

## Research Article

# TiO<sub>2</sub>-SiO<sub>2</sub>/Ph-POSS Functional Hybrids: Preparation and Characterisation

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The results of studies involving the innovative TiO<sub>2</sub>-SiO<sub>2</sub>/Ph-POSS hybrid were presented. An inorganic TiO<sub>2</sub>-SiO<sub>2</sub> oxide composite was precipitated from an emulsion media. The functionalisation of surface for the obtained composite was carried out with the use of TriSilanolPhenyl POSS (Ph-POSS) and a silane coupling agent—phenyltrimethoxysilane (PTMS). Electrokinetic and physicochemical as well as structural characteristics of obtained hybrids were evaluated. The zeta potential value has been determined, which provides relevant information regarding the interactions between colloid particles. Measurement of the zeta potential values allowed for an indirect assessment of stability for the studied hybrid fillers. In the next step, the degree of dispersion and surface morphology were evaluated based on the obtained particle size distribution curves and TEM images. The hydrophilic-hydrophobic character of the surface was assessed by analysing the wettability profiles. The modification degree of the TiO<sub>2</sub>-SiO<sub>2</sub> oxide composite was evaluated based on the infrared spectroscopy studies (FT-IR). Determination of the parameters of the porous structure was conducted by determining the specific surface area and the total volume and mean size of pores. Thermogravimetric measurements (TGA) were also carried out in order to measure the changes in sample mass as a function of temperature.

## 1. Introduction

Since the last decade, scientists work on the new organic-inorganic hybrid materials called silsesquioxanes. Polyhedral oligosilsesquioxanes (POSS) are considered a novel class of compounds with a general formula of  $(RSiO_{1.5})_n$  or  $R_nT_n$ , where R may stand for hydrogen, alkyl, aryl or other functional organic group. The inorganic skeleton may exhibit a completely condensed, closed, or open structure [1]. POSS is an intermediate product between silica (SiO<sub>2</sub>) and silicone (R<sub>2</sub>SiO) with a particle size ranging from several to dozens of nanometers, and its properties are determined by its composition and the type of organic substituents [2–4]. The specific structure of this type of compounds contributed to a broad range of applications [5–8].

Polyhedral oligosilsesquioxanes make for a significant base for the synthesis of novel functional materials and nanomaterials. Numerous researchers proved that POSS may

be successfully used for obtaining novel hybrid materials [9]. Since POSS compounds are costly fillers, several attempts have been made to combine them with inorganic oxide composites, such as: TiO<sub>2</sub>-SiO<sub>2</sub>, MgO-SiO<sub>2</sub>, ZnO-SiO<sub>2</sub>, or individual oxides for example, SiO<sub>2</sub> and TiO<sub>2</sub> [10–12]. Recently, the number of studies focused on obtaining such novel hybrid materials has considerably increased. Godinjavec et al. has confirmed that Trisilanophenyl-POSS may be integrated into a poly(methyl methacrylate) chain, which allows for obtaining a composite with excellent properties [1]. In our previously published researches, Ambrożewicz et al. obtained hybrid materials based on magnesium silicate and POSS compounds. The inorganic matrix (MgO-SiO<sub>2</sub>) was obtained according to the previously proposed method, described in [13]. The presented method in article [14] results confirmed that such products are thermally stable at the temperature of 600°C, which enables their use as fillers in the plastics industry.

TABLE 1: The POSS used for the surface modification of  $\text{TiO}_2\text{-SiO}_2$  oxide composite.

Chemical formula	Name of the POSS	Solvent solubility	Solvent insolubility
	TriSilanolPhenyl POSS (Ph-POSS)	THF, acetone, ethylacetate, toluene	Methanol, ethanol, water, acetonitrile, chloroform

In this study, the  $\text{TiO}_2\text{-SiO}_2$  oxide composite was selected as an inorganic carrier to be used in the process of obtaining hybrid filler due to its unique physicochemical properties. Such composites are often employed as efficient catalysts and photocatalyst which participate in various chemical reactions, such as the polycondensation of ethyl polyterephthalene, hydration of carbon oxide as well as selective oxidation in the liquid phase by organic peroxides. Additionally, these compounds serve as photocatalysts during the neutralisation of textile wastewater and production of nitriles, nylon, plastics and synthetic rubber [15–17].

In order to increase the possibility to use this type of oxide materials, the synthetic silicates are frequently subjected to surface modification with silane proadhesive compounds. Such surface functionalisation allows for the introduction of functional groups, which facilitate the bonding with polymers. The mechanism and modification method have been described in numerous scientific reports [18, 19].

When trying to evaluate the application potential of inorganic carrier/POSS hybrid materials (i.e., for the plastics industry), it is also important to determine their zeta potential values. The surface properties are a crucial factor which characterises nanoparticles, since, according to the DLVO theory, the parameters such as surface charge density, spherical interactions, or the Hamaker constant determine the dispersive properties in colloids [20].

The main aim of the presented studies was to obtain novel inorganic/organic hybrid fillers ( $\text{TiO}_2\text{-SiO}_2/\text{Ph-POSS}$ ), which may be successfully used in the constantly developing plastics industry. In the second stage of studies, a detailed characterisation of electrokinetic and physicochemical properties was carried out for the obtained hybrid materials.

## 2. Experimental Section

### 2.1. Preparation of the Functionalised

#### $\text{TiO}_2\text{-SiO}_2/\text{Ph-POSS}$ Hybrids

**2.1.1. Method of Obtaining the  $\text{TiO}_2\text{-SiO}_2$  Oxide Composite from an Emulsion Media.** The  $\text{TiO}_2\text{-SiO}_2$  oxide composites were precipitated in the emulsion system; this type of production was described detailed by Siwinska-Stefanska et al. [21].

**2.1.2. The Silane Proadhesive Agent.** Phenyltrimethoxysilane (PTMS) produced by Fluka was used in order to introduce functional groups which facilitate the bonding with other active substances on the surface of the  $\text{TiO}_2\text{-SiO}_2$  oxide composite. An adequate amount of the substance was first hydrolysed in a methanol : water (4 : 1, v/v) system and then applied on the surface of the silica according to the “dry method”, which is described in detail in [18, 22]. The surface of the oxide composite was modified with 3, 5, and 10 weight parts by mass of the applied silane.

**2.1.3. Surface Modification of the Precipitated  $\text{TiO}_2\text{-SiO}_2$  Oxide Composite with the Selected Silsesquioxane (Ph-POSS).** In the next experimental stage, the precipitated  $\text{TiO}_2\text{-SiO}_2$  oxide composite was subjected to the modification with the use of Ph-POSS (purchased in Hybrid Plastics) in order to change its surface properties (see Table 1).  $\text{TiO}_2\text{-SiO}_2$  oxide composite was introduced into the reactor, and afterwards the Ph-POSS (in an amount of 3, 5, and 10 parts by mass) was dissolved in 10 cm<sup>3</sup> of toluene was introduced into the reactor. Simultaneously, the dispersion with modifying agent was intensively stirred for 1 h. Upon introducing the Ph-POSS, the solution was transferred into a Büchi Labortechnik AG R-210 rotary evaporator in order to evaporate the organic solvent.

**2.2. Electrokinetic, Physicochemical, and Structural Analysis.** The zeta potential values have been determined with the use of the Zetasizer Nano ZS apparatus equipped with an autotitrator, which incorporates a combination of electrophoresis and laser determination of particle mobility based on the Doppler phenomena. The apparatus measures the speed of particle translocation in a liquid upon switching the electric field, which is referred to as electrophoretic mobility. Knowing this value, the zeta potential can be calculated from Henry's equation. The apparatus allows for determining the electrophoretic mobility of particles in the range of 5 nm to 100  $\mu\text{m}$ . The zeta potential was determined in a pH range of 1.5–11, in a 0.001 M NaCl electrolyte. Simultaneously, the changes in the conductivity and pH values of the studied suspension were also studied during the measurement. Prior

to the measurement, the apparatus was calibrated by determining the zeta potential of a latex suspension and measuring the pH of buffer solutions with a pH value of 4 and 9. The analysed dispersions were stabilised in the ultrasonic bath for 15 minutes. In order to avoid potential measurement errors each analysed sample was measured ten times and the general standard deviation was  $\pm 0.01$  mV (zeta potential) and  $\pm 0.01$  (pH).

The particle size distribution curves of the analysed hybrid fillers were obtained by using a Zetasizer Nano ZS apparatus (Malvern Instruments Ltd.). The equipment allows for a dispersive evaluation of particles with a diameter ranging from 0.6 to 6000 nm. The apparatus employs the NIBS (*non-invasive back scattering*) technique.

Studies focused on assessing the microstructure and morphology of the obtained powder substances were carried out in order to obtain data regarding the morphology of seeds, the structure of a given particle as well as the agglomeration and dispersion characteristics. The JEOL 1200 EX II transmission electron microscope was used during these studies.

Analysis of composition and the degree of modification was based on FT-IR spectra obtained with the use of the EQUINOX 55 spectrophotometer (Bruker). The analysed materials were studied as KBr tablets.

The wettability profiles in aqueous systems were determined with the use of the K100 tensiometer with a specialised software from Krüss in order to evaluate the hydrophilic-hydrophobic character of the powder surface. These measurements were carried at an equal time interval (10 minutes) for a constant sample mass (0.4 g).

The parameters of porous structure of the obtained hybrid fillers were carried out with the use of the ASAP 2020 apparatus (Micromeritics Instrument Co.). In order to do this, the parameters such as the specific surface area as well as the volume and mean the pore size were determined. Prior to the measurement, the samples were degassed at the temperature of approx. 120°C for 4 h. The specific surface area was determined with the use of a multipoint BET (Brunauer-Emmett-Teller) equation. In order to assess the pore volume and the mean pore diameter value, a BJH (Barrett-Joyner-Halenda) algorithm was employed. Measurement of the parameters of porous structure of the samples analysed was performed based on the low-temperature nitrogen adsorption.

The thermal analysis of the obtained fillers was carried out with the use of Jupiter 449 TG/DTA/DSC apparatus (Netzsch). The mass of the sample was approx. 10 mg. The sample was heated at 10°C/min (in the temperature range of 30–600°C). The analyses were carried out in the atmosphere of nitrogen, with a flow rate of 10 cm<sup>3</sup>/min.

### 3. Results and Discussion

**3.1. Zeta Potential of TiO<sub>2</sub>-SiO<sub>2</sub>/Ph-POSS, TiO<sub>2</sub>-SiO<sub>2</sub>/PTMS, and TiO<sub>2</sub>-SiO<sub>2</sub>/PTMS/Ph-POSS Hybrids.** Nanoparticles in dispersive systems exhibit a notable tendency to agglomerate, however this process may be successfully controlled by measuring the zeta potential (which allows for determining the value of electrostatic interactions between colloid particles

dispersed in aqueous solutions) and analysing the particle size distribution curves [23–25].

In the first experimental stage, the values of the zeta potential for the unmodified TiO<sub>2</sub>-SiO<sub>2</sub> oxide filler and the silsesquioxane (Ph-POSS) selected for subsequent surface modification were carried out (see Figure 1(a)). Next, the zeta potential values for the functionalised TiO<sub>2</sub>-SiO<sub>2</sub>/Ph-POSS hybrid fillers were measured, and the obtained results were presented in Figure 1(b). The measurement of the zeta potential values allows for determining the isoelectric point (i.e.p.), which is a crucial parameter for characterising solids dispersed in liquids. By knowing the i.e.p. value, the surface charge type can be recognised, that is, metal oxides exhibit a positive surface charge value in a pH range  $< \text{pH}_{\text{i.e.p.}}$  and a negative value in a pH range  $> \text{pH}_{\text{i.e.p.}}$ . This knowledge helps to understand the occurring coagulation and adhesion phenomena. Overall, the charge on the surface of metal oxides is influenced mainly by the pH and the ionic force of the solution. However, the charge and the overall course of the electrokinetic curve should not change as a result of changes in the electrolytes concentration [26]. The differences in acid-base properties of TiO<sub>2</sub>-SiO<sub>2</sub> oxide composites and their modified forms have a profound impact on the obtained zeta potential values [27]. Upon analysing the course of the electrokinetic curve for the unmodified TiO<sub>2</sub>-SiO<sub>2</sub> oxide composite it can be established that its zeta potential is decreasing with increasing the pH values, which confirms that the zeta potential value strongly depends on the pH value. The influence of the zeta potential on the distribution of the surface charge on oxide composites was presented detailed in previously published paper [13].

In our previously published studies [27], we reported that the zeta potential of unmodified TiO<sub>2</sub>-SiO<sub>2</sub> oxide composites reaches the value of the isoelectric point at a pH value of approx. 4.9 and exhibits zeta potential values from 30 to -30 mV in the whole studied pH range (1.7–11). The TiO<sub>2</sub>-SiO<sub>2</sub> oxide composite presented in the framework of this study is characterised by an isoelectric point at the pH value of 4.9 and reaches zeta potential values from 8 to -48 mV in the studied pH range. Marginal differences in the electrokinetic properties of the studied inorganic filler are a result of the proposed synthesis method and the percent composition of a given oxide. Lower i.e.p. value of the studied synthetic oxide composite is most likely caused by a higher percent composition of silica, which is characterised by an isoelectric point at a pH value of 2. The value of the point zero charge (PZC) and the isoelectric point for TiO<sub>2</sub> and SiO<sub>2</sub> has been an object of numerous studies and described in detail in several literature reports [28, 29].

The course of the electrokinetic curve for the analysed POSS compounds is similar to that obtained for SiO<sub>2</sub> [20]. Ph-POSS does not exhibit an i.e.p. value, however, the course of the curve suggests a tendency to reach i.e.p. at a pH value of approximately 1.0.

Upon analysing the results shown in Figure 1(b) it can be established, that the functionalisation of the TiO<sub>2</sub>-SiO<sub>2</sub> oxide composites surface with the selected silsesquioxane does not decrease the electrokinetic stability of the studied

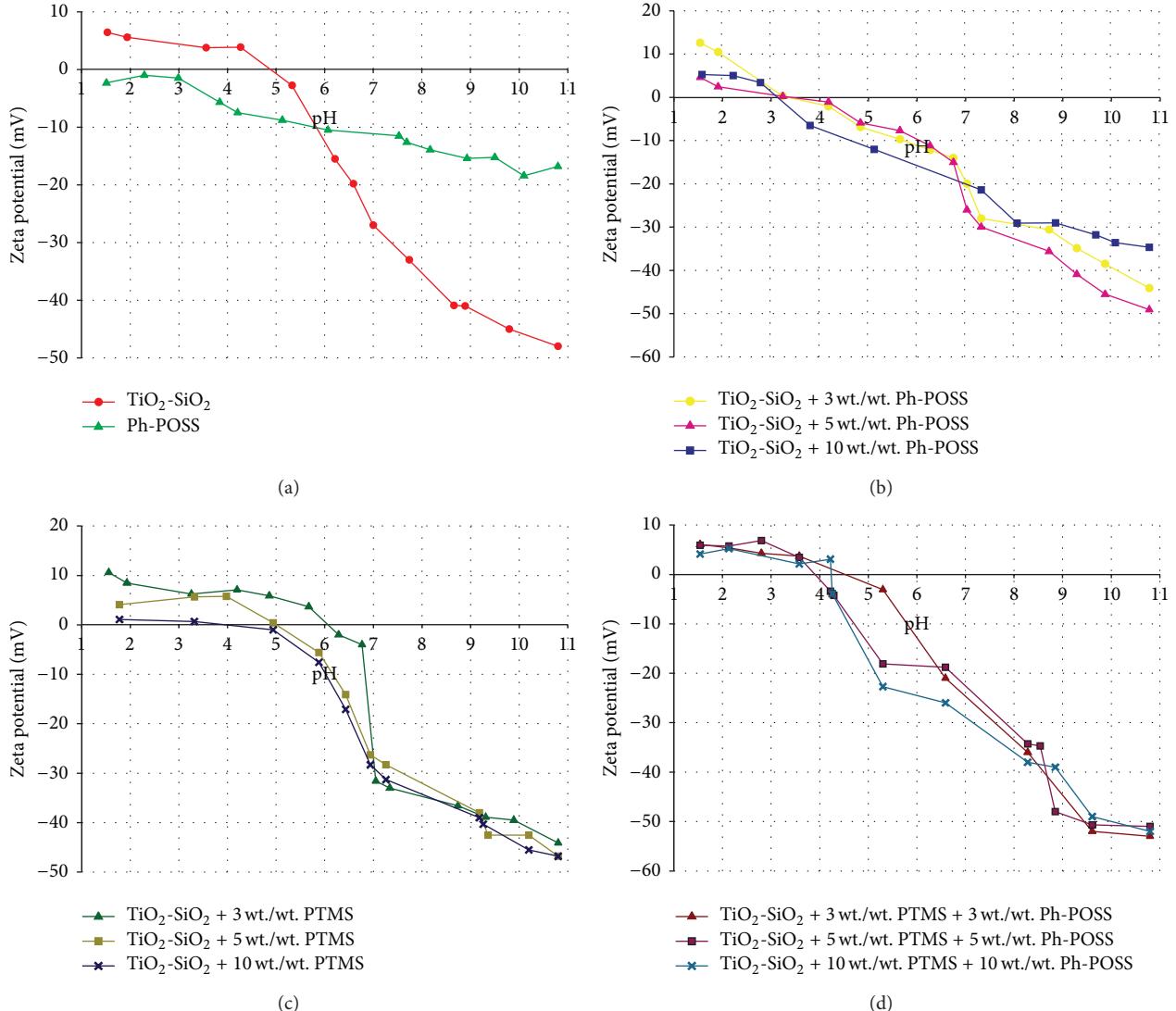


FIGURE 1: Zeta potential values as a function of pH for the (a) unmodified  $\text{TiO}_2\text{-SiO}_2$  oxide composite and the analysed silsesquioxane (Ph-POSS). Then, (b) for the inorganic composite modified with Ph-POSS, (c) PTMS, and (d) additionally functionalised with Ph-POSS.

oxide systems in the whole range of the studied pH and that the course of electrokinetic curves as well as the change of the obtained isoelectric point values confirms the effectiveness of the employed surface functionalisation method.

The electrokinetic curves obtained for the oxide composite modified with various amounts of the selected silane (PTMS) were shown in Figure 1(c). The obtained results were compared with the electrokinetic potential of the unmodified carrier. The surface functionalisation of the  $\text{TiO}_2\text{-SiO}_2$  oxide composite with the use of PTMS silane (see Figure 1(c)) did not contribute to any notable changes in the electrokinetic stability compared to the base oxide composite. The modified hybrid fillers are characterised by a zeta potential value ranging from 5 to  $-50$  mV, and their stability is high in the pH values from 6 to 11.

In the next experimental stage, the zeta potential values for the oxide composite modified with the use of the

selected silanes and further functionalised with the use of the silsesquioxane (Ph-POSS) were measured. The obtained results were presented in Figure 1(d). The proposed method of bifunctionalisation of the composite surface did not notably change the obtained zeta potential values.

**3.2. Particle Size Distributions and Surface Morphology and Microstructure Analysis.** In the next experimental stage the dispersive and morphological characteristics of the studied hybrid fillers were analysed. The particle size distribution curve in relation to the volume percent for the base inorganic filler (see Figure 2(a)) shows a single band in the range of 164–531 nm. The maximum volume percent (26.4%) was observed for particles with a diameter of 295 nm. The results obtained for the composite upon surface modification with 10 weight parts by mass of Ph-POSS led to a single broad band in

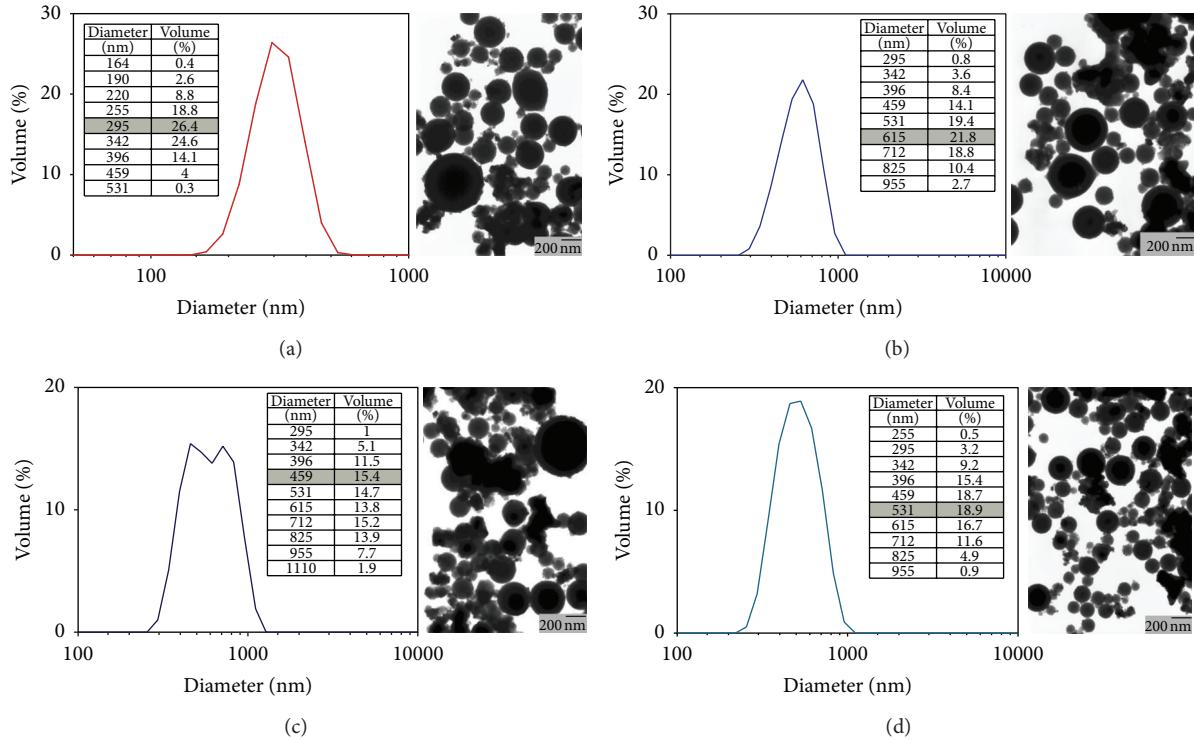


FIGURE 2: Particle size distribution curves and TEM images for (a) the unmodified TiO<sub>2</sub>-SiO<sub>2</sub> oxide composite, (b) the composite modified with 10 weight parts by mass of Ph-POSS, (c) PTMS, and (d) the TiO<sub>2</sub>-SiO<sub>2</sub> oxide composite bifunctionalised with 10 weight parts by mass of PTMS and Ph-POSS.

the range of 295–955 nm, with a maximum volume percent (21.8%) for particles with a diameter of 615 nm (Figure 2(b)).

Studies focused on assessing the microstructure and morphology of the obtained powder substances were carried out in order to obtain data regarding the morphology of seeds, the structure of a given particle as well as the agglomeration and dispersion characteristics. The presented TEM images of the analysed oxide systems (both for the unmodified composite and after modification with the POSS compound) show that the particles are characterised by a regular, spherical shape with a marginal tendency to form agglomerated structures. Upon analysing the TEM pictures, the Ph-POSS bonded to the surface of the inorganic carrier can also be observed. The particle size distribution curves and TEM images for the TiO<sub>2</sub>-SiO<sub>2</sub> synthetic composite modified with 10 weight parts by mass of PTMS were shown in Figure 2(c).

In the case of the particle size distribution curve in relation to the volume percent obtained for the oxide composite upon modification with 10 weight parts by mass of PTMS, a band in the range of 295–1110 nm can be observed. The maximum volume percent (15.4%) can be attributed to particles with a diameter of 459 nm. The obtained TEM images confirm that the particles had a spherical shape. A detailed procedure for the modification of the TiO<sub>2</sub>-SiO<sub>2</sub> oxide composite with silane proadhesive agents has been described in a previous publication [30].

In the next step, the morphological characteristics of the oxide composite modified with the PTMS silane and

additionally functionalised with the selected silsesquioxanes (Ph-POSS) have been carried out, and the obtained results were shown in Figure 2(d).

In the case of sample modified with 10 weight parts by mass of the PTMS and the POSS compound, a single band ranging from 255 to 955 nm could be observed. The maximum volume percent (18.9%) could be attributed to particles with a diameter of 531 nm. The TEM image showed that these particles were of regular spherical shape and a marginal tendency to form agglomeration structures.

**3.3. Water Wettability Profiles.** Analysis of the water wettability profiles for the synthetic TiO<sub>2</sub>-SiO<sub>2</sub> composite modified with a POSS compound showed that the studied samples exhibit a lower mass increase in time compared to unmodified samples (see Figure 3(a)).

The lowest mass increase was observed for samples modified with 10 weight parts by mass of Ph-POSS, which confirms that, with the increase of the surface functionalised with Ph-POSS, the hydrophobicity of the analysed oxide system is increased.

Analysing the water wettability profiles of samples modified with silane proadhesive agents and subsequently functionalised with the POSS compound (see Figure 3(c)), it can be observed that the lowest mass increase in time occurred for samples modified with 10 weight parts by mass of PTMS and Ph-POSS. This suggests that the increase of hydrophobic

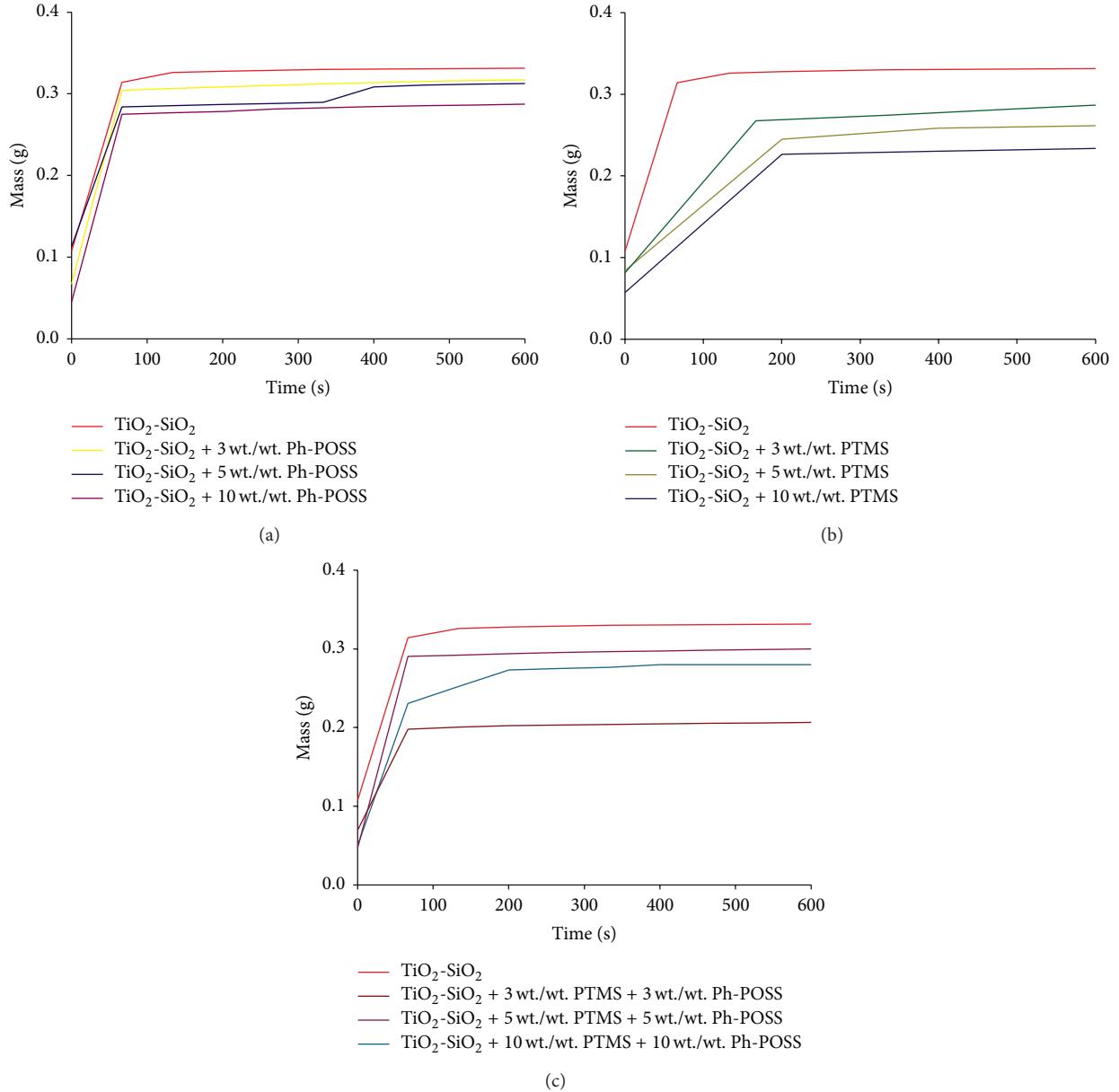


FIGURE 3: Water wettability profiles (a) for the unmodified  $\text{TiO}_2\text{-SiO}_2$  oxide composite and (b) composite modified with PTMS and (c) for the composite bifunctionalised with PTMS and Ph-POSS.

properties in comparison to the unmodified composite was greatest in this case.

**3.4. FT-IR Evaluations.** The spectroscopic studies were carried out in order to evaluate the efficiency of the modification process (appearance of characteristic functional groups) for the selected samples of unmodified and modified  $\text{TiO}_2\text{-SiO}_2$  composite. The obtained spectra were shown in Figure 4.

The carried out FT-IR analysis proved that the modification of the base sample with the use of Ph-POSS leads to a decrease of intensity for the  $-\text{OH}$  band with a wavenumber of approx.  $3620 \text{ cm}^{-1}$  which is proportional to the amount of the POSS compound used for the modification of the

carriers surface. The broad band between 500 and  $800 \text{ cm}^{-1}$  is associated with the  $\text{Ti-O-Ti}$  group. The bands corresponding to the silsesquioxane “cages” can be observed at approx.  $1118 \text{ cm}^{-1}$ . Other visible bands include  $\text{CH}_2$  ( $2927 \text{ cm}^{-1}$ ) and  $\text{CH}_3$  ( $2954$  and  $2871 \text{ cm}^{-1}$ ) groups [31].

The FT-IR spectra for the unmodified  $\text{TiO}_2\text{-SiO}_2$  oxide composite and the modified 10 parts by mass were shown in Figure 4(a); sample unmodified and bifunctionalised were shown in Figure 4(b). The presented spectra confirm the efficiency of the surface functionalisation process for the analysed oxide composite.

The Si-OH absorption bands of silicate matrix are shown at  $3750 \text{ cm}^{-1}$  as well as width bands related in the range of

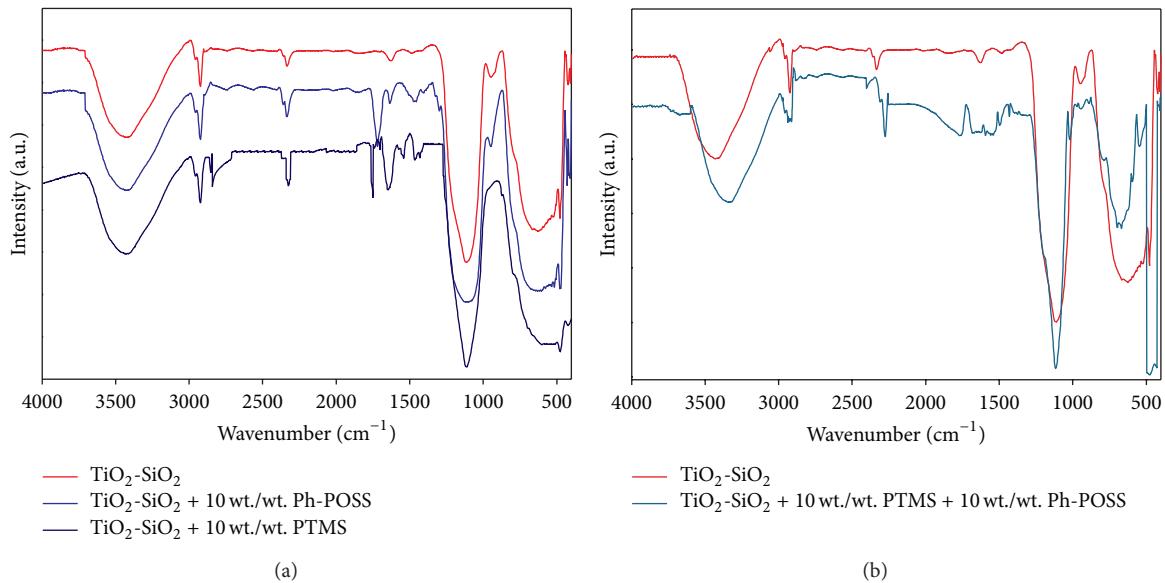


FIGURE 4: FT-IR spectra obtained (a) for the unmodified  $\text{TiO}_2\text{-SiO}_2$  oxide composite and composite modified with Ph-POSS and PTMS, (b) for the composite bifunctionalised with PTMS and Ph-POSS.

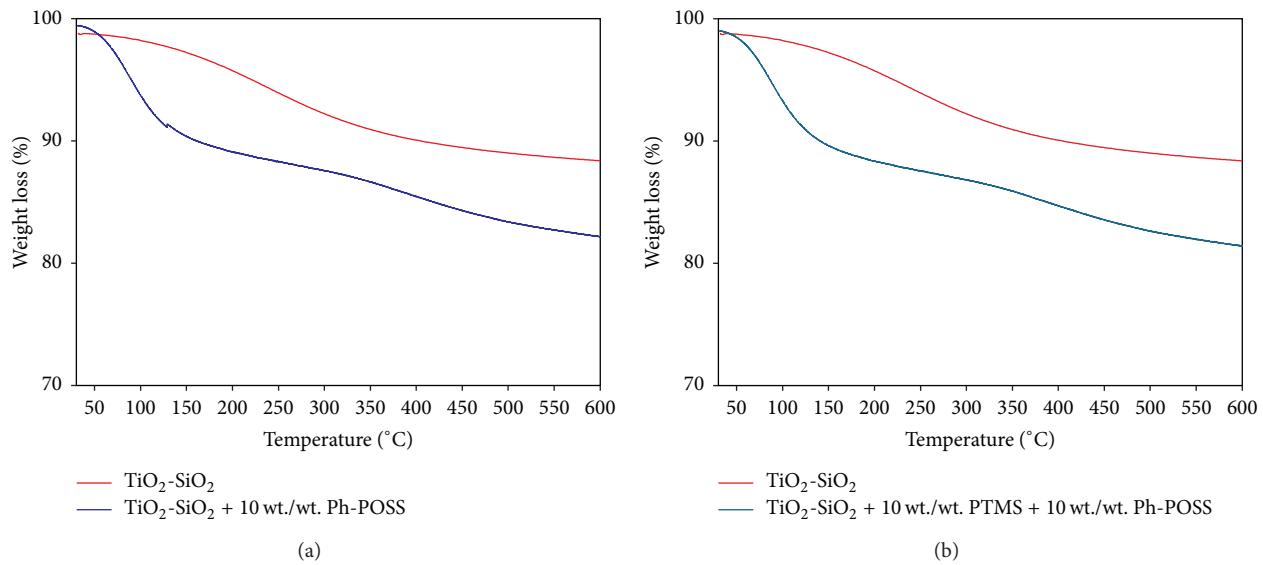
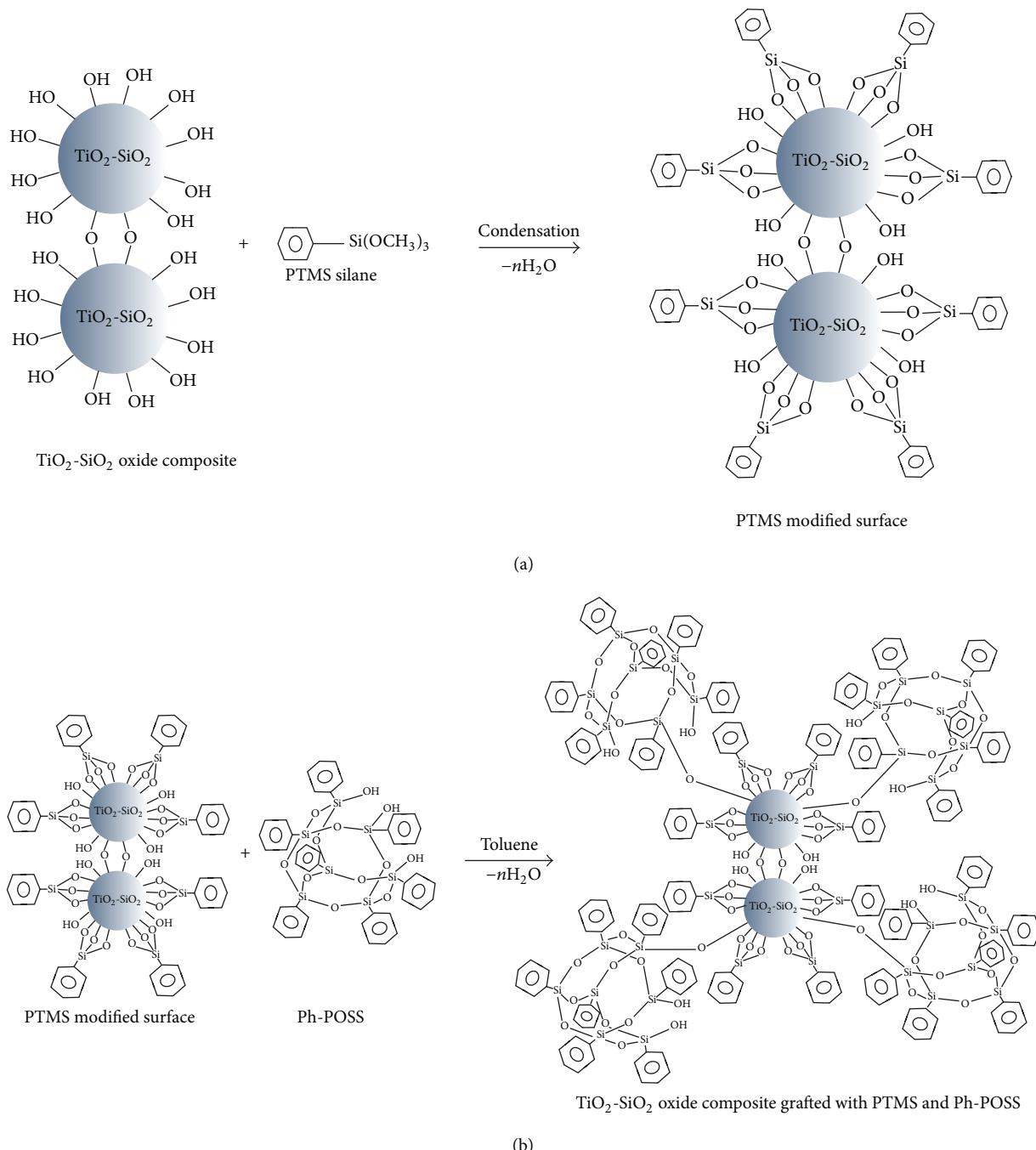


FIGURE 5: TGA curves obtained (a) for the unmodified  $\text{TiO}_2\text{-SiO}_2$  oxide composite and composite modified with Ph-POSS and (b) composite bifunctionalised with 10 weight parts by mass of PTMS and Ph-POSS.

$3500\text{--}3000 \text{ cm}^{-1}$  with physically adsorbed water has been noted. The band at  $1106 \text{ cm}^{-1}$  can be associated with the stretching vibration of Si-O-Si groups. A visible band corresponding to Ti-O-Si groups is also visible at  $970$  and  $1400 \text{ cm}^{-1}$ . The band at  $1106 \text{ cm}^{-1}$  can be associated with the stretching vibration of Si-O-Si groups. For the sample modified PTMS, we can observe the peaks at  $3044 \text{ cm}^{-1}$  (CH stretching vibrations) and  $1580$ ,  $1554$ , and  $1542 \text{ cm}^{-1}$  (C=C vibrational stretching of phenyl groups). Two distinct changes can be observed in the FT-IR spectra of POSS silanol (TriSilanolPhenyl POSS). The absorption peaks of the Si-OH

groups at  $3750\text{--}3000 \text{ cm}^{-1}$  as well as the width band at  $3500\text{--}3000 \text{ cm}^{-1}$  decrease in intensity obviously. This suggests that the condensation reaction of the Si-OH group between POSS silanol and hydroxyl-terminated on silicate surface has taken place. Another distinct change is the peak intensity between  $1000$  and  $1300 \text{ cm}^{-1}$ . The intensity of the Si-O-Si absorption band increases with the incorporation of POSS silanol. A visible band corresponding to Ti-O-Si groups is also visible at  $970$  and  $1400 \text{ cm}^{-1}$ . A band of the trisilanol-silsesquioxane cage appeared at  $1118 \text{ cm}^{-1}$  and was accompanied by  $\text{CH}_2$  ( $2927 \text{ cm}^{-1}$ ) and  $\text{CH}_3$  ( $2954$  and  $2871 \text{ cm}^{-1}$ ) stretching and



**SCHEME 1:** Mechanism of PTMS silane modification (a) and Ph-POSS grafting of  $\text{TiO}_2\text{-SiO}_2$  oxide composite (b).

corresponding deformational modes (1461, 1350, 1230, and  $839\text{ cm}^{-1}$ ). Band corresponding to  $\text{CH}_3$  at 2950 and  $1230\text{ cm}^{-1}$  indicates the occupation of the free sites on the surface.

In Scheme 1, proposed mechanism of PTMS modification and grafting with Ph-POSS of  $\text{TiO}_2\text{-SiO}_2$  oxide composite is presented.

**3.5. Structural Properties.** In the next experimental stage, the parameters of the porous structure of the unmodified and

modified  $\text{TiO}_2\text{-SiO}_2$  oxide composite have been determined, and the obtained results were shown in Table 2.

The value of specific surface area of the unmodified  $\text{TiO}_2\text{-SiO}_2$  composite sample was at  $24.8\text{ m}^2/\text{g}$ , while the pore volume was at  $0.040\text{ cm}^3/\text{g}$ . The average pore diameter value was  $5.9\text{ nm}$ . Subjecting the  $\text{TiO}_2\text{-SiO}_2$  oxide composite to modification with the selected silsesquioxane contributed to a notable decrease of the basic adsorptive parameters. Upon modification with 10 weight parts by mass of Ph-POSS, the studied oxide composite reached a specific surface area value

TABLE 2: Parameters of porous structure of both unmodified and modified  $\text{TiO}_2\text{-SiO}_2$  oxide composite.

Sample	$A_{\text{BET}}$ ( $\text{m}^2/\text{g}$ )	$V_p$ ( $\text{cm}^3/\text{g}$ )	$S_p$ (nm)
$\text{TiO}_2\text{-SiO}_2$	24.8	0.040	5.9
$\text{TiO}_2\text{-SiO}_2 + 10$ weight parts by mass of Ph-POSS	7.0	0.030	17.1
$\text{TiO}_2\text{-SiO}_2 + 10$ weight parts by mass of PTMS	6.6	0.020	12.6
$\text{TiO}_2\text{-SiO}_2 + 10$ weight parts by mass of PTMS + 10 weight parts by mass of Ph-POSS	3.3	0.008	10.4

of  $7.0 \text{ m}^2/\text{g}$  and a pore volume of  $0.030 \text{ cm}^3/\text{g}$ . The average pore diameter value for the oxide composite modified with 10 weight parts by mass of Ph-POSS was 17.1 nm.

Measuring the specific surface area showed that the changes occurring on the surface of the  $\text{TiO}_2\text{-SiO}_2$  oxide composite subjected to the functionalisation process with POSS type compounds are very notable. Due to this process the active centers on the surface of the composite are blocked.

In the next experimental stage, the obtained functionalised  $\text{TiO}_2\text{-SiO}_2/\text{PTMS/POSS}$  hybrid fillers were subjected to an analysis of their structural properties. The obtained results suggest that the use of silanes (PTMS) for functionalisation of the oxide composite surface contributes to a decrease of the BET specific surface area. This effect is a result of blocking active centres present on the surface of the composite. Due to subsequent modification of the functionalised composite with POSS compounds, a further decrease of the specific surface area was observed. The obtained results may also be used for an indirect confirmation of the proposed modification methods efficiency.

**3.5.1. Thermogravimetric Analysis.** Thermal analysis is an important method which enables the determination of the thermal durability or lifetime for the studied materials and allows for evaluating the thermodynamic and kinetic parameters of the reaction. Due to this fact, the thermal analyses are frequently employed in several branches of science and industry. In the framework of the presented studies the TGA technique was used, which allows for registering the changes in sample mass as a function of temperature.

The thermogravimetric curves obtained for the unmodified  $\text{TiO}_2\text{-SiO}_2$  oxide composite and the composite modified with 10 weight parts by mass of Ph-POSS were shown in Figure 5(a). The total decrease of mass for the analysed samples changes with the increase in temperature. The highest decrease of mass for the  $\text{TiO}_2\text{-SiO}_2/\text{Ph-POSS}$  hybrid filler was observed at  $150^\circ\text{C}$ . On the other hand, the highest decrease of mass for the unmodified oxide composite was observed at approx.  $300^\circ\text{C}$  [32].

The thermogravimetric curves obtained for the unmodified  $\text{TiO}_2\text{-SiO}_2$  oxide composite and the composite modified with 10 weight parts by mass of PTMS and Ph-POSS were shown in Figures 5(a) and 5(b). It was observed that up to the temperature of  $150^\circ\text{C}$ , the physically and chemically bound

water is removed from the sample, while for samples modified at  $300^\circ\text{C}$ , the degradation of groups from the open cage occurs. Since the cages consist of 8 silica atoms, they are more thermally stable compared to POSS with open cages, which tend to bond more easily but are less thermally resistant.

## 4. Conclusions

In the framework of the presented studies, the efficiency of the proposed surface modification method for  $\text{TiO}_2\text{-SiO}_2$  oxide composites with POSS compounds and bifunctionalisation of surface with POSS and selected silane proadhesive agents has been presented and confirmed by the results of FT-IR and TGA analyses.

Based on the obtained results, it was established that bifunctionalisation leads to the deterioration of dispersive-morphological properties compared to samples modified with the use of silsesquioxanes only. The samples obtained upon modification with silanes and subsequent modification with POSS exhibit a higher tendency to form agglomeration structures, which is why the disappearance of nanometric particles can be observed. This fact becomes especially visible with increasing amounts of the silane used for modification. The electrokinetic studies have shown that the samples modified with POSS only exhibit better stability. Modification of the  $\text{TiO}_2\text{-SiO}_2$  oxide composite with the mentioned silsesquioxane improves its hydrophobic properties, as confirmed by the water wettability studies. It was established that the bifunctionalisation with PTMS and POSS leads to a marginal increase of the hydrophobic properties for the analysed hybrid fillers.

To summarize, from the point of future applications of this type of functionalised hybrids, better electrokinetic and physicochemical properties were exhibited by oxide composites modified only with POSS-type compounds. Based on the obtained results, it can be established that the proposed  $\text{TiO}_2\text{-SiO}_2/\text{Ph-POSS}$  hybrids may be successfully applied in the constantly developing plastics industry and others applications.

## Conflict of Interests

The authors declare no conflict of interests in respect of their submitted paper.

## Authors' Contribution

The authors equally contributed in this paper.

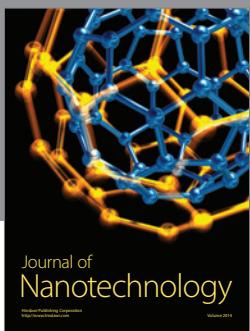
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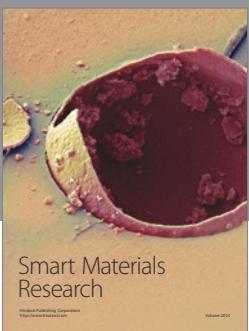
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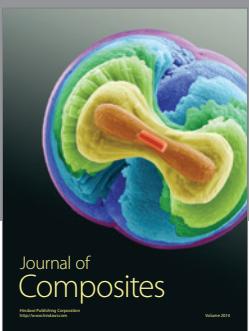
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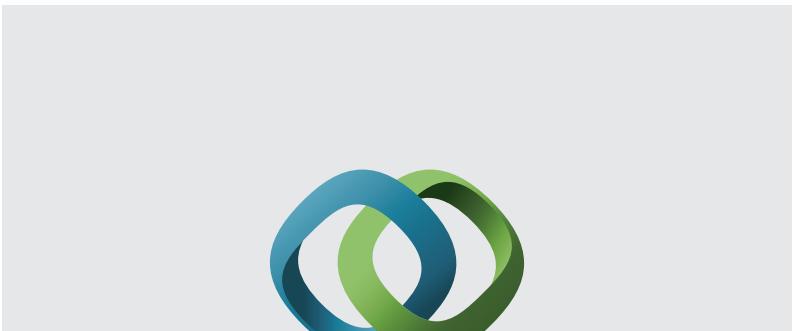
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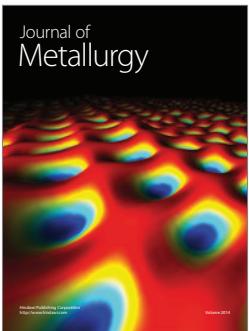


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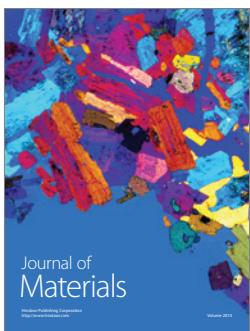
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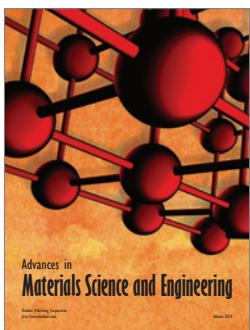
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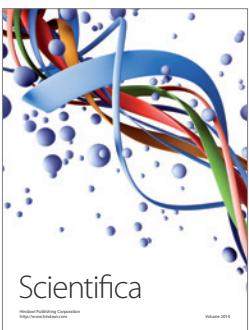
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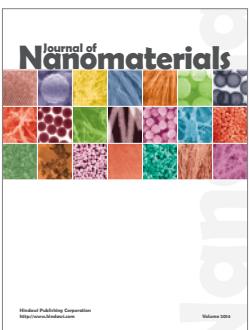
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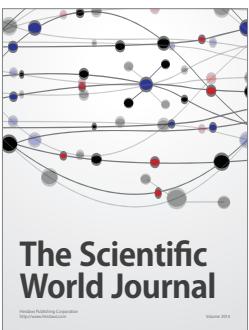
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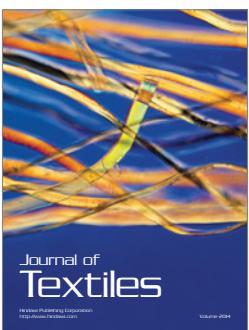
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