

A novel functional $\text{MgO} \cdot \text{SiO}_2$ /polyhedral oligomeric silsesquioxane hybrids as an active filler of polypropylene

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New organic/inorganic hybrid fillers were obtained by mechanical modification of magnesium silicate with selected polyhedral oligomeric silsesquioxane and characterized afterwards. $\text{MgO} \cdot \text{SiO}_2$ was precipitated in a water system. The effect of chemical modification of magnesium silicate surface on their physicochemical properties was determined. Functionalization was carried out with the use of different amount 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). The polypropylene composites of 0.5, 1.0 and 1.5 wt.% modified by 10 weight parts by the mass of the filler were also produced. For the obtained polypropylene composites measurements of the tensile strength, Young's modulus and elongation at break were performed.

Keywords: Hybrids fillers, Magnesium silicate, Polyhedral oligomeric silsesquioxane, Polypropylene, Polymer composites, Mechanical properties.

INTRODUCTION

Organic-inorganic hybrid fillers combine two worlds of chemistry (organic and inorganic) and significantly contribute to the field of materials science due to their characteristic properties that result in diverse advantages. The main idea when developing hybrid materials is to take advantage of the best properties of each component that forms the hybrid. In particular, they may also be called polymer hybrids to emphasize that polymer constituents are involved. However, in order to distinguish them from the conventionally known composites that are mere mixtures, it is necessary to call the products "hybrid materials" when the level of mixing of the different types of materials is at the nanometer or micro level, or sometimes at the molecular level¹. It is possible to expect very interesting characteristics that are not found in the organic polymer or the inorganic material independently. For example, they can have features such as being flexible like a plastic but have excellent mechanical strength and thermal stability. That is why such hybrid materials have attracted attention. It has become possible to carry out high precision molecular design (structural control) even at the nanometer levels. Instruments have been developed that are capable of characterization of nanometer or even higher sizes. Interesting and unique phenomena have been found one after another in the nanometer region, such as energy movement, opto-chemistry, etc. Many natural materials consist of inorganic and organic building blocks distributed on the (macro) molecular or nanoscale. In most cases the inorganic part provides mechanical strength and an overall structure to the natural objects while the organic part delivers bonding between the inorganic building blocks and/or the soft tissue². Typical examples of such materials are bone or nacre. Hybrids based on polyhedral oligosilsesquioxanes are the most popular materials these days. Polyhedral oligosilsesquioxanes (i.e. $[\text{RSiO}_{3/2}]_n$) are an interesting class of three-dimensional silsesquioxanes derived from the hydrolytic polycondensation of trifunctional organo-

silicon monomers (i.e. RSiX_3 , X = Cl, OMe, OEt). The use of inorganic cage compounds as molecular building blocks for the rational design of materials is an attractive and challenging avenue for the material chemists. One example is the silicate cage compounds $(\text{RSiO}_{3/2})_n$, R = organic or inorganic group), which are potentially a very useful class of compounds. They were used as three-dimensional building block units for the synthesis of new materials such as precursors for ceramics and models in various fields³⁻⁴. One of the ways in which the research has been conducted is the application of polyhedral oligomeric silsesquioxanes as fillers for polymeric materials⁵⁻⁷. The POSS fillers are used for developing nanocomposites with a polyolefin matrix (polypropylene, polyethylene)⁸⁻⁹. The manufacturing process of thermoplastic polymer/nanofiller composites is usually carried out in a molten state with using homogenization techniques: twin-screw extruders and periodic mixers¹⁰⁻¹¹. The addition of POSS to polyolefins aims to modify their thermal, electrical, mechanical and rheological properties. A type of modification results directly from a structure of the POSS nanofiller, and usually occurs at a much smaller amount compared to the commonly used fillers in a macro scale^{5, 8, 11}. One of the ways to obtain active fillers with certain properties is the modification of hybrid systems using POSS compounds. The utilization of hybrid systems, modified with polyhedral oligomeric silsesquioxanes, as fillers for polymers allows a certain modification of composites' properties.

Despite a large number of research concerning the production of hybrid systems and their use as fillers/modifiers for polymers, there is no data regarding polymer composites containing synthetic magnesium silicate modified with POSS compounds. Therefore, in this article the research results were presented, and their aim was to obtain the modified hybrid systems and attempt their application.

EXPERIMENTAL

Hybrid filler: Preparation, modification and physicochemical characteristic

The following substrates were used in order to obtain a highly dispersed magnesium silicate: sodium silicate (27.18% of silicon dioxide, 8.50% of sodium oxide, density of 1.39 g/cm³ and silicate modulus – 3.3; VITROSILICON SA). An inorganic salt – magnesium sulfate hexahydrate (density of 2.66 g/cm³; POCh SA) – was used as a basic precipitating agent.

The precipitation of the highly dispersed magnesium silicate was carried out in a reactor (volume of 10 dm³; QVF Miniplant PILOT-TEC) equipped with a high speed stirrer (1000 rpm) at room temperature. A 5 dm³ 5% aqueous solution of magnesium sulfate was placed in the reactor and afterwards a 5 dm³ 5% aqueous solution of sodium silicate was dosed at a fixed flow rate (0.0002 dm³/min) with the use of a peristaltic pump. The precipitation process lasted for approx. 5 hours.

The obtained precipitate was separated from the reaction mixture by vacuum filtration. Afterwards the product was rinsed with 10 dm³ of hot redistilled water in order to flush out residual salts and then the precipitate samples were dried at 105°C.

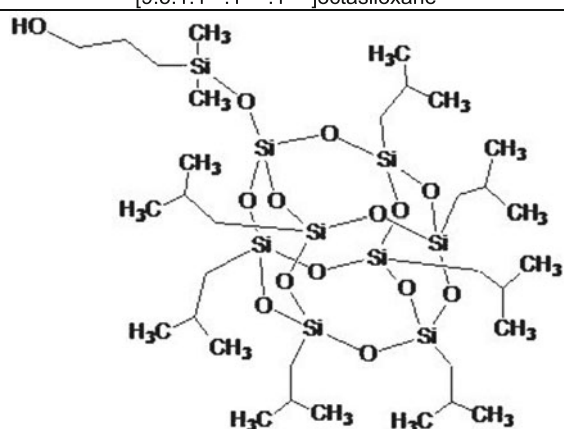
Synthesis of POSS modifier

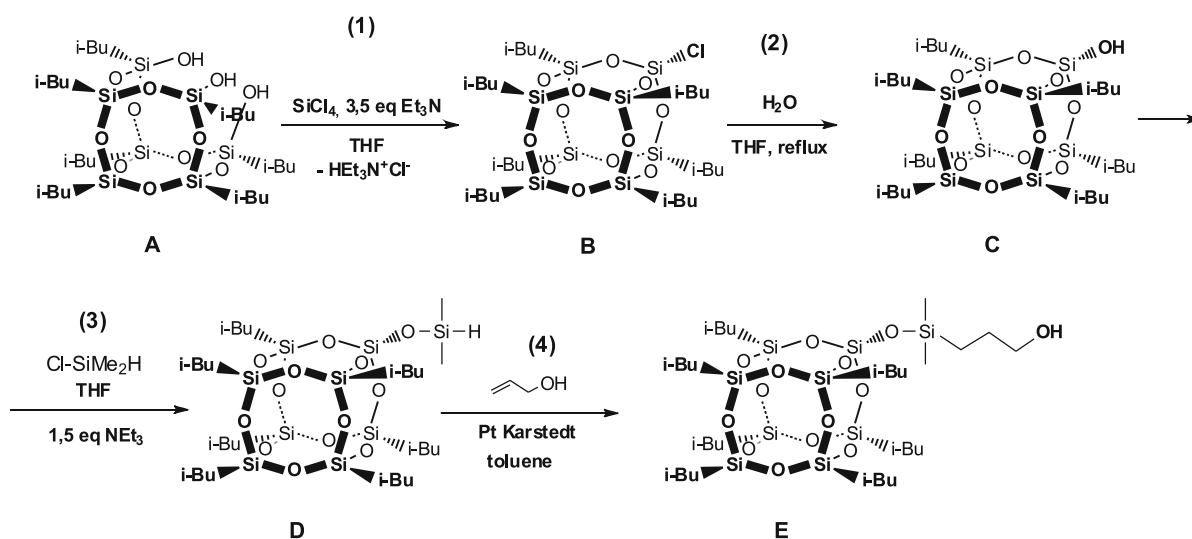
All synthesis and manipulations were carried out under argon using standard Schlenk-line and vacuum techniques. ¹H, ¹³C, ²⁹Si NMR spectra were recorded on Bruker Avance 400 MHz and 500 MHz in CDCl₃. FT-IR spectra were recorded on a Bruker Tensor 27 Fourier transform spectrophotometer equipped with a SPECAC Golden Gate diamond ATR unit. In this case 16 scans at a resolution of 2 cm⁻¹ were collected to record the spectrum.

All solvents and liquid reagents were purchased from Sigma-Aldrich, they were dried and distilled under argon prior to use. The structure and synthetic route to 1-(3-hydroxypropyl)dimethylsiloxo-3,5,7,9,11,13,15-hepta(isobutyl)pentacyclo-[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane (later called iBu-POSS) is shown in the Scheme 1 and in Table 1.

The syntheses of T₈R₇R' derivatives from partially condensed silsesquioxanes all follow the same general reaction scheme, where a partially condensed silsesquioxane R₇Si₇O₉(OH)₃ reacts with a chloro- or alkoxy silane, often in the presence of a base such as NEt₃. The partially condensed trisilanol species have been known since 1965¹². Much of the early work on these differently substituted POSS species was conducted by Feher et al.¹³. The synthesis of T₈R₇R' (R = iBu, R' = OSiMe₂(CH₂)₃OH) is performed by the condensation (Scheme 1. Reaction (1)

Table 1. Structure of POSS used for modification process

Molecular formula	(1-(3-hydroxypropyl)dimethylsiloxo-3,5,7,9,11,13,15-hepta(isobutyl)pentacyclo-[9.5.1.1 ^{3,9} .1 ^{5,15} .1 ^{7,13}]octasiloxane
Structural formula	



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

to get (B) and hydrolysis of chloro-substituted silsesquioxane (B) yielding (C), followed by next condensation to receive (D), according to original procedure¹⁴. The final step of the preparation of E is the most frequent method of silsesquioxane functionalization, *i.e.* hydrosilylation (Scheme 1. Reaction (4)) of allyl alcohol with 1-hydrodimethylsiloxy-3,5,7,9,11,13,15-hepta(isobutyl)pentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]-octasiloxane (D) in the presence of Pt Karstedt catalyst^{15–17}. The reaction proceeds with high yield and selectivity.

Analysis of iBu-POSS

¹H NMR (CDCl₃, δ ppm): 0.13 (s, SiCH₃); 0.56–0.64 (m, 14H SiCH₂CH(CH₃)₂, 2H SiCH₂CH₂CH₂OH); 0.95–0.97 (dd, 42H SiCH₂CH(CH₃)₂); 1.58–1.66 (m, SiCH₂CH₂CH₂OH); 1.81–1.90 (m, 7H SiCH₂CH(CH₃)₂); 3.59–3.62 (tr, SiCH₂CH₂CH₂OH)

¹³C NMR (CDCl₃, δ ppm): 0.37 (SiCH₃); 13.48 (SiCH₂CH₂CH₂OH); 22.45, 22.23, 23.85, 26.59 (SiCH₂CH(CH₃)₂); 26.35 (SiCH₂CH₂CH₂OH); 65.52 (SiCH₂CH₂CH₂OH);

²⁹Si-NMR (CDCl₃, δ ppm) : 11.5 ; –66.7 ; –67.0 ; –67.8 ; –109.6

IR (ATR): 3400–3320, 2955–2872, 1231, 1170–1097, 1078, 839, 772, 741, 563 cm^{–1}.

Mechanical modification method

During the next experimental step the obtained precipitate samples were subjected to modification process in order to change their surface properties. In the mechanical modification method, the POSS compound was used as modifying agents at an amount of 3, 5 and 10 weight parts by mass. The unmodified inorganic filler and the modifying mixture were placed in ball mill (Pulverisette 6 made by Fritsch). The modification process lasted for 1 hour.

Analysis and Characterization

The obtained functional fillers were subjected to measurements of particle size distributions with the help of Zetasizer Nano ZS (NIBS method). The analysis of composition and modification degree for the fillers were evaluated using a FT-IR EQUINOX 55 spectrophotometer (Bruker). The fillers were analyzed in IR by incorporating the KBr pellets technique. The amount of the applied POSS-type organic compound was indirectly determined by elemental analysis Vario EL Cube (Elementar Analysensysteme GmbH).

Polymer Composites: Preparation and Determination of Mechanical Properties

In the current study the following polymeric material (applied as a polymer matrix) was investigated: homopolymer polypropylene (PP) Moplen HP456J (produced by the Basell Orlen Polyolefins Sp. z o.o.) with a density of 0.90–0.92 g/cm³ (23°C) and a melt flow rate of (MFR_{2,16 ; 230}) 3.4 g/10min.

A two-step mixing process was conducted to aid the fillers dispersion in the PP matrix. The first step was to prepare the composites, during 15 min melt blending at 160°C and 20 rpm, using the Brabender internal mixer. In the first stage three types of composites: PP + iBu-POSS; PP + MgO · SiO₂ and PP + MgO · SiO₂ · iBu-POSS(10

wt./wt.) were obtained by preparing 10 wt.% filler/PP masterbatch. Then the masterbatch was used to generate granulated composites that contained 0.5, 1.0 and 1.5 wt.% of the filler. The composites in the form of spun filaments were prepared by melt extrusion of PP and the masterbatch in suitable ratios. To get the above compositions a co-rotating twin-screw extruder was used, model EH16.2D (L = 16 mm; L/D = 40), manufactured by the ZAMAK. The polypropylene and the masterbatch were dosed to the first zone of the cylinder (there were nine zones in total). For all the systems used the temperature range was maintained between 160 and 230°C, and the screw speed was set at 120 rpm. The extrudate was solidified by quenching it in a water bath, maintaining 10–15°C. After that it was chopped into pellets using plastic granulator and dried for 8 h at 80°C.

A single-screw extruder with a slit die (width 120 mm and slit h = 0.5 mm) and a pull-out line with a *chill roll* cooling unit was used to produce films from all blends by slit die extrusion¹⁸. The following parameters were set up on the film extrusion line: a screw rotation speed of 25 rpm, a barrel–die temperature of 230°C, a pull-out velocity of 0.011 m/s and a chill roll temperature of 35°C. As a result, 80 μm thick and 90 mm wide films were produced under these conditions. The mechanical properties were determined via tensile tests using the Zwick (model Roell Z020), a common testing machine, with a touchless extensometer video and a measurement head of 100 N, operated with a stretching velocity of 100 mm/min (PN-EN ISO 527-1-3).

Scanning electron microscopy (SEM) observations were performed with a Zeiss EVO40 instrument (Germany) with a contrast of secondary electrons (SE) at the acceleration voltage 15 kV, to observe the possible agglomerations and dispersion level of the filler. The scanning electron microscopy observations were performed on the cryogenic fracture surface.

RESULTS AND DISCUSSION

Fillers Characteristics

In first step of the studies the comparison of dispersive-morphological properties was carried out for unmodified silicate and samples functionalized with 3, 5 and 10 weight parts by mass of the POSS compound obtained with mechanical method (Fig. 1). The particle size distribution curves relative to their volumetric ratio for unmodified silicate (Fig. 1a) and samples modified with 3 (Fig. 1b), 5 (Fig. 1c) and 10 (Fig. 1d) weight parts by mass of iBu-POSS are shown in Fig. 1. The unmodified magnesium silicate was characterized by a broad range of size distribution, and particles with a diameter of 2330 nm accounted for the most intensive volumetric ratio in the whole sample (27.7%). The mechanical surface modification process resulted in a decreased abundance of secondary agglomerates in the samples modified with 3, 5 and 10 weight parts by mass of iBu-POSS. The silicate samples modified by 3 weight parts by mass of iBu-POSS (Fig. 1b) were characterized by a particle size distribution profile, which differed greatly from the unmodified filler. The highest volumetric ratio was observed for the particles with a diameter of 825 nm for samples modi-

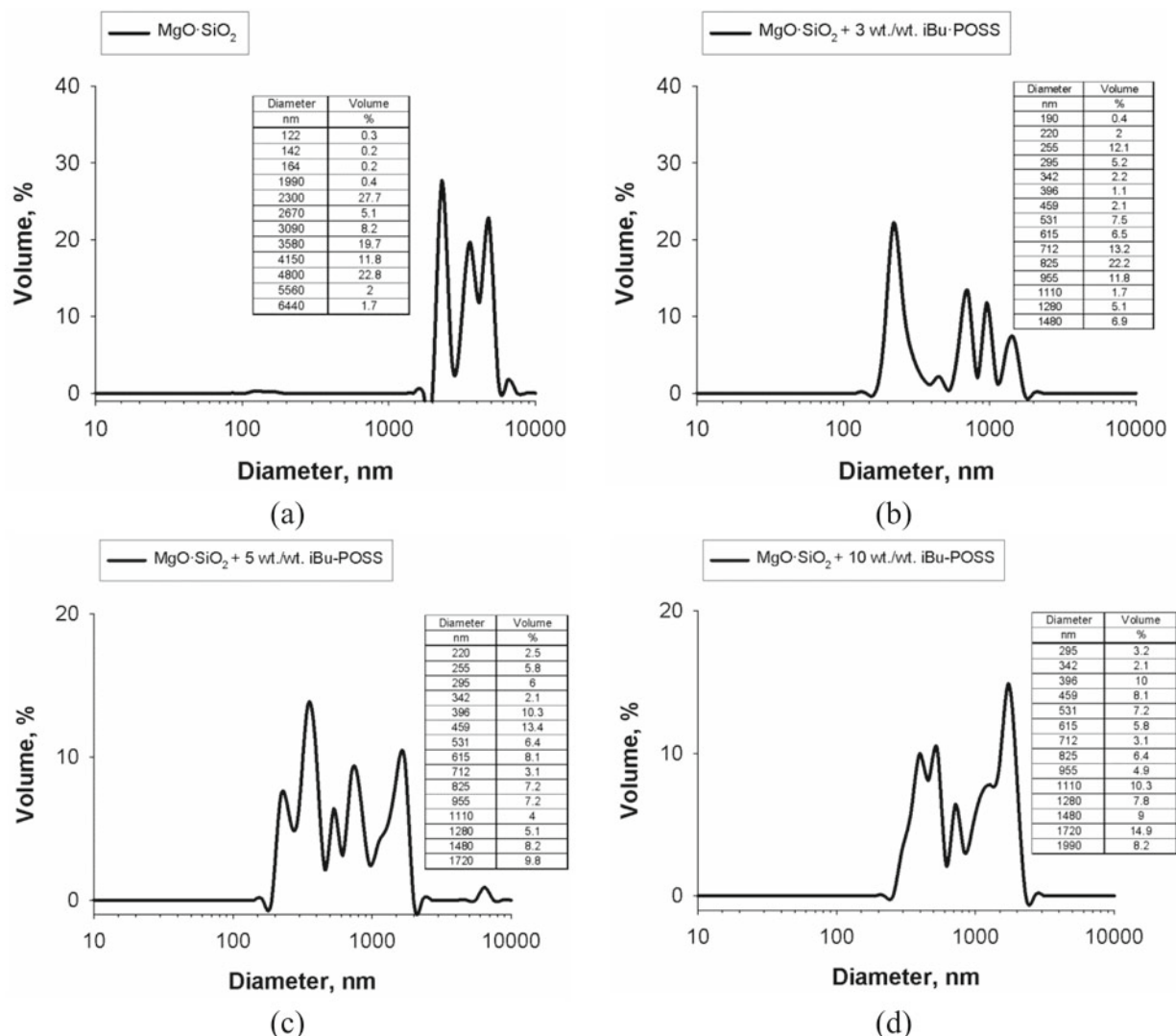


Figure 1. Particle size distributions of unmodified filler (a) and samples modified with iBu-POSS: MgO · SiO₂ + 3 wt./wt. iBu-POSS (b), MgO · SiO₂ + 5 wt./wt. iBu-POSS (c), MgO · SiO₂ + 10 wt./wt. iBu-POSS (d) relative to their volumetric ratio

fied with 3 wt./wt. iBu-POSS (22.2%), while for sample modified 5 wt./wt. iBu-POSS (Fig. 1c) 459 nm were most intensive (13.4%), and 1720 nm (14.9%) for sample modified 10 wt./wt. (Fig. 1d) has highest volumetric ratio for 1720 nm (14.9%).

The absorption intensity of the free hydroxyl groups (-OH) from inorganic matrix at 3620 to 3200 cm⁻¹ decreased upon increasing the amount of iBu-POSS. The C-O stretching frequency from iBu-POSS chain is split into bands at 1763 and 1735 cm⁻¹ was present, and its intensity increased gradually with the increase of amount of used modifier. The Si-O-Si linkages of POSS cages exhibit significant absorption peaks at 1110 cm⁻¹, and 1223 cm⁻¹ and Si-C vibrations for iBu-POSS absorption at 734 cm⁻¹ and 781 cm⁻¹ are due to an CH₃ group¹⁹. FT-IR results sufficiently clear that there was no need to confirm the structure using other techniques.

In order to evaluate the efficiency of the modification process with the POSS-type compounds the elemental analysis was carried out. The obtained data regarding the carbon and hydrogen elemental content allowed for the surface composition of the samples to be characterized.

The elemental contents of the above-mentioned elements in the analyzed samples are shown in Table 2. Based on the obtained data, it can be concluded that the amount of carbon and hydrogen in the sample is increased with the increasing amount of POSS-type compounds.

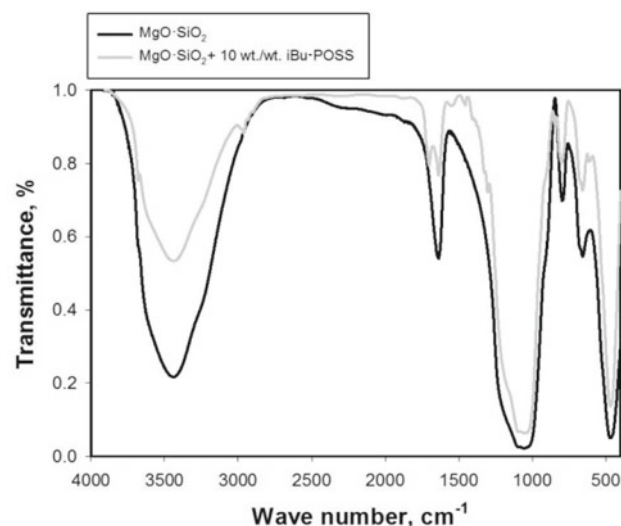


Figure 2. Comparison of FT-IR spectra of the unmodified filler and modified with 10 weight parts by mass of iBu-POSS

It can be observed, that with the increased amount of POSS used for the modification of the nonorganic filler, the amount of carbon is also increased – from the base value of 0 for the unmodified silica filler to the value of 5.416 for the chemically modified samples with 10 weight parts by mass of iBu-POSS, accordingly. On the

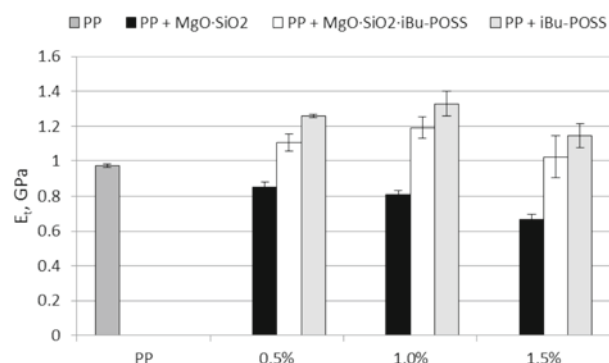
Table 2. The results of the elemental analysis

Sample	Elemental content [%]	
	C	H
MgO · SiO ₂	–	3.034
MgO · SiO ₂ + 3 wt./wt. iBu-POSS	2.302	0.209
MgO · SiO ₂ + 5 wt./wt. iBu-POSS	4.285	0.465
MgO · SiO ₂ + 10 wt./wt. iBu-POSS	5.416	0.725

other hand, it was observed that the increase of carbon and hydrogen in the mechanically modified samples was minor.

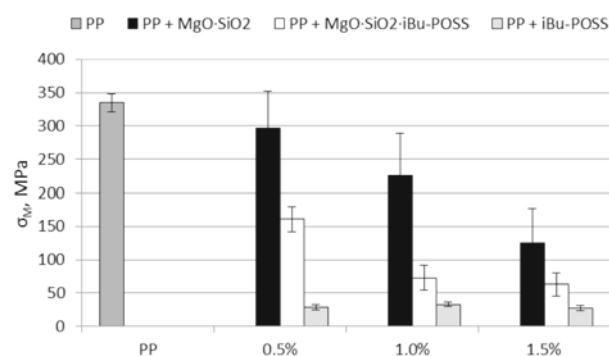
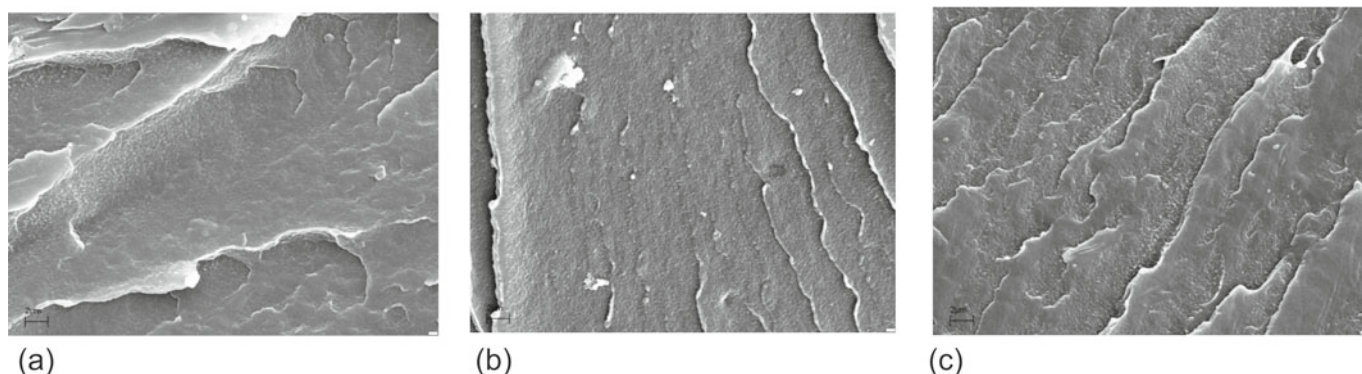
Polymer Composites

As a result of tensile tests, a direct impact of fillers addition on the Young's modulus (E_t), the strength (σ_M) and the elongation at break (ϵ_B) of produced composite films was found. Figure 3 summarizes the values of Young's modulus as a function of a type and amount of the filler. Analyzing the changes of the E_t , it can be noted that the highest increase of modulus was obtained for polypropylene films with iBu-POSS nanofiller addition of 0.5 and 1.0 wt.%. The values of the modulus range from 0.973 GPa for pure films to 1.33 GPa for composite films with a filler amount of 1.0 wt.%. In the case of magnesium silicate addition, a decrease in the modulus of elasticity value together with an increase of filler amount in a system was observed. The lowest value of the E_t occurred for film that contained 1.5 wt.% of MgO · SiO₂ (approximately 0.67 GPa). A decrease of the Young's modulus is assigned to heterogeneity of composite film structure (inclusions), which resulted from filler agglomeration (MgO · SiO₂) that led to development of local weaknesses – notches. Modification of the magnesium silicate with the POSS nanofiller improved quality of films (a lack of inclusions – better homogenization) and contributed to an increase of the Young's modulus (Fig. 4). In terms of all amounts of the modified filler used (MgO · SiO₂ · iBu-POSS), the Young's modulus ranges between the values obtained from the films that contain non-modified filler (MgO · SiO₂) and from those that contain the modifier (iBu-POSS). In this case, it can be stated that the iBu-POSS used to modify the magnesium silicate acted as a compatibilizer in polymer versus filler (MgO · SiO₂ ↔ PP) relationship²⁰. Analyzing the changes of the E_t according to the amount of filler used, a following correlation can be observed – an increase of the modulus for composite films that contain the nanofiller (PP + iBu-POSS) and films that include the modified hybrid filler (PP + MgO · SiO₂ · iBu-POSS) occurs up to a maximum of 1.0 wt.%. This kind of dependence may

**Figure 3.** The Young's modulus (E_t) as a function of various fillers amounts in composites

occur due to certain/limited amount of filler/nanofiller in composite, above which a deterioration of properties is noted. Observations of this type were presented by Baldi⁷ and Zhou²¹ in their research.

In Figure 4 the maximum film strength, obtained in static stretching conditions, was presented. The addition of fillers, regardless of their type, resulted in decreasing the composite film's strength in comparison to PP film, which strength was about 335 MPa. The strength of films that contained iBu-POSS was constant (around 30 MPa) regardless of the amount of added nanofiller, but it was 91% lower in comparison to PP films. In case of the two remaining fillers the strength decreased sharply together with increased content of the filler. The strength of the films obtained from PP + MgO · SiO₂ · iBu-POSS composites was between σ_M of the films modified with hybrid fillers and nanofillers, as it was in the case of the E_t . Regarding the composites that contain MgO · SiO₂ filler, high standard deviation values were observed, which was a result of inclusions in the film structure (Fig. 5).

**Figure 4.** The tensile strength (σ_M) as a function of various fillers amounts in composites**Figure 5.** SEM microphotographs of (a) PP, (b) PP+MgO · SiO₂, and (c) PP+ 1.0 wt.% MgO · SiO₂ · (10 wt./wt.)iBu-POSS

Filler addition resulted in anticipated changes in terms of elongation of the composite film samples, i.e. the ϵ_B value decreased in comparison to the PP films (Fig. 6). The results analysis proved that the films that contained iBu-POSS nanofiller showed the smallest elongation during stretching. For PP + iBu-POSS films the ϵ_B value was 52% (regardless of the filler concentration), which indicated that the parameter had dropped seven times in comparison to PP films. Regarding PP + MgO · SiO₂ and PP + MgO · SiO₂ · iBu-POSS films, the elongation decreased together with an increase of the filler content in the composite. Modification of the filler resulted in a decrease of the value of the elongation at break in

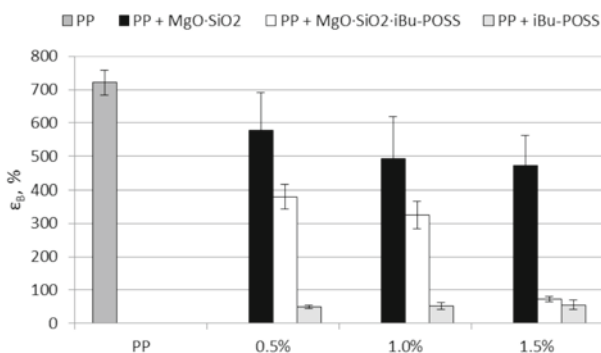


Figure 6. The elongation at break (ϵ_B) as a function of various fillers amounts in composites

comparison to a film filled with a non-modified magnesium silicate.

CONCLUSIONS

A new route to develop novel materials using organic/inorganic hybrids was introduced. MgO · SiO₂/POSS hybrids were synthesized by a mechanical method with the use of a ball mill. The mechanical modification method with the use of a ball mill was used to obtain new types of inorganic/organic hybrid materials with particle sizes decrease relatively to unmodified sample (190 nm – 0.4%, for the samples modified with 3 weight parts by mass of iBu-POSS). In order to validate the modification of inorganic filler surface with POSS-type compounds FT-IR and elemental analyzes were carried out. The results of these studies revealed that organic groups originating from POSS compounds appeared on the inorganic matrix, the carbon and hydrogen content was increased and the surface area value of the obtained powder products changed.

The obtained results showed a direct impact of MgO · SiO₂ addition and its modification on quality and properties of polypropylene composite films. Modification of magnesium silicate with 10 wt./wt. of iBu-POSS caused an increase of stiffness in comparison to a polypropylene film and to a system containing the same amount of a unmodified filler. The modification of the filler decreased the composite strength and the value of elongation at break. The modification of magnesium silicate simplified the dispersion and reduced the phenomenon of filler agglomeration in a polymer matrix. Determination of the full scope of impact of magnesium silicate and its modification on film properties requires further research. However, the results of tensile tests indicated that the

developed system could be applied as a modifier of polypropylene film properties.

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