loses a bit over 20% of the total mass.

Elemental analysis of the samples studied (Figs. 11 and 12) has proved that the content of carbon increased with increasing mass of the POSS modifier, which was also related to increasing degree of surface coverage. The latter parameter was calculated from the Berendsen and de Golan formula.

The hybrid systems (Fig. 11) obtained as a result of functionalisation with octakis({3-glycidoxypropyl}dimethylsiloxy)octasilsesquioxane have the highest percent content of carbon. For Sample 4 the carbon content is 5%, while the degree of coverage for the same sample is 0.738 μmol/m^2. The smallest degree of coverage was found for the hydrated silica functionalised with octakis({3-glycidoxypropyl}dimethylsiloxy)octasilsesquioxanes (Samples 5-7). The hybrids obtained on the basis of the silica precipitated from the emulsion system showed a similar tendencies (see Fig. 12).

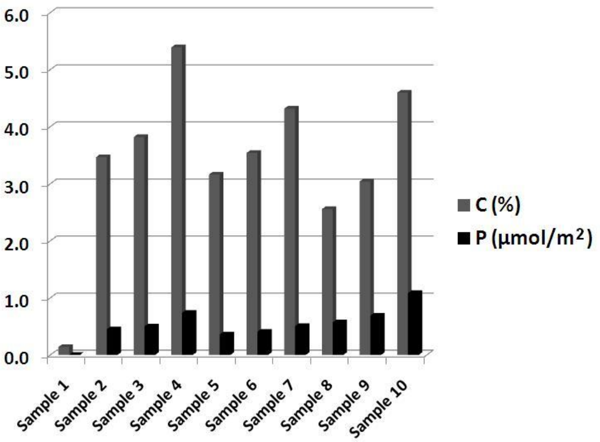


Fig. 11. Carbon content and coverage degree for the unmodified hydrated silica and based on it functionalised hybrids

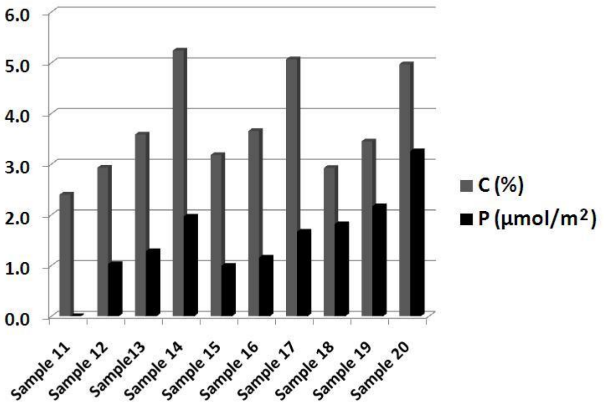


Fig. 12. Carbon content and coverage degree measured for the unmodified silica precipitated in the emulsion system and based on it hybrids

4. Conclusions

The products obtained by the proposed method of mechanical modification in general had more beneficial dispersion properties than the pure silicas. Functionalisation of the silica surface with G-POSS gave hybrid materials made of smaller size particles than those of the silica, irrespective of the amount of the modifier used. With increasing amount of the POSS modifier, the products revealed increasing hydrophobicity, which is beneficial from the point of view of their application as polymer fillers.

The specific surface area BET was observed to decrease from 110 m^2/g for the unmodified silica to 24 m^2/g for some hybrids. Thermal stability of the hybrids was found to depend on the thermal degradability of the functional groups of the silsesquioxanes used. Modification of silica surface with POSS leads to an increase in the degree of coverage, which is reflected in the percent content of carbon in the hybrids. This increase is particularly pronounced for the samples functionalised with octakis({3-glycidoxypropyl}dimethylsiloxy)octasilsesquioxanes.

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