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COMPOSITES
THEORY AND
PRACTICE

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APPLICATION OF ONE-POT SOL-GEL METHOD TO PREPARE POLYOLEFIN FILLERS

The application of silica-based fillers for polymers and nanocomposites is a subject of extensive research, mostly due to the demand for new materials of improved physicochemical, mechanical or thermal properties. In this paper we present a new, *one-pot sol-gel* (OPSG) method to synthesize fillers for polyolefins. The developed method assumes direct synthesis of the filler together with its modification upon the addition of organofunctional silane. It allows fillers with controlled porosity and hydrophobic properties to be obtained, which undergo better dispersion in a polymer matrix. The characteristics of the obtained composites were defined by thermal analysis, as well as tensile and impact tests. The contact angle was measured by the sessile drop technique to determine the hydrophobic-hydrophilic properties of the fillers. Morphological analyses were performed using SEM, surface area and pore volume measurements. The *one-pot* method is a preferred alternative to the multi-step synthesis methods for synthetic fillers.

Keywords: one-pot, sol-gel, polyolefins, Stöber silica, composite

ZASTOSOWANIE METODY ONE-POT ZOL-ŻEL DO OTRZYMYWANIA NAPEŁNIACZY DO POLIOLEFIN

Zastosowanie napełniaczy krzemionkowych w materiałach kompozytowych ma swoją długoletnią tradycję, wynikającą z uniwersalności tego powszechnie stosowanego napełniacza. Pomimo wieloletnich badań nad systemami kompozytowymi opartymi o krzemionkę, nadal istnieje zapotrzebowanie na nowe metody jej modyfikacji i funkcjonalizacji, zarówno w obszarze struktury i morfologii cząstek, jak i obróbki powierzchniowej. W prowadzonych przez nas badaniach koncentrujemy się na jednoetapowej metodzie zol-żel, w literaturze określanej jako *one-pot sol-gel* (OPSG). Najważniejszą różnicą w porównaniu do tradycyjnych metod otrzymywania funkcjonalnych napełniaczy jest to, że etap syntezy napełniacza oraz modyfikacja chemiczna odbywają się w tym samym naczyniu reakcyjnym (lub reaktorze) bez konieczności suszenia i preparacji napełniacza. Metoda ta pozwala na otrzymanie napełniacza zaprojektowanego pod indywidualne potrzeby finalnego materiału kompozytowego, zapewniając większą adhezję do osnowy, lepsze zwilżanie czy wreszcie, co bardzo istotne, dobrą dyspergowalność przy mieszaniu z osnową. W pracy zaprezentowano metodę syntezy sferycznej krzemionki Stöbera modyfikowanej jednoetapowo z użyciem organofunkcyjnego silanu. Na osnowie polipropylenu otrzymano kompozyty z zastosowaniem tak otrzymanego napełniacza. Kompozyt został scharakteryzowany z punktu widzenia właściwości mechanicznych i termicznych. Przeprowadzono również wszechstronną charakterystykę napełniacza w porównaniu do standardowej krzemionki typu Stöbera. Podsumowując, jednoetapowa metoda zol-żel jest interesującą alternatywą dla klasycznych metod syntezy napełniaczy funkcyjnych materiałów kompozytowych.

Słowa kluczowe: one-pot, sol-gel, poliolefiny, krzemionka Stöbera, kompozyt

INTRODUCTION

Due to their wide range of applications, composites based on polyolefin matrices are a subject of continuous research and development. Composite systems bear a number of qualities such as increased durability, toughness, chemical resistance and more. The presence of a well-dispersed filler in an organic matrix allows one to not only acquire better performance parameters, but also to create systems with new properties, unobtainable for pure polyolefins [1]. Introducing SiO_2 into the PE matrix enables one to obtain material with new application possibilities [2, 3], mostly due to improvement of the mechanical properties of the material or its abrasion resistance [1]. Obtaining composite materials, despite many well-known, dedicated techniques at hand, is still a challenge. The choice of the preparation method is determined by the composition, shape and performance parameters of the composite. Introducing fillers is difficult because of their tendency to agglomerate. To overcome such issues, different techniques are used, e.g. *in situ* polymerization or *melt mixing* [1, 4-14]. In this work, a new method of synthesizing a silica-based filler is presented and is called *one-pot sol-gel* (OPSG). In the classical approach, modification of the filler is performed in a separate reaction system than its synthesis, often in different solvents and under different conditions. In the proposed method, the filler is synthesized and modified directly with organofunctional silane. The effectiveness of the *one-pot* method is generally high and enables purification procedures to be omitted, which corresponds to smaller amounts of produced chemical waste, a shorter preparation time and less labour-intensive work [15]. The *one-pot* method is a good alternative to multistep filler synthesis. The proposed procedure is based on the classical approach proposed by Stöber [16]. In the modification process, methyltrimethoxysilane is introduced to the system, as upon hydrolysis and condensation reactions it modifies the surface of spheroidal Stöber silica, rendering it more hydrophobic and lowering its agglomeration capacity. Such an obtained filler has been used to prepare a PE-based composite.

EXPERIMENTAL PROCEDURE

Materials

Synthesis was based on a modified Stöber method. The synthesis was performed in a thermostatic glass reactor (working capacity 20.000 cm^3). For the reaction solution, 9000 cm^3 of isopropyl alcohol, 4000 cm^3 of ethyl alcohol, 600 cm^3 of distilled water and 600 cm^3 of a 25% aqueous solution of ammonia were used. At the temperature of 2°C, ethyl silicate - Silanil Si40 BRB (Fig. 1) (d = 1.05 g/cm^3) was added to the stirred solution. Ethyl silicate is a hydrolyzed and oligomerized form of tetraethoxysilane. It is a mixture of monomers, oligomers and cyclic polysiloxanes. In addition to chain condensates, it also contains branch-shaped and ring-shaped condensates. Ethyl silicate is a transparent liquid containing 40% silica (SiO_2) by mass.

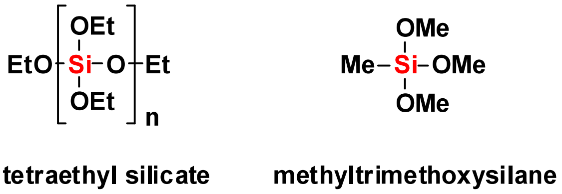

Fig. 1. Structural formulas of organofunctional silanes used as raw materials to prepare spheroidal Stöber silica

Rys. 1. Wzory strukturalne organofunkcyjnych silanów używanych jako surowiec do otrzymywania sferoidalnej krzemionki typu Stöbera

Innosilica3 was obtained as follows: the dosing rate of the ethyl silicate (a very important parameter for the morphology of the final product) was 200 cm^3/h in the first 18 hours of the process and 350 cm^3/h for a further 4 h. The total amount of added ethyl silicate was 5000 cm^3. Next, Silanil 118 BRB (methyltrimethoxysilane, Fig. 1), was added to the reaction mixture after 5 hours, with the dosing rate at 100 cm^3/h. The total amount of added Silanil 118 was 500 cm^3. Once the dosing stage ended, the slurry was stirred for 24 h at 20°C and then evaporated using a rotary evaporator to obtain a white powder. Next, the powder was placed in a laboratory dryer and left to dry at 160°C for 24 h. After the drying process, the mass of the resulting filler was stored under hermetic conditions. Innosilica1 was prepared by the method described in literature [17]. Malen E FABS 23-D022 low density polyethylene (PE-LD) was chosen for the matrix of the studied composites, and obtained from *Basell Orlen Polyolefins Sp. z.o.o.* Its characteristics are a melt flow rate (MFR$_{(190;\ 2.16)}$) of 2 g/10 min and density 0.921 g/cm^3.

In the first stage of composite preparation, for both types of fillers, masterbatch concentrates were produced with a 75:25 matrix to filler ratio. For this purpose, a *ZAMAK MERCATOR* two-roll mill was used. The concentrates were ground in a *SHINI SG*-1417 low-speed mill and dried for 2 h at 90ºC. The such prepared materials (PE-LD/Innosilica1; PE-LD/ Innosilica3; 75/25) were then diluted to 1, 5 and 10% filler concentrations in a twin screw extrusion process with cold granulation using a *ZAMAK* EH16.2D (L = 16 mm, L/D = 40) extruder.

In order to prepare experimental samples in their final form, to study the mechanical properties, a hydraulic injection molding machine from the *BATTENFELD* company, model PLUS 35/75, was used, which was equipped with a double socket mold to prepare normalized test dumbbells consistent with the PN-EN ISO 527-2 norm (type 1A). Neat PE-LD was used as the reference material. The tested systems are presented in Table 1.

TABLE 1. **List of composites with designations**
TABELA 1. **Zestawienie kompozytów z oznaczeniami**

Sample	Designation of sample with 1% filler	Designation of sample with 5% filler	Designation of sample with 10% filler
PE-LD	-	-	-
PE-LD/Innosilica1	I1 1%	I1 5%	I1 10%
PE-LD/Innosilica3	I3 1%	I3 5%	I3 10%

Methodology

The obtained materials were characterized by low-temperature nitrogen adsorption (surface area, material texture), contact angle (hydrophobic-hydrophilic properties), electron microscopy with X-ray spectroscopy (the level of filler dispersion uniformity in the composite).

For the cross-section observation, the composite was frozen in liquid nitrogen. Imaging of the surface was performed by SEM (Quanta 250 FEG, FEI).

The surface area of the silicas was measured by N_2 adsorption using BET, with a Micromeritics Instrument Corporation Model ASAP 2010. The samples were degassed at 423 K for 48 hours under vacuum. Contact angle measurements of the obtained materials were performed at room temperature, under atmospheric pressure using a Krüss DSA 100 goniometer, 10 µl water drops were used.

To measure the tensile strength of the composites and starting material under conditions of a constant strain rate, a universal testing machine Zwick Roell Z020 was used. The measurements were conducted according to the current norm PN-EN ISO 527-1. For the measurements, clamps of a maximal load force of 20 kN were used and the crosshead speed was set at 100 mm/min.

Hardness measurements were conducted with a Zwick analog Shore durometer (D scale) with a cone indenter, according to the current norm PN-ISO 868:2005. Flammability tests were performed according to the current norm PN-EN 60695-11-10 on samples of the obtained composites and the starting material. For full characteristics of the performed tests, a Testo 890 thermal imaging camera was used to measure the maximum combustion temperature.

Designations

PE-LD - low density polyethylene
PE-LD/Innosilica - low density polyethylene with Innosilica composite
PP/SiO_2 - polypropylene with SiO_2 composite
E_t - Young's modulus
σ_M - tensile strength
ε_B - relative elongation at break
HS - Shore hardness

RESULTS AND DISCUSSION

A new type of amorphous spherical hydrophobic silica (Innosilica3, average particle size of 585 nm) was obtained by the *one-pot sol-gel* method. Previous studies [17] proved the spheroidal structure of SiO_2 obtained by the modified Stöber method, which had a crucial impact on the homogeneity of the PP/SiO_2 composite. For filler modification with organofunctional silane, the *one-pot* method also enables preparation of a spheroidal filler (Fig. 2), aggregation of the spheroidal particles on the surface of the micrometric granules is shown.

The morphological differences in the microscale and submicroscale are minor and visual distinction of the silica species is impossible.

The next important performance parameter of the filler, which may have an impact on the composite properties and its miscibility with the organic matrix, is its surface area. For both fillers, the types of porous structure (which are extrapolated from adsorption isotherms, Fig. 3) do not differ much from each other. Innosilica3 has a slightly smaller surface area, which is due to the smaller number of micropores (Table 2), whose contribution to the structure of the filler is substantial.

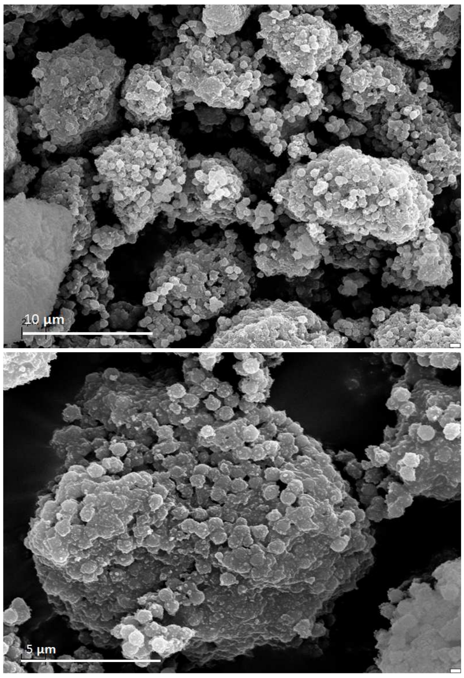

Fig. 2. SEM micrograph of Innosilica3
Rys. 2. Zdjęcia SEM Innosilica3

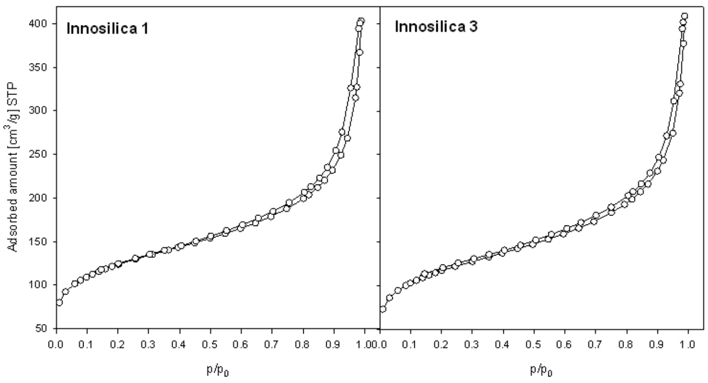

Fig. 3. Nitrogen adsorption/desorption isotherms for Innosilica1 and Innosilica3
Rys. 3. Izotermy adsorpcji/desorpcji azotu dla Innosilica1 i Innosilica3

TABLE 2. **Textural parameters of Inosilica1 and Innosilica3 obtained by low-temperature nitrogen adsorption technique**

TABELA 2. **Parametry teksturalne Innosilica1 i Innosilica3 uzyskane w pomiarach techniką niskotemperaturowej adsorpcji azotu**

Sample name	BET surface area [m^2/g]	Micropores area [m^2/g]	Pore volume [cm^3/g]	Micropores volume [cm^3/g]	Pore diameter [nm]
Innosilica1	437	132	0.55	0.058	8.1
Innosilica3	407	98	0.56	0.045	8.4

This observation is crucial for further analysis of the interactions between the filler and the matrix. Micropores have no important impact on the interaction with the matrix and their disappearance may be attributed to migration and condensation of methyltrimethoxysilane inside the pores or closing of their entrances. No decrease in the number of mesopores was observed, which is significant as they are a more important factor in forming interactions with the polymer matrix.

The difference in the chemical nature of the two fillers (Fig. 4) resulting from material modification with hydrophobic silane, is reflected by the contact angle measured for the obtained composites (Fig. 5). Silica modified with methyltrimethoxysilane (Fig. 5B) clearly shows its hydrophobic character (132 ± 1°) in contrast to classic Stöber silica (Fig. 5B), for which immediate sorption of water rendered measurement of the contact angle impossible.

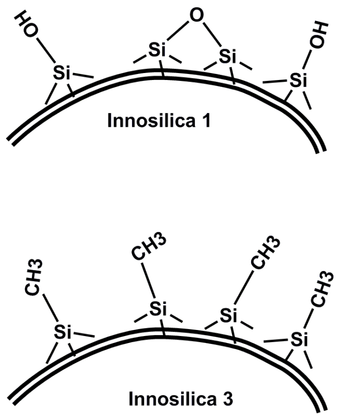

Fig. 4. Difference between surface functional groups of hydrophilic (Innosilica1) and hydrophobic (Innosilica3) silicas

Rys. 4. Różnice w powierzchniowych grupach funkcyjnych dla krzemionki hydrofilowej (Innosilica1) i krzemionki hydrofobowej (Innosilica3)

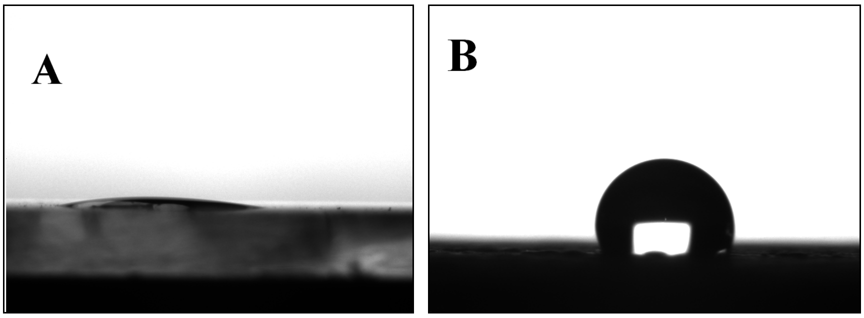

Fig. 5. Picture of water drop placed on surface of Innosilica1 (A), Innosilica3 (B)

Rys. 5. Zdjęcie kropli wody na powierzchni Innosilica1 (A), Innosilica3 (B)

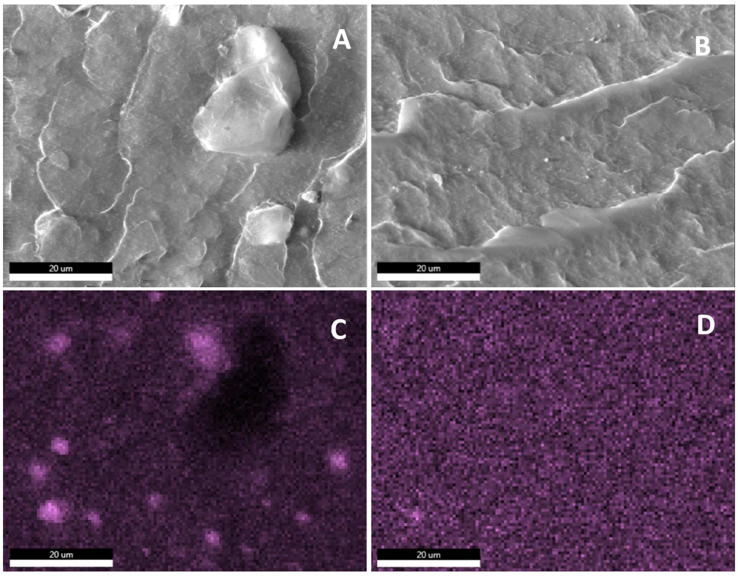

Fig. 6. SEM micrographs of PE-LD/Innosilica1 (10%) (A), PE-LD/Innosilica3 (10%) (B), EDS maps of PE-LD/Innosilica1 (10%) (C), PE-LD/Innosilica3 (10%) (D)

Rys. 6. Zdjęcia SEM PE-LD/Innosilica1 (10%) (A), PE-LD/Innosilica3 (10%) (B), Mapy EDS PE-LD/Innosilica1 (10%) (C), PE-LD/Innosilica3 (10%) (D)

Microscopic images of the obtained composites (Fig. 6) show their high homogeneity, which corresponds to very good dispersion of the filler in the polymer matrix. Nonetheless, for the hydrophobic silica-based composite, the homogeneity is much higher as the filler is dispersed completely uniformly in the organic matrix.

Generally, the available literature data in [18] clearly show that modifying powder fillers with compounds introducing hydrophobic functional groups onto their surface not only improves the homogeneity of the resulting composites (Fig. 6D), but also increases adhesion on the filler-polymer matrix interface (Fig. 6B). It directly translates into a change in the mechanical properties of the newly produced materials. The results of the composite tensile strength measurements under conditions of a constant strain rate and their Shore D scale hardness measurements are presented in Figure 7.

As expected, it was observed that the Young's modulus, tensile strength and Shore hardness of the obtained composites increased together with an increasing content of both the tested fillers. The property which decreased upon addition of the filler (also according to its content) was the relative elongation at break. The observed relationship is typical for polymer-based composites with powder fillers [19, 20].

Interesting relationships were observed when the impact of both fillers on the mechanical parameters of the obtained composites was analyzed. Analysis of the obtained results revealed that introducing 1% by mass of either of the fillers to the polyethylene matrix reduced the Young's modulus (Fig. 7A) as well as tensile strength (Fig. 7B) in comparison to the reference sample, but it increased the relative elongation at break (Fig. 7C). The obtained results suggest that regardless of its surface modification, Innosilica introduced to the polymer matrix in a small amount (1% by mass) has a plasticizing effect on the material. The shore hardness measurements also confirm this observation, as the HS values are lower for I1 1% and I3 1% than for the pure PE-LD. Reports on the plasticizing effect of powder fillers used in small quantities to produce polymer materials can be found in literature [21-23]. An increase in the amount of applied fillers to 5% by mass strongly changes the impact of Innosilica on the mechanical parameters of polyethylene. In such loading Innosilica1 still works as a plasticizer, lowering the E_t and σ_M values of the Innosilica1 5% composites. With the same loading, the Innosilica3 composites are characterized by higher values of Young's modulus (Fig. 7A) and tensile strength (Fig. 7B) in comparison to the reference sample. It suggests that from a 5% content, the silica I3 behaves like a typical reinforcing filler, increasing the composite stiffness. This is also confirmed by other mechanical parameters, i.e. an increase in ε_B and decrease in HS for I1 5% and an opposite trend of both parameters for I3 5%. At 10% loading, both types of Innosilica behave the same, i.e. their character is typical of reinforcing fillers.

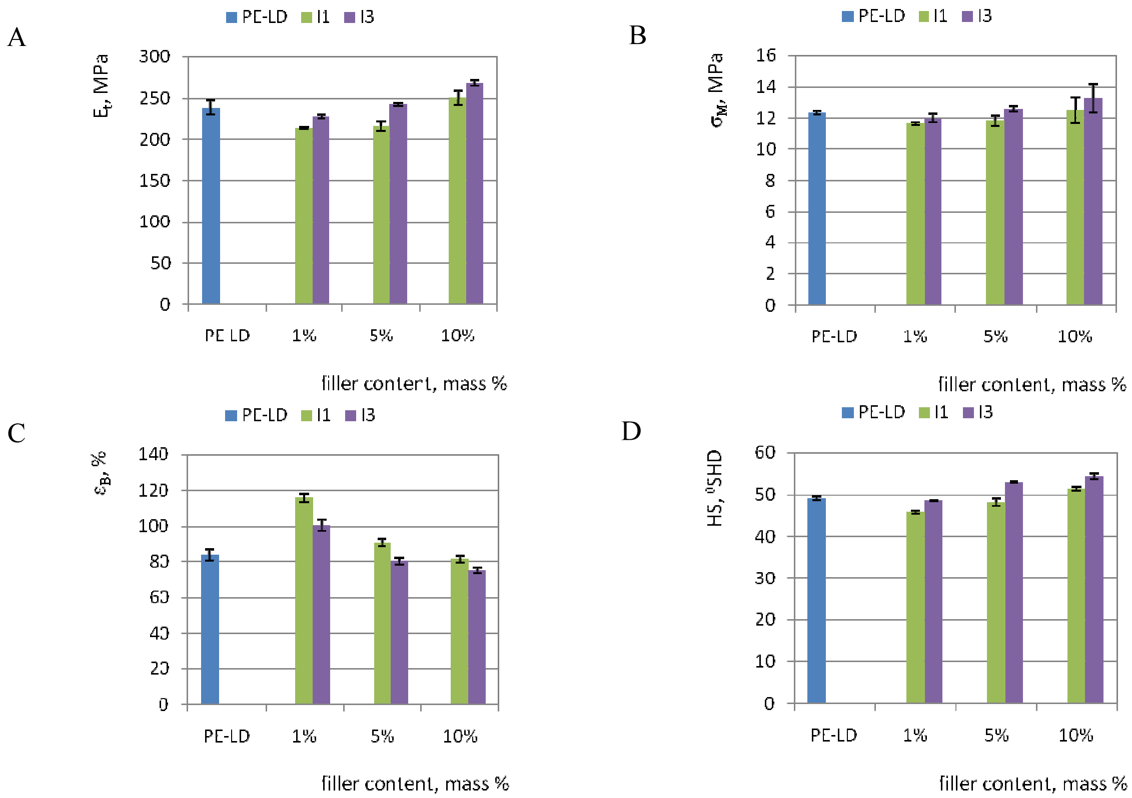

Fig. 7. Influence of filler content on mechanical properties of composites and reference material: A) modulus of elasticity, B) tensile strength, C) elongation at break, D) Shore D scale hardness

Rys. 7. Wpływ zawartości napełniacza na właściwości mechaniczne badanych kompozytów oraz materiału odniesienia: A) moduł sprężystości wzdłużnej, B) wytrzymałość, C) wydłużenie względne przy zerwaniu, D) twardość Shore'a w skali D

It is important to note that regardless of the filler loading, as long as it is equal to or above 5%, higher values of Young modulus, tensile strength and Shore's hardness, and lower values of relative elongation at break, were observed when the surface-modified Innosilica3 was applied as a filler. It proves that this filler is characterized by stronger adhesion at the silica-polyethylene interface - such prepared composites have a more homogeneous structure than PE-LD/Innosilica1 systems, which is also confirmed by the SEM (Fig. 6B and 6D) presented earlier.

From the application point of view, an important parameter describing the new composite materials is their flammability. The results of the linear burning rate and maximum combustion temperature were recorded with the thermal imaging camera during the combustion experiments of the composite and the reference samples. Results are presented in Figure 8.

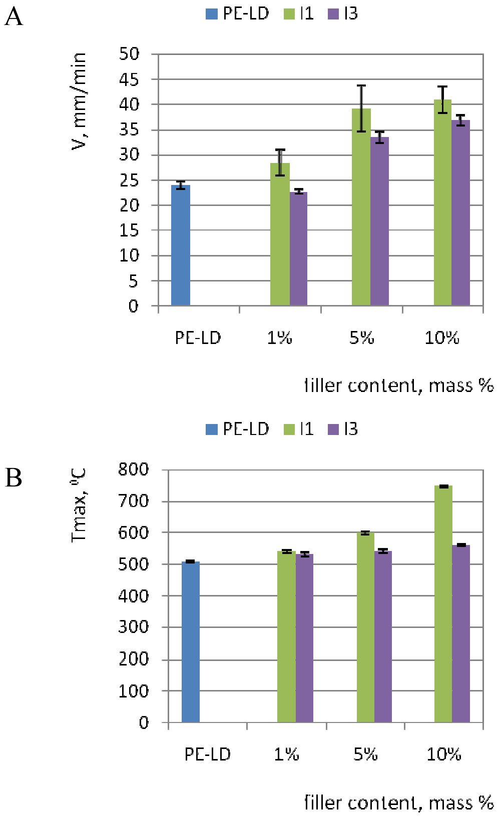

Fig. 8. Influence of filler content on: A) linear burning rate and B) maximum combustion temperature of tested composites and reference material

Rys. 8. Wpływ zawartości napełniacza na: A) liniową szybkość palenia oraz B) maksymalną temperaturę spalania badanych kompozytów oraz materiału odniesienia

Upon analysis of the collected data, it was observed that both the linear burning rate and maximum combustion temperature increase accordingly with a rising loading of either of the fillers. Notwithstanding, better results were obtained by the Innosilica3-filled systems. For the PE-LD/Innosilica1 systems, an increase in the V and T_{max} values was observed in comparison to pure PE-LD, regardless of the filler loading. For example, for composites containing 10% Innosilica1, a 71% increase in V and 47% increase in T_{max} were measured. At the same loading of Innosilica3, the increase in the linear burning rate was 54% and the maximum combustion temperature increase was only 10%. It is also worth noting that the V value for I3 1% is 5% lower than that of PE-LD and the T_{max} values of the Innosilica3 composites increase very slowly with an increase in filler loading, from 532 ±7.8°C for I3 1% to 559 ±2.8°C for I3 10%.

Regardless of the rise in the composite linear burning rate for both filler types, the measured V values are less than 75 mm/min, which classifies them as HB 75 type materials in flammability classification.

CONCLUSIONS

A new, effective, *one-pot sol-gel* method for the synthesis and surface modification of a silica-based filler for polyolefins was presented. The influence of silica on polyethylene was studied using inorganic fillers. The study showed that the mechanical properties of silica-filled polyethylene material depend on the weight ratio of the individual components of their constituent. Innosilica3 has a slightly smaller surface area, which is due to the reduced number of micropores (Table 2), whose contribution to the total porous structure of the filler is substantial. This observation is very important in terms of our interpretation of the filler-matrix interaction. Micropores have no significant impact on this interaction and a decrease in their number may be attributed to migration and condensation of methyltrimethoxysilane inside the pores or closing of their entrances. The number of mesopores, which play an essential role in creating filler-matrix interaction, is not affected by the material modification presented in this work.

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