

The new functional filler TiO₂-SiO₂/polyhedral oligomeric hybrid silsesquioxane as a potential modifier of polyethylene

Arkadiusz Kloziński^{1,*)} (ORCID ID: 0000-0002-2025-699X), Damian Ambrożewicz¹⁾, Paulina Jakubowska¹⁾ (0000-0002-8638-1216), Beata Dudzic^{2),3)} (0000-0001-6344-0298), Ewa Andrzejewska¹⁾ (0000-0002-6940-1289), Bogdan Marciniak³⁾ (0000-0001-5203-1376), Teofil Jesionowski¹⁾ (0000-0002-7808-8060)

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Abstract: The paper presents preliminary application studies of the innovative TiO₂-SiO₂/ POSS filler as a potential low-density polyethylene modifier. It was found that the addition of the filler increases the stiffness and hardness of the composite and slightly changes the intensity of its color.

Keywords: polymer composites, polyethylene, hybrid fillers, POSS, mechanical properties.

Nowy funkcjonalny napełniacz hybrydowy TiO₂-SiO₂/wielościenny oligomeryczny silseskwioxan jako potencjalny modyfikator polietylenu

Streszczenie: Przedstawiono wstępne badania aplikacyjne innowacyjnego napełniacza TiO₂-SiO₂/POSS jako potencjalnego modyfikatora polietylenu małej gęstości. Stwierdzono, że dodatek napełniacza powoduje wzrost sztywności i twardości kompozytu oraz nieznacznie zmienia intensywność jego barwy.

Słowa kluczowe: kompozyty polimerowe, polietylen, napełniacze hybrydowe, POSS, właściwości mechaniczne.

Many natural materials are highly integrated hybrid materials which are characterized by various properties (mechanical properties, density, color, hydrophobicity). A characteristic feature of hybrid materials is that their properties are not only associated with their chemical nature of organic and inorganic compounds but are also dependent on their synergy. This is why a connection between organic and inorganic parts strongly influences their properties. Hybrids may be characterized by a type or size of organic or inorganic precursors. The precursors may consist of two separate monomers which are not connected [1–5]. However, uniform hybrids reveal the best properties both organic and inorganic. During last few decades many researchers focused on producing new hybrid materials, such as POSS. Polyhedral oligo-

meric silsesquioxanes (POSS) are characterized by monodisperse size, low density, high thermal stability, and controlled functionality which make them ones of the most frequently used compounds for the preparation of nanomaterials [6–12]. They lead to substantial improvement in their physicochemical properties, *i.a.* increased thermal and mechanical properties, *e.g.* hardness as well as the reduction of flammability, heat evolution, viscosity during processing, *etc.* [13, 14]. Monofunctional POSS may be used as polymer modifiers introduced into polymer chain during polymerization. Monofunctional POSS with methacrylate functional groups may be also used as monomers in copolymerization of other acrylate monomers and offer novel branches for their applications, *e.g.* in dentistry [12, 15–17]. Bifunctional POSS derivatives may be utilized as monomers in polycondensation reaction for production of polymers containing POSS groups in their structure. On the other hand, multifunctional POSS derivatives are widely used for production of cross-linked polymer/POSS nanocomposites [14, 18]. A higher amount of POSS in composites is responsible for lower dielectric constant in obtained products. However, the amount of POSS which may be introduced into nanocomposites is limited due to compatibility between POSS and polymer [19, 20]. Nanofillers, such as POSS, are also used for production of nanocomposites based on thermoplas-

¹⁾ Institute of Chemical Technology and Engineering, Faculty of Chemical Technology, Poznan University of Technology, Berdychowo 4, 60-965 Poznań, Poland.

²⁾ Department of Organometallic Chemistry, Faculty of Chemistry, Adam Mickiewicz University in Poznań, Uniwersytetu Poznańskiego 8, 61-614 Poznań, Poland.

³⁾ Centre for Advanced Technologies, Uniwersytetu Poznańskiego 10, 61-614 Poznań, Poland.

*) Author for correspondence:

Arkadiusz.Klozinski@put.poznan.pl

tic matrix (polyolefins) [21–28]. In this case, the process of composites production is conducted in a molten state with the use of homogenization processing techniques [29–32]. The addition of polyhedral oligomeric silsesquioxanes to polyolefins causes changes in mechanical, thermal, electrical as well as rheological properties with using considerably lower content of nanofiller in comparison to commonly used fillers [24, 29, 33–38].

The increasing demand for materials with strictly designed properties determines researches on creation of brand new hybrid systems or modification of already existing ones [25]. One way to obtain modern active fillers is a method of modification of hybrid systems with POSS compounds which are composed of T silicon units [39, 40]. The use of hybrid systems modified with POSS as polymer fillers allows for highly targeted modification of properties of produced composites.

One compound that plays an important role in various modern industries and applications is titanium dioxide (TiO_2). Apart from its main use as an excellent white inorganic pigment in paint production, titanium dioxide is an important compound in the food industry, pharmacy, cosmetics, textile industry, ceramics, packaging industry (polymer films), and other modern technologies [41, 42]. Titanium dioxide is also one of the most important inorganic pigments used in polymeric materials. The highest consumption of titanium dioxide is observed in the processing of poly(vinyl chloride) and polyolefins, mainly polyethylene. In case of polyethylene films high hiding power and strong coloring power of TiO_2 are used [43]. A big problem in the use of titanium dioxide, similar as in case of silicate fillers, is its tend to form aggregates and agglomerates in polyolefin matrices [44–46]. This effect is generally a result of very strong interactions between the hydrophilic filler particles and their weak interactions with the hydrophobic polymer chains [44]. Increasing the adhesion at the polymer-filler interface is achieved often by modifying the filler surface [45, 46]. Increasing the compatibility between the components of composites can also be obtained by the use of POSS nanofillers, especially with long alkyl substituents [35, 44]. Therefore, it is justified to do researches based on the use POSS nanofillers, aimed at improving the compatibility and homogeneity of the dispersion of filler particles in polymeric matrix, as a one of the main factors determining the improvement of composites properties.

There is a lack of data concerning composites containing TiO_2 - SiO_2 oxide fillers modified with POSS compounds in articles focused on the production of hybrid systems and their application in polymeric materials. Therefore, the aim of this research is to produce an innovative hybrid system (TiO_2 - SiO_2 /POSS). Presented results are the description of the filler synthesis, its physicochemical characteristics and the attempt at this application. Results on the influence of the hybrid filler on selected polyethylene functional properties (strength, hardness, color, wettability) described in this paper are preliminary

tests – the purpose of which is to determine the possibility of using the TiO_2 - SiO_2 /POSS system as a potential modifier of the properties of polyethylene products.

EXPERIMENTAL PART

Materials and methodology

The chemicals were purchased from the following sources: silicon tetrachloride, chlorodimethylsilane, Karstedt's catalyst ($[\text{Pt}_2(\text{dvds})_3]$ solution in xylene with 2% of Pt), allyl alcohol, ammonium chloride, magnesium sulfate, triethylamine (Et_3N), toluene, tetrahydrofuran (THF), methanol, *n*-hexane, chloroform, chloroform-*d*, silica gel -MN-Kieselgel 60 from Sigma-Aldrich. $\text{iBu}_7(\text{Si}_7\text{O}_9)(\text{OH})_3$ from Hybrid Plastic.

All preparations for the synthesis of 1-(3-hydroxypropyl)dimethylsiloxy-3,5,7,9,11,13,15-hepta(isobutyl)pentacyclo-[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane (marked as 3 in Fig. 1) were conducted under argon atmosphere using standard Schlenk-line and vacuum techniques. ^1H , ^{13}C and ^{29}Si NMR spectra were performed with Bruker Ultrashield 400 MHz spectrometer, using CDCl_3 as a solvent and the chemical shifts are reported in ppm with reference to the residual solvent peaks for ^1H and ^{13}C and to TMS for ^{29}Si . Toluene and amine were dried over CaH_2 and THF over Na with benzophenone before use and stored under argon in Schlenk.

Synthesis procedure for the preparation of 1-(3-hydroxypropyl)dimethylsiloxy-3,5,7,9,11,13,15-hepta(isobutyl)pentacyclo-[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane

$\text{iBu}_7(\text{Si}_7\text{O}_9)(\text{OH})_3$ (15.48 g, $19.56 \cdot 10^3$ mol), anhydrous THF (300 cm^3) and Et_3N (9.54 cm^3 , $6.85 \cdot 10^3$ mol) were added to a two-neck round-bottom flask equipped with a magnetic stirrer and placed in an ice-water bath, purged with argon, after which SiCl_4 (2.3 cm^3 , $19.90 \cdot 10^3$ mol) was added and left for 24 hours at room temperature. Next, the insoluble solid of triethylammonium chloride was removed by filtration and the precipitate was washed with THF and the solvent was evaporated. The residue (marked as 2a in Fig. 1) was again dissolved in a mixture of THF (100 cm^3) and water (20 cm^3) and heated at 65°C for 24 h. After this time, the THF was evaporated and the remains were extracted with *n*-hexane (100 cm^3), water, and brine. The organic phase was collected and dried with MgSO_4 . Evaporation gave the analytically pure monosilanol $\text{iBu}_7(\text{Si}_8\text{O}_{12})(\text{OH})$ in the form of a white solid which was put in a two-neck round-bottom flask, purged with argon along with anhydrous THF (300 cm^3), Et_3N (1.5 cm^3 , $28.70 \cdot 10^3$ mol) and chlorodimethylsilane (2.24 cm^3 , $20.16 \cdot 10^3$ mol), and left with stirring for 24 h at room temperature. The triethylammonium chloride solid was removed by filtration and the crude product was precipitated in cold methanol. After methanol removal, the 16.57 g of solid 2c was dried *in vacuo* and obtained with 97% yield.

In the final step of the synthetic route, a mixture consisting of 2c (16.57 g, $18.60 \cdot 10^{-3}$ mol), toluene (150 cm^3) and allyl alcohol (1.40 cm^3 , $20.10 \cdot 10^{-3}$ mol) was placed in a round-bottom flask equipped with a condenser and $[\text{Pt}_2(\text{dvds})_3]$ was added ($181 \cdot 10^{-3} \text{ cm}^3$). Afterwards it was heated to 95°C and left with stirring for 24 h. Then, the volatiles of toluene and unreacted allyl alcohol were evaporated and the crude product was purified on a column chromatography on silica gel, eluting with CHCl_3 . Solvents evaporation gave pure 16.7 g (95%) of 1-(3-hydroxypropyl)dimethylsiloxy-3,5,7,9,11,13,15-hepta(isobutyl)pentacyclo-[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane (3). The ^1H , ^{13}C , ^{29}Si NMR analysis confirmed the formation of the desired product and was analogous to the reported ones [17, 40, 47].

TiO_2 - SiO_2 /POSS filler synthesis

TiO_2 - SiO_2 preparation

TiO_2 - SiO_2 was used to produce hybrid systems in this research. A co-precipitation of TiO_2 - SiO_2 inorganic filler was conducted in an emulsion system. For this purpose, two emulsions, E1 and E2, were prepared. Firstly, the E2 emulsion was prepared and it contained cyclohexane as an organic phase, and titanium sulfate (titanium precursor) and nonionic surfactants as emulsifiers. The emulsion components were uniformed for 15 minutes using a homogenizer Basic Ika Werke type T25 operated at about 16 000 rpm. Secondly, the E1 emulsion was prepared and it consisted of cyclohexane, 5 % sodium silicate of 3,3 modulus (silicon source), and nonionic surfactants. The emulsion was subjected to the same homogenization procedure as the previous one. The co-precipitation process was conducted in a system that consisted of a reactor with a capacity of 2 dm^3 , homogenizer and peristaltic pump. The precipitation involved an introduction of the second emulsion containing sodium silicate into a reactor filled with acidic E2 emulsion which in turn was homogenized with a speed of 16 000 rpm. The E1 emulsion was dosed using a peristaltic pump at a constant speed. After the introduction of the whole volume of the E1 emulsion, the system was further homogenized for 20 minutes just in case the reaction was not completed. The resulting product with TiO_2 - SiO_2 precipitate underwent a process of breaking of an emulsion form in order

to separate its components. Destabilization was carried out at 80°C . As a result, the product split into three phases. The TiO_2 - SiO_2 precipitate with aqueous phase was in the lower part of the system, while an upper part consisted of cyclohexane which in turn was separated from the rest through vacuum distillation. The obtained product was separated from post-reaction mixture using a low pressure filtration process. The filtrated precipitate was dried at 105°C for 18 h. Then it was parched in a furnace Nabertherm type Controller P320 in order to obtain a defined crystalline form of titanium dioxide in the final composite. Calcination was proceeded at 950°C for 1 h. After drying and calcination, the last step included preparation of the obtained product for physicochemical analysis. For this purpose, the TiO_2 - SiO_2 powders were ground in a mechanical mortar grinder. The final product was characterized and used in the novel hybrid filler preparation.

Synthesis of POSS

1-(3-hydroxypropyl)dimethylsiloxy-3,5,7,9,11,13,15-hepta(isobutyl)pentacyclo-[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane (3) was used as a nanofiller and a modifying agent for TiO_2 - SiO_2 . Its structure and synthetic route are presented in Figure 1. The titled compound 3 was obtained in a sequence of reactions, starting from commercially available open-cage trisilanol iBuPOSS ($\text{iBu}_3(\text{Si}_7\text{O}_9)(\text{OH})_3$) and its use in corner-capping hydrolytic condensation with SiCl_4 , hydrolysis and consecutive hydrolytic condensation with ClSiMe_2H to obtain Si-H functionalized silsesquioxane derivative (2c). Finally, 2c was used as a hydrosilylating agent of allyl alcohol in a Pt-Karstedt's catalyzed reaction to gain 3 with a 95% yield and its synthetic procedure is described in the experimental part.

The mono(3-hydroxypropyl)-functionalized silsesquioxane was reported as an additive for the modification of MgO - SiO_2 and further modifier of polypropylene [40]. It is also a perspective reagent for further conversion *i.e.* introduction of methacrylate group or alkylcarboxy functionality and used as a modifier of polymethacrylates and polylactides respectively or others [17, 48, 49]. It was shown that the surface properties of the hybrid coatings of resulting materials were strongly modified even for very low content of POSS (1 or 2 wt%).

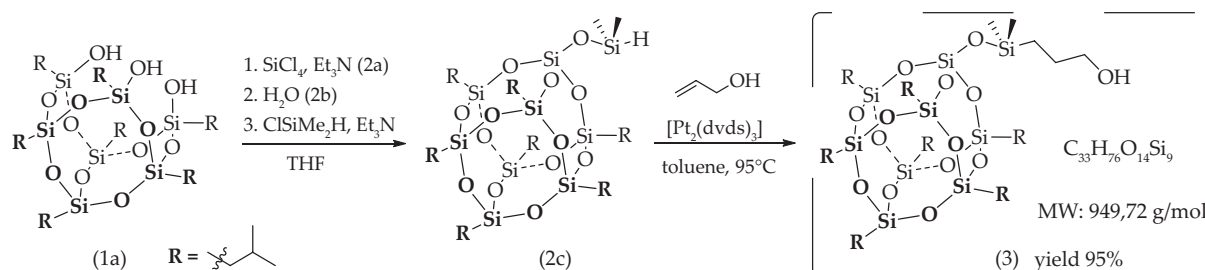


Fig. 1. Reaction path for the synthesis of 1-(3-hydroxypropyl)dimethylsiloxy-3,5,7,9,11,13,15-hepta(isobutyl)pentacyclo-[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane

1-(3-hydroxypropyl)dimethylsiloxy-3,5,7,9,11,13,15-hepta(isobutyl)pentacyclo-[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane was applied to the carrier (TiO₂-SiO₂) in an amount of 3, 5 and 10 parts by weight applying a hydrolytic-condensing method of modification with toluene evaporation using a vacuum evaporator. The modification process of ceramic filler with the use of POSS nanofiller was described in a previous paper [50]. The modified filler was utilized to produce polymeric composites based on polyethylene matrix. Filler systems containing 3 and 5 parts by weight POSS did not show any influence on the functional properties of polyethylene. Therefore, the test results for composites containing titanium silicate modified with 10 parts by weight of POSS and non-modified titanium silicate as a reference filler will be discussed.

Polymer matrix

The commercial low-density polyethylene (LDPE Malen E FABS 23-D022), with MFR_(2.16; 190) = 2.00 g/10 min and density of 0.921 g/cm³ from Basell Orlen Polyolefines (Poland) was used as polymeric matrix.

Homogenization

Homogenization process of composites was conducted in two steps. During the first step, concentrates with 10 wt% of the filler (TiO₂-SiO₂ and TiO₂-SiO₂/POSS) were obtained by using a Brabender type measuring mixer operated at 160°C and 20 rpm for 15 minutes. Next, concentrates were diluted to a concentration of 0.15, 0.5 and 1.0 wt% of the filler by a twin-screw extrusion process. A co-rotating twin-screw extruder, model EH16.2D, by Zamak Mercator (Poland), with a screw diameter of $D = 16$ mm and L/D ratio of 40 was employed. The extrusion process was conducted at 120 rpm, in the barrel temperature range between 100 and 190°C. The material was first palletized (cold granulation) and then injection molded using a Battenfeld hydraulic injection molding machine, model PLUS 35/75. Dumbbell shape specimens were produced as per ISO 527-2 – type 1A. The specimens were tested, among others, for mechanical properties under static tension, hardness, contact angle, and color changes.

Methods and procedures for the physicochemical and mechanical properties characterization

Filler

A comprehensive characteristics of the TiO₂-SiO₂/POSS hybrid systems was made by a direct determination of particle size, morphology, and microstructure of grains as well as tendency to agglomeration. Moreover, FT-IR examinations were performed and a profile of wetting the surface with water was determined. The measurements of particle size distribution of the powders were conducted using Zetasizer Nano ZS analyzer manufac-

tured by Malvern Instruments Ltd. The device allows to analyze dispersion of particles of sizes in the range between 0.6 to 6000 nm. The wettability measurement was conducted using K100 tensiometer, equipped with an attachment device for estimating wettability of the solid particles, produced by Krüss. The FT-IR spectra of the fillers were conducted using a Bruker spectrophotometer, model Vertex 70, applying infrared radiation which range was between 4000 and 400 cm⁻¹. Morphological and structural observations of obtained hybrid fillers were conducted using TEM (Jeol 1200 EXII).

Composites

To assess the strength properties of composites under static tension a two-column Zwick testing machine, model Roell Z020 (Germany), was used. All the tests were carried out at a constant crosshead speed of 50 mm/min. The following mechanical properties were determined: Young's modulus (E_f , MPa); stress at the maximum force (σ_{Mf} , MPa) and elongation at break (ϵ_{Bf} , %). The hardness of composites was determined using a Shore D hardness tester manufactured by Zwick (as per ISO 868:2005). The hardness was designated in the measuring section, on the surface of dumbbell shape specimens. The composite surface wettability was tested throughout a determination of the contact angle value – an evaluation of drop shape (water) with accuracy of ± 0.01 mN/m at 25°C using a device produced by Krüss, model DSA 100. The color measurements of the composites were conducted using a Specbos 4000 colorimeter produced by Yeti Technische Instrumente GmbH.

RESULTS AND DISCUSSION

Characteristics of physicochemical and structural properties of fillers

The particle size distributions and selected TEM images of obtained fillers are presented in Figure 2.

The analysis of the results revealed that unmodified sample was characterized by a monomodal particle distribution and particles of 295 nm size occupied 26.4% of volume in the sample. However, a modification of the filler with 3, 5 and 10 parts by weight of POSS caused an appearance of particles with larger diameters (255–1100 nm) which was confirmed by the appended particle size distributions and a TEM image (Figure 2). The FT-IR analysis was conducted for the systems to prove rightness of the modification process. In the FT-IR spectra (Figure 3) an appearance of bands typical for organic groups attached to silicon cage as well as POSS silicon--oxygen cages themselves was observed. An intensity of free OH groups at a wavelength of 3620 cm⁻¹ decreased. However, the bands deriving from C-H, CH₂ and CH₃ bonds appeared at wavelengths of 2918 and 2849 cm⁻¹ – these derived from the organic substituents attached to the sil-

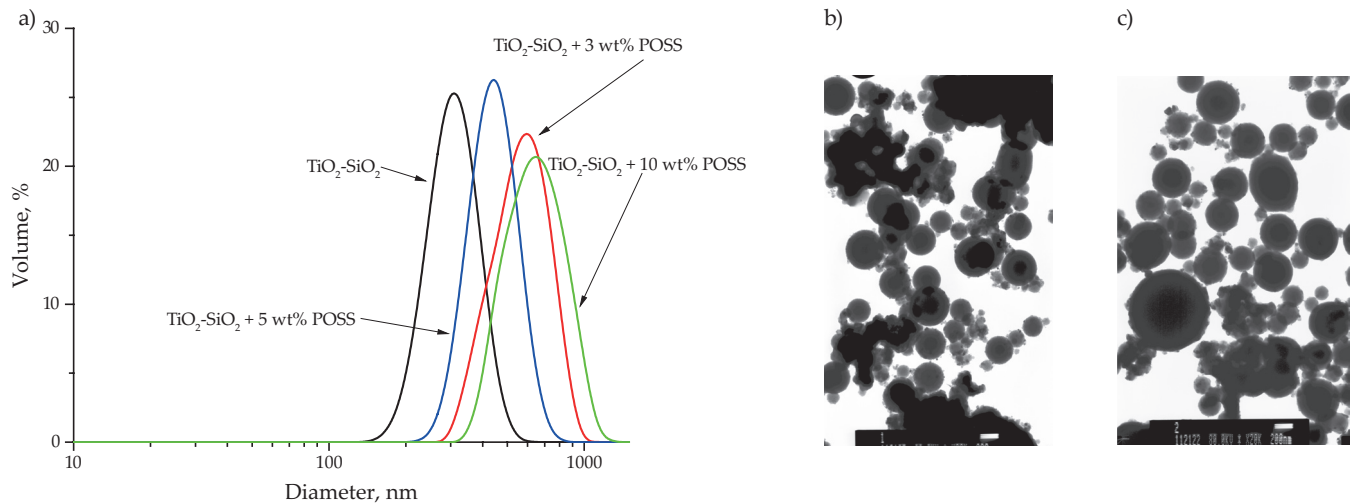


Fig. 2. The particles size distributions (in volume contribution) of the $\text{TiO}_2\text{-SiO}_2$ samples of unmodified and modified by 3, 5 and 10 wt% POSS (a) and TEM micrographs of (b) unmodified sample and (c) modified by 10 wt% POSS sample

icon-oxygen cage. The Si-O-Si bonds, originating from POSS, were observed at wavelengths of 1110 cm^{-1} and 1223 cm^{-1} , while the Si-C bonds were noticed at wavelengths of 734 cm^{-1} and 781 cm^{-1} .

Modification of synthetic oxide system with POSS compound directly influenced a capability of its interaction with the polar solvent (water). The analysis of water wettability profiles (Figure 4) revealed that modified samples had a smaller increase of mass in time in comparison to unmodified sample. The sample that contained 10 wt% of POSS revealed the smallest growth in mass. It may be observed that an increasing amount of the modifier increased the sample hydrophobicity. In practice, this may result in increased interactions at the polymer-filler interface, thus better homogenization of filler in the polymer matrix and improved composite properties. The influence of fillers on the properties of the composite

depends not only on their concentration and the size and shape of the particles, but most of all on the interaction with the polymer matrix [51].

Properties of polymeric composites

The analysis of mechanical measurements conducted under static extension revealed that an addition of the fillers caused changes in Young's modulus. The course of changes in the value of elastic modulus (E_p) in a function of content and type of the filler is presented in Figure 5. An increase in stiffness of polyethylene was observed when at least 0.15 wt% of the filler was added. An addition of 1.0 wt% of the filler caused an increase in Young's modulus equal to 8% for the unmodified filler and 6% for modified one. For every of the filler concentrations used (0.15, 0.5 and 1.0 wt%), greater Young's modulus values

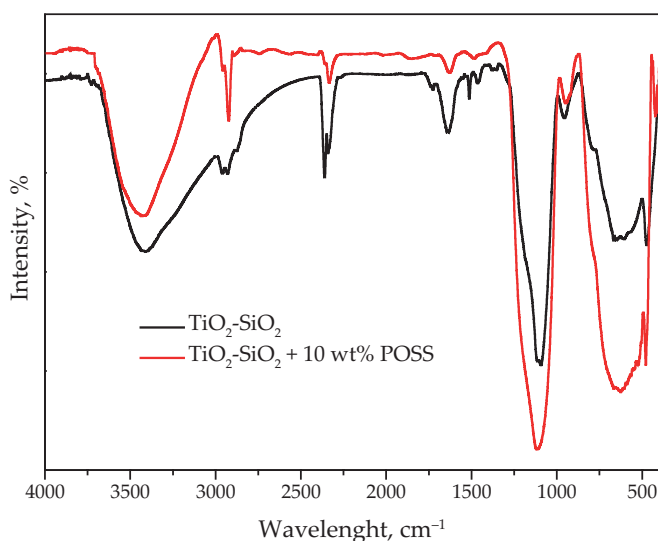


Fig. 3. Comparison of FT-IR spectra of the unmodified filler ($\text{TiO}_2\text{-SiO}_2$) and modified with 10 wt% POSS

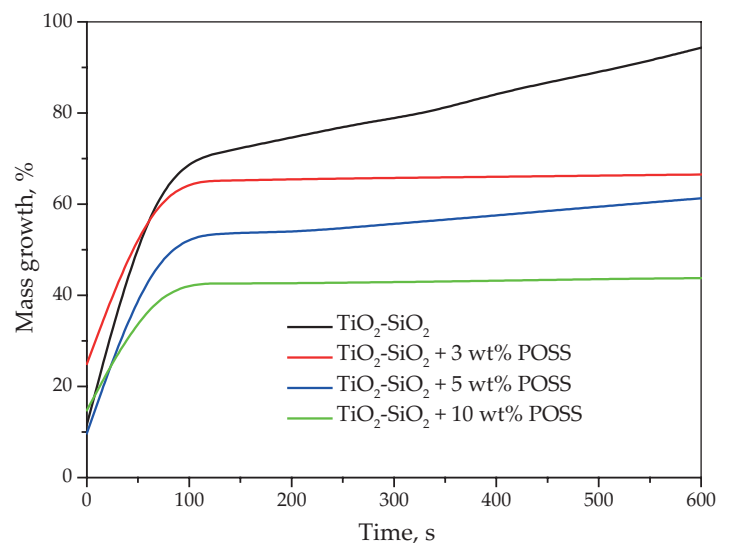


Fig. 4. Water wettability profiles for unmodified and grafted with 3, 5 and 10 wt% POSS samples of $\text{TiO}_2\text{-SiO}_2$

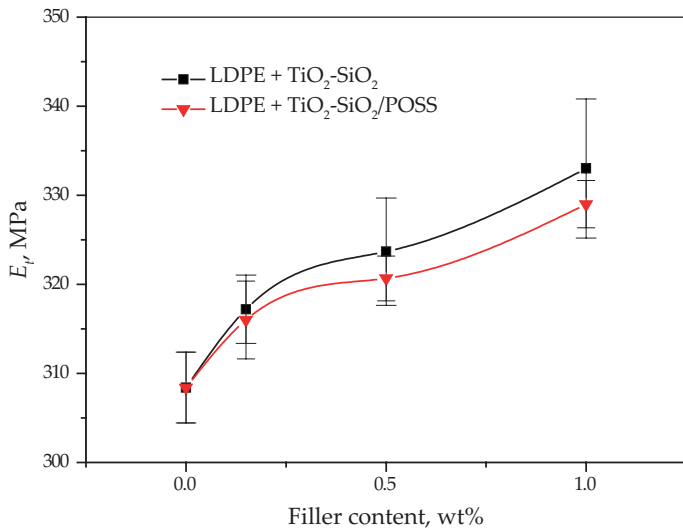


Fig. 5. The Young's modulus (E_f) as a function of filler content and type

for composites that contained unmodified TiO₂-SiO₂ were noted. Modification of the filler, causing a decrease in stiffness of the composite, may result from the construction of the organic substituents (R) of the POSS modifier. Similar dependencies were presented in the publication of Baldi *et al.* [36]. They discussed an impact of a type and amount of the organic substituents in POSS nanofillers on mechanical properties of polypropylene composites.

Changes in Young's modulus values influenced directly the elongation at break in the composites (Figure 6). No changes in the ϵ_B values in a function of filler content were noted. However, an elongation for LDPE + TiO₂-SiO₂ composites decreased in comparison to unfilled LDPE and increased in case of composites that contained titanium silicate (LDPE + TiO₂-SiO₂). Modification of the filler caused a decrease in composite stiffness ($E_f \downarrow$) and an increase in elongation conducted under static tensile

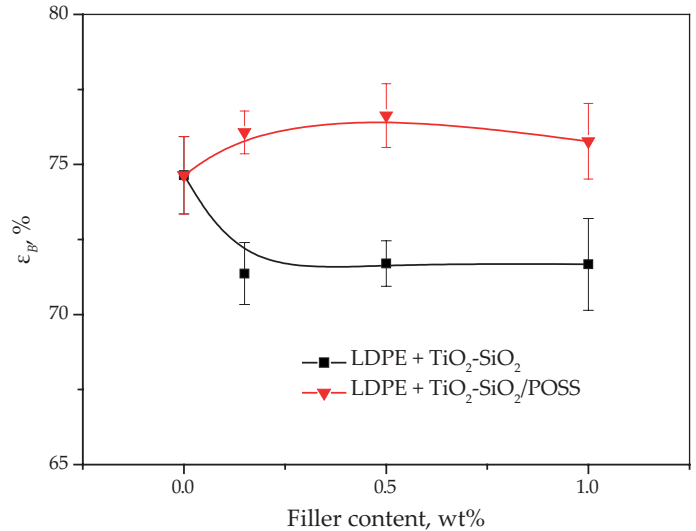


Fig. 6. The elongation at break (ϵ_B) as a function of filler content and type

test ($\epsilon_B \uparrow$). Modification of titanium dioxide with nano-filler in this case caused a slight increase in elasticity of the composite, which may result from previously mentioned structure of the POSS substituents [36].

An addition of the fillers did not affect the durability of the composites in comparison to pure LDPE. There was no effect of the filler modification or changes in its content on the σ_B value (Figure 7).

The obtained composites were subjected to surface properties tests. Moreover, hardness, wettability, and color change for composites were determined. The hardness was defined using Shore apparatus (D scale). The changes in Shore hardness as a function of the filler content (Figure 8) allowed to conclude that even 0.15 wt% of the filler improved composites hardness in comparison to pure LDPE. An increase in hardness values for the composites with increasing amount of the filler in the

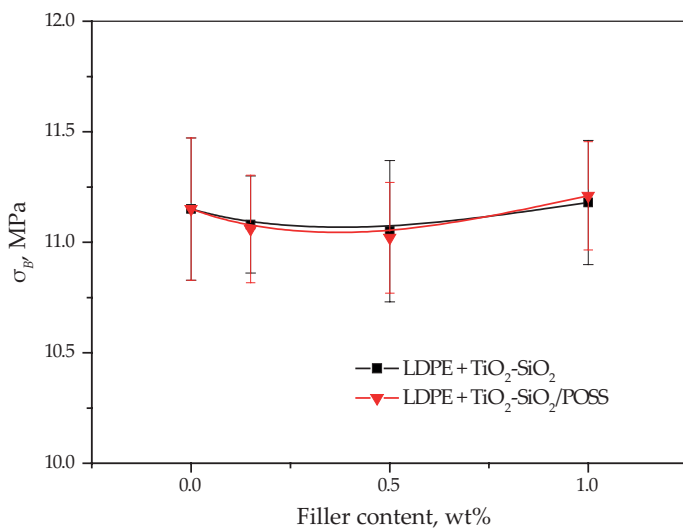


Fig. 7. The strength at break (σ_B) as a function of filler content and type

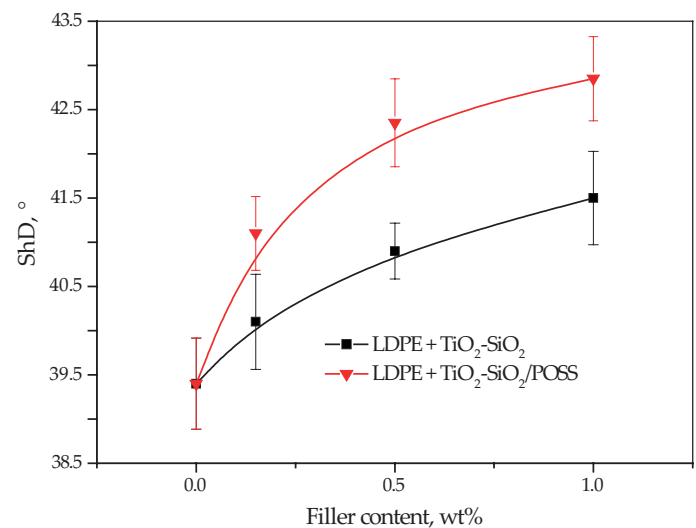


Fig. 8. The Shore hardness as a function of filler content and type



Fig. 9. Images of water drop on the surface of: a) LDPE, b) LDPE + 1 wt% $\text{TiO}_2\text{-SiO}_2$, c) LDPE + 1 wt% $\text{TiO}_2\text{-SiO}_2/\text{POSS}$

system was noted. The changes in hardness also indicated a beneficial effects of silicate modification on the property discussed above. When modifying the filler ($\text{TiO}_2\text{-SiO}_2/\text{POSS}$), regardless of its amount, an improvement in composites hardness by about $1,5^\circ$ in comparison to unmodified filler ($\text{TiO}_2\text{-SiO}_2$) was noted. The used system is not a typical reinforcing filler, such as glass fiber [52, 53] or basalt fibers [54, 55], therefore a significant improvement in hardness or the mechanical properties described above cannot be expected. However, it should be emphasized that even with such low filler content as used in the presented researches, its influences on the mechanical properties of LDPE were observed. Among others this may be a result of the influence of the filler on the supermolecular structure of the polymer, including degree of crystallinity [25, 38]. The influence of the presented filler on the degree of crystallinity, morphology, and mechanical properties of polyethylene will be discussed in detail in the next publication.

The assessment of the wettability degree on the surface was conducted through determining the contact angle – images of a water drop on the surface of the polyethylene and composite samples are presented in Figure 9. The contact angle value for LDPE was qualified as partially wettable ($84,4 \pm 1$) $0^\circ < \theta < 90^\circ$. The addition of modified and unmodified titanium silicate did not cause any significant changes in wettability of the composites – contact angle changes were in a range of $\pm 1^\circ$ in comparison to contact angle of LDPE.

The composites were also evaluated for changes in color by determining the brightness parameters L^* and ΔE responsible for the overall color change of the composites. With increasing volume fraction of the unmodified filler, an increase in brightness values from 41.34 for LDPE up to 77.93 for LDPE + 1 wt% $\text{TiO}_2\text{-SiO}_2$ was noted. However,

a utilization of modified system ($\text{TiO}_2\text{-SiO}_2/\text{POSS}$) caused a slight decrease in brightness for the composites in comparison to LDPE + $\text{TiO}_2\text{-SiO}_2$. For the modified fillers similar changes in color were observed as for the composites produced with unmodified titanium silicate. The results of color changes are presented in Figure 10.

CONCLUSION

The modification of synthetic oxide system $\text{TiO}_2\text{-SiO}_2$ with POSS nanofiller resulted in obtaining the system with increased hydrophobic properties in comparison to the unmodified inorganic matrix. Modification caused a slight agglomeration of particles. A positive impact of modification could be observed on the FT-IR spectrum because the bands that derive from the groups attached to the silicon-oxygen cage were visible.

The obtained results revealed a direct influence of the $\text{TiO}_2\text{-SiO}_2$ addition and its modification on the properties of the composites based on polyethylene matrix. The filler addition caused an increase in composite stiffness, hardness and a change in its color. Modification of titanium silicate with 10 wt% of POSS caused a decrease in composite stiffness in comparison to the system that contained the same amount of the unmodified filler, which is a consequence of a modifier chemical structure. The modification of the filler had a positive effect on improving the hardness of composites and slightly on the intensity of color change which is of particular importance for the application of titanium silicate as polymers' pigment.

The presented preliminary application studies have shown that the developed innovative $\text{TiO}_2\text{-SiO}_2/\text{POSS}$ filler may be a potential modifier of low-density polyethylene. Further researches in the area of improving the barrier and sealability of polyethylene films (LDPE) were carried out. The results of experimental studies and a description of the extrusion technology trials with the use of the developed filler will be presented in the next publication.

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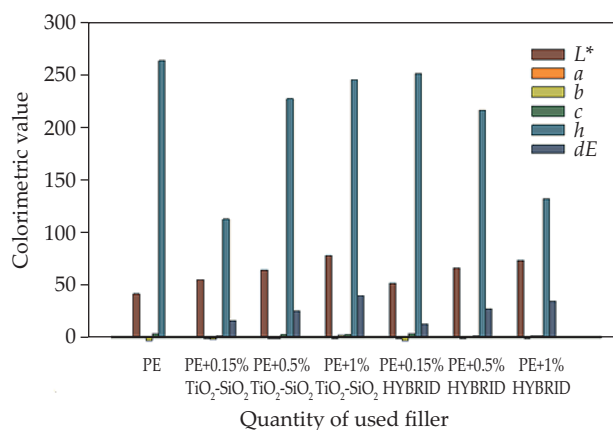


Fig. 10. The colorimetric analysis of the polyethylene and composites

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