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PREPARATION AND CHARACTERIZATION OF SiO_2/SILANE/POSS FUNCTIONAL HYBRIDS

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Abstract: Novel SiO_2/silane/POSS functional hybrids have been synthesized via an immobilization method. Hybrid materials were obtained through a connection of emulsion silica with defined dispersive and morphological properties with (3-isocyanatepropyl)triethoxysilane and selected mono- or octasubstituted POSS compounds in organic solvent. Modification effectiveness of the obtained SiO_2/silane/POSS hybrid systems was confirmed with the use of the Fourier transform infrared spectroscopy (FTIR). In order to determine the influence of bifunctionalization on coverage degree of the selected POSS compounds, elemental analysis (C, H, N contents) was performed. Moreover, parameters of porous structure of the obtained products were determined: BET surface area, total volume and mean size of pores. During analysis the thermal stability of silsesquioxanes cage, unmodified silica support, and hybrid systems have been investigated. For this purpose dispersive and morphological characterization (particle size distribution and TEM images) was performed.

Keywords: *SiO_2/silane/POSS hybrids, silica support, silsesquioxanes cage, bifunctionalization process*

Introduction

Nanotechnology is a modern science, which is focused mainly on designing and creation of structures, of which at least one dimension is in nanometric scale (Swiderski, 2008; Szwarc-Rzepka, 2013). Among nanofillers particularly interesting are various silica products, silsesquioxanes, fullerens and carbon nanotubes. Those compounds are especially susceptible to various kinds of modifications (Zurawska, 2003).

One of the most popular modifiers, next to silane coupling agents (Andrzejewska, 2004; Jesionowski, 2003; Jesionowski, 2010; Karim, 2012), are polyhedral oligomeric silsesquioxanes (POSS) (Wu, 2009). POSS is a group of compounds build of inorganic and organic part. The inorganic core is made of silicon-oxygen cage. On the

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other hand, organic fragments, located at the corners of the cage, might be composed of alkil, alkylen, epoxy, hydroxyl, acryl, methacrylate or other organic groups and their derivatives (Kuo, 2001; Li, 2001; Ipoh, 1995). Usually, oligomeric silsesquioxanes are colorless, crystalline substances in the 1–100 nm particle size range (Zhang, 2009; Iyer, 2007; Utracki, 2004). They crystallize from solution usually in form of white powders. However, they might also appear in form of colorless oil or waxes (Ye, 2006; Kickelbick, 2007).

Dynamic development of nanotechnology have had a significant influence on a formation of novel synthesis method of functionalized nanofillers. Addition of materials of particle size lower than 100 nm to organic, as well as inorganic matrix is often a reason for improvement or maintaining constant properties of final components (Thostenson, 2005).

Bianchini and Galland (2005) have modified surface of silica with polyhedral oligomeric silsesquioxanes, where amines are part of side functional groups. Goal of the research was to point at catalytic properties of metallocene and POSS modified silica in ethylene polymerization process. Equally interesting examples were obtained by Carniato et al. (2008). They have dealt with problems concerning surface bifunctionalization of an ordered mesoporous silica (SBA-15), and unordered silica (SiO_2-Dav). For modification purpose (3-isocyanatepropyl)triethoxysilane and monosubstituted POSS with amine group, have been used. Obtained hybrid systems were utilized as a heterogenic catalysts in a limonene epoxydation reaction.

In this paper grafting of traditional inorganic support, namely silica, with well known silane proadhesive compound, and modern modifying agents, that is cage silsesquioxanes, was performed on the basis of the bifunctionalization process. Due to the fact, that single cubic structure T_8 is able to attach as much as eight reactive organic groups (Lee, 1998), properties of the obtained compounds, such as thermal stability, mechanical strength, catalytic activity etc., are improved.

Experimental

Materials

The material studied was SiO_2 filler precipitated in the emulsion system, in analogy to previously described procedure by Jesionowski (2009).

The inorganic filler surface was grafted with selected alkoxysilane (purchased from Sigma-Aldrich) (Table 1) and also with Methacryl POSS® Cage Mixture and AminoethylaminopropylIsobutyl POSS® (purchased from Hybrid Plastics® Co.) (Table 2) in the amounts of 3, 5 or 10 weight parts by mass of SiO_2.

Table 1. Alkoxysilane used for inorganic filler surface grafting

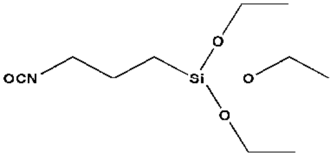
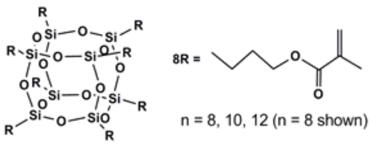
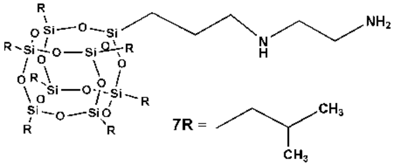
Name	(3-isocyanatepropyl)triethoxysilane
Formula	$(C_2H_5O)_3Si(CH_2)_3NCO$
Structure	
Molecular weight	247.36
Form	liquid
Density (g/cm^3)	0.999 (temperature 25 °C)
Color	transparently

Table 2. POSS compounds used for inorganic filler surface functionalization

Name	Methacryl POSS® Cage Mixture	AminoethylaminopropylIsobutyl POSS®
Formula	$C_{56}H_{88}O_{28}Si_8$	$C_{33}H_{76}N_2O_{12}Si_8$
Structure		
Molecular weight	1433.97	917.65
Form	liquid (oily)	powder
Density (g/cm^3)	1.200 (temperature 20 °C)	1.170 (temperature 20 °C)
Color	transparently	white

SiO_2/silane/POSS hybrids synthesis

Silica filler was submitted to the bifunctionalization via immobilization in organic solvent method. Schematic diagram of the bifunctionalization process has been presented in Fig. 1.

The process consisted of two stages. To a four-necked flask, supplied with a high-speed stirrer and mounted in a water bath, an appropriate fraction of emulsion silica was introduced into organic solvent – toluene. Nitrogen has been introduced in order to ensure inert atmosphere. When temperature in water bath reached 50 °C, modification process started. With the use of a peristaltic pump, a proper amount of organosilane (3, 5 or 10 weight parts by mass of silica) was dosed into toluene with rate equal to 1 cm^3/min (1). Afterwards, selected POSS compound in organic solvent has been introduced into the system (2) with set rate of dosing.

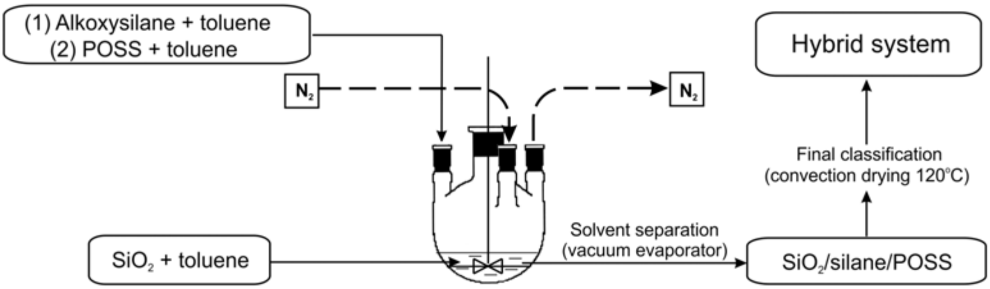


Fig. 1. Schematic diagram of SiO_2/silane/POSS hybrid systems preparation

After that time mixture remained in the reactor for 2 h under stirring (ca. 800 rpm). Then, the organic solvent was separated by distillation. Obtained powders has been dried in a convectional dryer in temperature as high as 120 °C for 48 h.

Evaluation of physicochemical properties

The final products were characterized by a number of methods. The effectiveness, degree of bifunctionalization of SiO_2 with silane and selected POSS compounds were estimated using the FTIR IFS 66v/S spectrophotometer made by Bruker.

The chemical composition of the functionalized SiO_2 systems were determined using a Vario EL Cube apparatus (Elementar Analysensysteme GmbH).

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 BET equations the specific surface area BET (S_{BET}) was calculated and the pore size (D_P) and total pore volume (V_P) were found from the BJH algorithm.

Thermogravimetric analyses were performed using a Jupiter STA 449 F3 (Netzsch GmbH). Samples weighing approximately 10.0 mg were placed in an Al_2O_3 crucible, and heated at a rate of 10 ºC/min from 30 to 1000 ºC in a nitrogen atmosphere.

The particle size distributions of the samples were measured using Zetasizer Nano ZS made by Malvern Instrument Ltd., enabling measurements in the range 0.6–6000 nm (NIBS method). Microstructure of the samples was analyzed by using the transmission electron microscopy images (Joel 1200 EX II).

Results and discussion

In the first stage of investigation Fourier transform infrared spectroscopy has been performed.

Figure 2 shows the FTIR spectra of emulsion silica (ES) and the hybrid obtained after silica modification with 5 weight parts by mass of isocyanatesilane, and 10 weight parts by mass of methacryl POSS compound (HS-I5.M10). The spectra presented prove a high efficiency of modification and change in the chemical character of the SiO_2 surface. Emulsion silica presents two characteristic absorptions bands at 1100 and 595 cm^{-1}, which are assigned to Si–O–Si stretching vibration, respectively. The spectrum of unmodified silica also shows adsorption band around 1640 cm^{-1}, which is assigned to the bending mode of physically adsorbed water molecules, in analogy to (Hong, 2007). Additionally, the intensity of the band at 3600–3200 cm^{-1}, assigned to the stretching vibrations of –OH groups, is coming from physically adsorbed water.

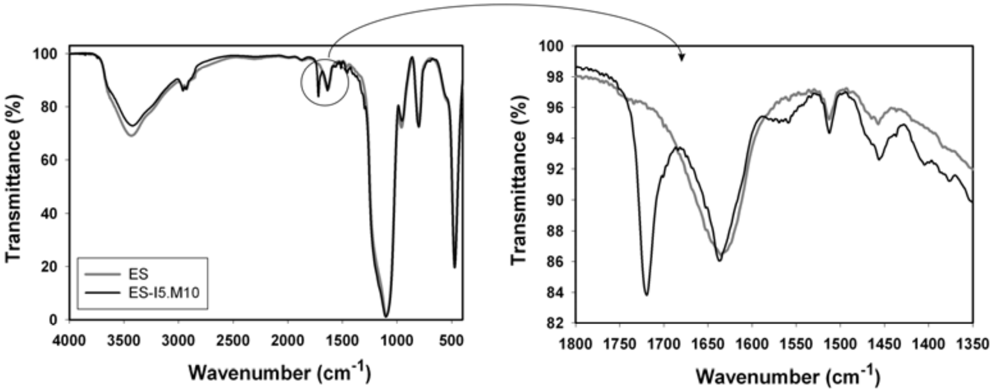


Fig. 2. FTIR spectra of unmodified emulsion silica (ES) and the hybrid obtained via modification with 5 weight parts by mass of (3-isocyanatepropyl)triethoxysilane and 10 weight parts by mass of Methacryl POSS® Cage Mixture (ES-I5.M10)

As a result of the performed bifunctionalization process a change in the band intensity at 3700–3200 cm^{-1} in the spectrum of the ES-I5.M10 sample has been observed and assigned to the stretching vibrations of –OH group, which might be related to changes in the hydrophilic–hydrophobic properties of the specimen. Moreover, the reduction of the intensity of this band confirms a chemical bonding of the modifier to silica surface and an effective substitution of double vicinal groups by its molecules. Besides, spectrum of the produced hybrids contains the stretching vibration band ν(C–H) in the range of 2950–2850 cm^{-1}. The band at 1720 cm^{-1} arises from the carbonyl stretching vibrations (ν(=C=O)) which corresponds to isocyanatesilane and methacrylate groups. Noteworthy is the presence of a weak absorption band at 1550 cm^{-1}, which most likely relate to appearing of ν(C=C). Finally, absorption band corresponding to the stretching vibration of N=C=O group at 2250 cm^{-1} for the hybrid was not observed, because these groups have been effectively substituted by molecules of POSS with methacrylate groups. Analogical situation and suggested mechanism of SiO_2/modifier interactions, has been presented in our earlier work (Ciesielczyk, 2013).

Additionally, in Fig. 3 FTIR spectra of the ES and the hybrids obtained as a result of the bifunctionalization of silica support with 5 weight parts by mass of isocyanatesilane and 10 weight parts by mass of AminoethylaminopropylIsobutyl POSS® (ES-I5.N10). A change in the band absorption intensity characteristic for physically adsorbed water molecules has been observed. Moreover, because of masking effect of the intensive band sourcing from –OH group, absorption band characteristic for stretching vibrations of N–H in 3500–3250 cm^{-1} range has not been observed. Additionally, raise in band intensity of ν(C–H) bonds in the range of 2950–2850 cm^{-1} has been noted. Moreover, a formation of a very weak band assigned to secondary and primary amines has been also confirmed (Fig. 3).

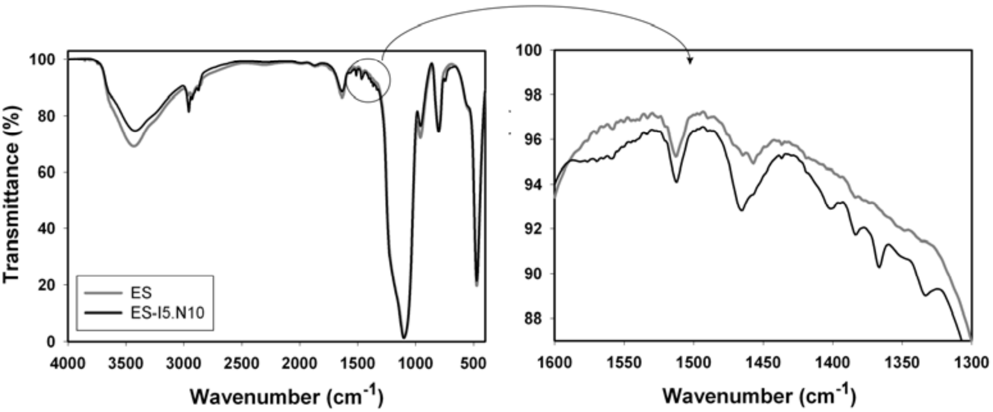


Fig. 3. FTIR spectra of unmodified emulsion silica (ES) and the hybrid obtained by their modification with 5 weight parts by mass of (3-isocyanatepropyl)triethoxysilane and 10 weight parts by mass of AminoethylaminopropylIsobutyl POSS® (ES-I5.N10)

Furthermore, chemical composition of the obtained materials was determined using elemental analysis (Table 3). The procedure was performed in order to verify the effectiveness of the modification process and to calculate the surface coverage degree of the silica support with (3-isocyanatepropyl)triethoxysilane and selected POSS compounds. The degree of coverage was calculated from the Berendsen and de Golan equation (1978).

As a result of the silica supports bifunctionalization with silane and Methacryl POSS® Cage Mixture, the content of carbon and hydrogen was found to increase with rising the applied amounts of POSS modifier (in weight parts by mass). Since the degree of coverage depends on the specific surface area of the initial support, lower values were obtained for emulsion silica modified with 5 weight parts by mass of the organosilane and 3, 5, 10 weight parts by mass of the methacryl POSS compound, i.e. 0.505 μmol/m^2, 0.548 μmol/m^2, and 0.717 μmol/m^2, respectively (Table 3). In the case of hybrid systems made from emulsion silica modified with 5 weight parts by mass of (3-isocyanatepropyl)triethoxysilane and 3, 5 or 10 weight parts by mass of AminoethylaminopropylIsobutyl POSS®, the content of carbon, hydrogen, and nitrogen also was found to increase with the applied amounts of POSS modifier. The obtained values of the coverage degree are as high as 0.927 μmol/m^2, 1.078 μmol/m^2, and 1.690 μmol/m^2.

Table 3. Elemental content of carbon, nitrogen and hydrogen and parameters of the porous structure of unmodified silica and silica-based fillers grafted with alkoxysilane and different amounts of Methacryl POSS® Cage Mixture and AminoethylaminopropylIsobutyl POSS®

Acronym	Elemental content (%)			Degree of coverage (μmol/m^2)	Parameters of porous structure		
	N	C	H		S_{BET} (m^2/g)	V_P (cm^3/g)	D_P (nm)
ES	–	2.398	1.227	–	77	0.23	8
ES-I5.M3	–	4.875	1.712	0.505	76	0.18	9
ES-I5.M5	–	5.075	1.762	0.548	55	0.16	10
ES-I5.M10	–	5.838	1.885	0.717	46	0.12	11
ES-I5.N3	0.289	5.374	1.939	0.927	77	0.18	8
ES-I5.N5	0.315	5.824	2.026	1.078	75	0.17	9
ES-I5.N10	0.459	7.560	2.366	1.690	55	0.14	10

In a further part of the research, an attempt to interpret the parameters of porous structures, such as specific surface area (S_{BET}), total pore volume (V_P) and mean size of pores (D_P) of unmodified emulsion silica, as well as alkoxysilane and POSS modified silica filler has been undertaken. Investigation results have been set in Table 3. Additionally, adsorption/desorption isotherms of nitrogen and pore size distribution of selected samples have been determined. Obtained results of selected powders have been presented in Fig. 4. Analysis of the data shown in Table 3 allows to state, that the obtained emulsion silica can be characterized with relatively high value of specific surface area equal to 77 m^2/g, taking under consideration spherical shape of the particles. The product can be included into mesoporous adsorbents group. Pores volume equal to V_P = 0.23 cm^3/g, and pores diameter D_P = 8 nm serves as a confirmation for the statement. From these data one can conclude that the process of emulsion silica bifunctionalization with use of silanes and oligomeric silsesquioxanes, caused significant changes in basic adsorption parameters. For samples bifunctionalized with 3, 5 or 10 weight parts by mass of methacryl POSS compound a decrease in pores volume has been noted, and reached values equal to 0.18 cm^3/g, 0.16 cm^3/g, and 0.12 cm^3/g, respectively. For the hybrids obtained with the use of amino POSS compound, smaller changes have been noted in comparison to final silica filler. Worth mentioning is also fact, that the kind and amount of used modifier, undoubtedly have impact on adsorption properties of the produced hybrid systems.

Analyzing data in Fig. 4 it has been stated that from isotherms set-up, according to IUPAC, are of type IV type with the hysteresis of type H3. It has been observed, that amount of adsorbed nitrogen on surface of the non-modified emulsion silica (Fig. 4a) slightly raises, until it reaches the value of relative pressure equal to 0.6. After exceeding the value of characteristic pressure rapid increase in adsorbed nitrogen has been observed, reaching maximum value as high as 122 m^2/g at p/p_0 = 1. For the presented hybrid systems functionalized with 3 or 10 weight parts by mass of POSS compounds (see Figs. 4b and 4c) an analogical dependence has been observed.

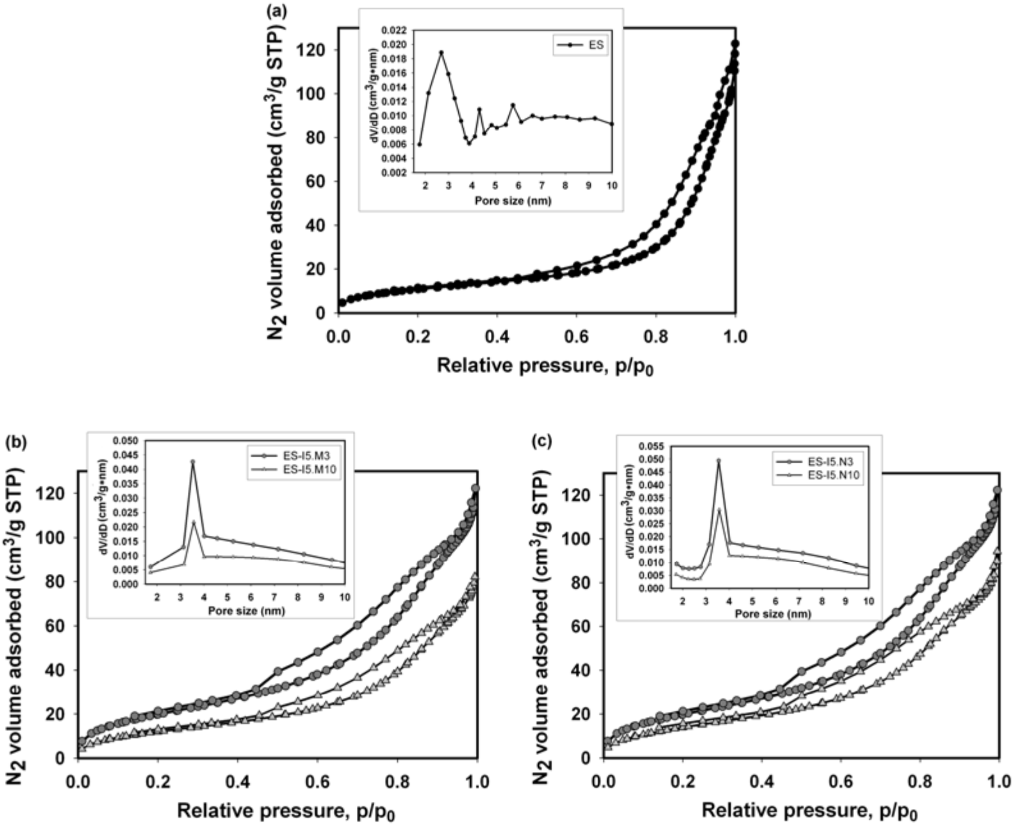


Fig. 4. Nitrogen adsorption/desorption isotherms and pore size distributions for (a) unmodified emulsion silica and hybrid systems obtained using 5 weight parts by mass of the (3-isocyanatepropyl)triethoxysilane and (b) 3 or 10 weight parts by mass of the Methacryl POSS® Cage Mixture (ES-I5.M3, ES-I5.M10), and (c) 3 or 10 weight parts by mass of the AminoethylaminopropylIsobutyl POSS® (ES-I5.N3, ES-I5.N10)

Up to the value of relative pressure equal to $p/p_0 = 0.4$, a slight increase in the amount of adsorbed nitrogen has been noted. After exceeding this value, the amount of adsorbed nitrogen rises rapidly. When value of relative pressure reached its maximum, i.e. 1.0, the amount of adsorbed gas molecules was equal to 122 cm^3/g for ES-I5.M3 (Fig. 4b), 85 cm^3/g for ES-I5.M10 (Fig. 4b), 122 cm^3/g for ES-I5.N3 (Fig. 4c), and 95 cm^3/g for sample ES-I5.N10 (Fig. 4c).

Examination of the bifunctionalization process effectiveness has been broaden by thermal analysis TG/DTA (Fig. 5) of the pure POSS compounds, final silica support, and selected hybrid materials. The results from TG/DTA analysis allowed to estimate temperatures range, which correspond to important chemical and structural transitions of the obtained hybrids.

Figure 5a shows a TGA thermograms of pure silsesquioxanes used for the hybrids obtained. As it can be seen, the TGA curve of pure Methacryl POSS® Cage Mixture revealed a mass loss of about 43% at 550 °C. The process continued until total degradation of the methacrylate groups substituted at the silicon atoms of the POSS skeleton. The rapid mass changes are accompanied by exothermic effects in temperature range from 300 to 700 °C. In the case of AminoethylaminopropylIsobutyl POSS® a two-stage degradation process has been observed. At the first stage an insignificant mass loss is most likely related to humidity evaporation, which has been captured by the compound as a result of heating process. The second change begins at 400 °C, and is accompanied by strong exothermic effect. At temperature as high as 500 °C sample mass stabilizes, and further increase in temperature does not cause considerable mass change. Total mass loss is equal to ~95%.

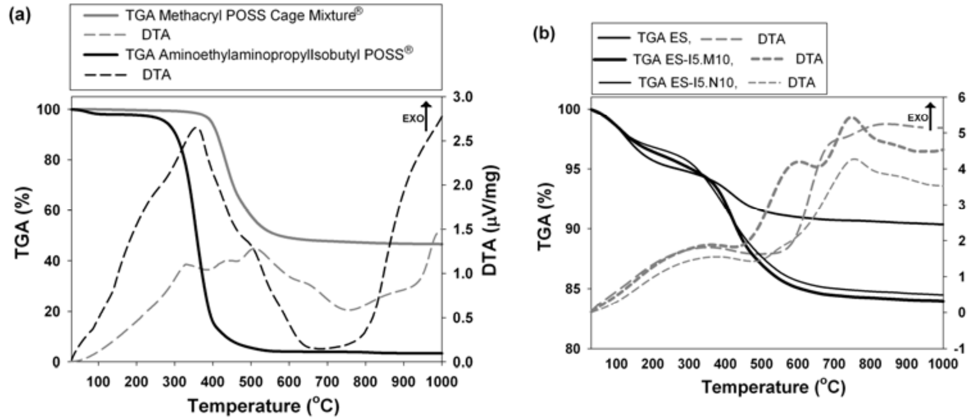


Fig. 5. Thermograms of (a) pure Methacryl POSS® Cage Mixture and AminoethylaminopropylIsobutyl POSS® and (b) unmodified emulsion silica, and hybrids functionalization with 5 weight parts by mass of isocyanatosilane and 10 weight parts by mass of selected POSS compounds

Figure 5b shows TGA thermograms of the unmodified emulsion silica and hybrids obtained by silica functionalization with 5 weight parts by mass of isocyanatesilane, and 10 weight parts by mass of the selected POSS compounds. Analysis of the hybrid systems has been performed in order to determine thermal stability. The obtained thermograms were compared with curves characteristic for pure POSS modifiers. In case of the unmodified silica filler first mass loss is observable in temperature range from 30 to 300 °C, and most likely corresponds to loss of physically and chemically bound water. At this point mass loss is slightly above 10%. The mass change is also connected with endothermic effect. In further part of thermogram mass loss equal to 7% is observable, which is reflected by exothermic effect on the DTA curve (Fig. 5b). Observable thermal effect in the temperature range 300–700 °C corresponds to a loss of constitutional water. Afterwards only slight mass loss have been registered. For the selected hybrid systems (ES-I5.M10 and ES-I5.N10) two-stage degradation process has been observed as well. First mass loss for both systems is somewhat smaller and equal to ~8%. Additionally, the change is accompanied with endothermic effect. Second change characterize with exothermic effect (from 300 to 700 ^{o}C), and likely corresponds to degradation of the organic substituents, which appears in the corners of silsesquioxane. Noteworthy is fact, that no significant changes in the thermogravimetric curves, resulting from change of the cage modifier, have been observed. As can be noted for this example, mass loss for sample functionalized with AminoethylaminopropylIsobutyl POSS® (ES-I5.N10) is slightly lower in comparison to the hybrid bifunctionalized with methacryl POSS compound, and is equal to 16% of total mass sample.

Moreover, for the final support and SiO_2/silane/POSS functionalized hybrids dispersive and morphological characteristics have been performed. These parameters determine potential application of such systems, e.g. as a polymers filler. The particle size distribution according to volume contribution obtained for the unmodified SiO_2 is presented in Fig. 6a. One band covering the particle diameters from 342 to 712 nm with the maximum volume contribution of 32.2% comes from particles of 459 nm in diameter.

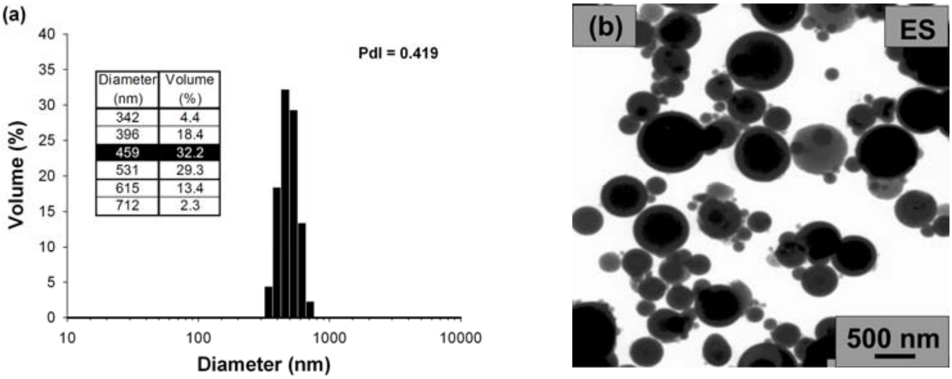
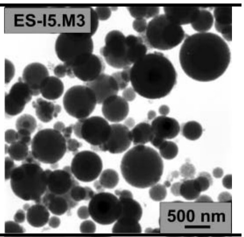
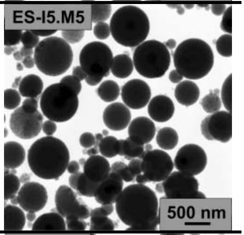
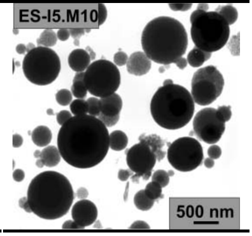


Fig. 6. PSD (a) and TEM microphotograph (b) of the unmodified SiO_2 precipitated in the emulsion system

The polydispersity index (PdI) of this filler is equal to 0.419. The TEM microphotograph of the studied sample is presented in Fig. 6b. The picture serves as a confirmation for the presence of particles with small diameters (corresponding to those indicated in the particle size distributions), significant homogeneity, spherical shape, and showing low tendency to form agglomerate structures.

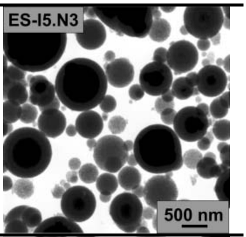
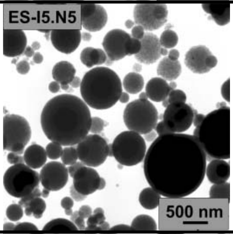
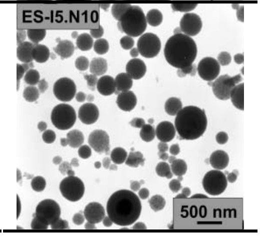
Table 4 presents dispersive and morphological characteristics of hybrids obtained as a result of SiO_2 modification with 5 weight parts by mass of organosilane and Methacryl POSS® Cage Mixture in different amounts. The results prove that the bifunctionalization has caused significant changes in dispersive character of the hybrid systems obtained.

Table 4. Dispersive and morphological characteristics of hybrid fillers obtained after SiO_2 modification with (3-isocyanatepropyl)triethoxysilane and Methacryl POSS® Cage Mixture in different amounts

Acronym	Amounts of modifiers (weight parts by mass)		Dispersive properties			TEM microphotograph
	Silane	POSS	Diameters range (nm)	Dominant particles diameter (nm)	PdI	
ES-I5.M3	5	3	396–955; 1110–2300	712 (18.5%)	1.000	
ES-I5.M5		5	459–955	712 (33.6%)	0.647	
ES-I5.M10		10	531–1280	825 (28.6%)	0.674	

Analyzing data collected and set-up in Table 4 it has been concluded that filler obtained after 2-hour functionalization with use of 5 weight part (3-isocyanatepropyl)triethoxysilane, and various amounts of the methacryl POSS compound can be described with different particles sizes. All samples presented in Table 4 show high tendency to particles agglomeration. For presented systems an increase in the polidispersity index in comparison to the final support has been observed. For instance, sample modified with 5 weight parts by mass of the silane and 3 weight parts by mass of POSS with methacrylate groups has PdI value equal to 1.

Table 5. Dispersive and morphological characteristics of the hybrid fillers obtained after SiO_2 modification with (3-isocyanatepropyl)triethoxysilane and AminoethylaminopropylIsobutyl POSS® in different amounts

Acronym	Amounts of modifiers (weight parts by mass)		Dispersive properties			TEM microphotograph
	Silane	POSS	Diameters range (nm)	Dominant particles diameter (nm)	PdI	
ES-I5.N3	5	3	295–955; 1110–6440	396 (18.8%)	1.000	
ES-I5.N5		5	825–2300	1280 (31.4%)	0.897	
ES-I5.N10		10	255–825	456 (17.3%)	0.714	

The most attractive dispersive parameters are observed for the hybrid synthesized with use of 5 weight parts by mass of Methacryl POSS® Cage Mixture. Data analysis suggests that the sample is characterized with the monomodal particle size distribution in particles diameter range 459–955 nm and with volume fraction maximum equal to 33.6% pointing at particles with diameter as high as 712 nm, its polidispersity index is equal to 0.647.

Furthermore, Table 5 presents data of systems obtained with use of 5 weight parts by mass of (3-isocyanatepropyl)triethoxysilane and Aminoethylamino-propylIsobutyl POSS® in different amounts. The bifunctionalization contribute to a significant rise of analyzed particles size, with exception for sample ES-I5.N10, modified with 10 weight parts of amino POSS, which shows the most analogous dispersive character to the unmodified emulsion silica (see Fig. 6a). Analysis of the presented results let us to notice a monomodal particles size distribution in the diameter range of 255–6440 nm for SiO_2 modified with 5 weight parts by mass of silane, and 10 weight parts by mass of POSS. The highest volumetric fraction (17.3%) in the sample corresponds to particles diameter equal to 456 nm and the PdI of these sample was 0.714.

Conclusions

As a result of the investigation, novel SiO_2/silane/POSS functional hybrids have been obtained. It was stated that proposed modification route is an effective process, and it significantly contributes to changes in their physicochemical parameters. It was confirmed by the presented FTIR results.

Bifunctionalization of emulsion silica with POSS compounds increases coverage degree along with an increase in the applied amounts of the POSS modifiers. This was confirmed by the content of carbon and hydrogen. Higher values of the coverage degree were obtained in case of utilization of monosubstituted POSS, i.e. AminoethylaminopropylIsobutyl POSS®.

Examined parameters of porous structure of hybrid materials synthesized with utilization of N-POSS are higher than values noted for the hybrid obtained with use of Methacyl POSS® Cage Mixture.

SiO_2/silane/POSS hybrids acquired via immobilization in organic solvent are characterized with small shift in thermal stability. However, a change in the bifunctionalized samples mass loss, in comparison to native silsesquioxane cage, has been observed.

Performed process of the emulsion silica bifunctionalization with organofunctional silane and POSS modifier have contributed to a change in dispersive character of the obtained fillers.

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