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## THERMAL PROPERTIES OF PP-SiO<sub>2</sub> COMPOSITES FILLED WITH STÖBER SILICA

The paper analyses the impact of ceramic particles on the thermal properties and flammability of polymer composites. The research subject concerns polypropylene-based composites. Polypropylene was modified with Aerosil 200 commercial silica and Innosilica silica obtained by means of a modified Stöber method. The input material with a variable content of SiO<sub>2</sub>: amounting to 1, 5 and 10% was produced during injection. The heat resistance of the obtained composites was specified by the determining the Vicat softening temperature (VST) and heat deflection temperature (HDT), and based on differential scanning calorimetry (DSC) measurements, thermogravimetric analysis (TG) and thermal diffusivity (D<sub>f</sub>). A fire resistance test of the studied composites was also carried out. It was found that silica added to the polypropylene matrix has a favourable influence on or does not worsen the heat resistance of the studied composites. It was also noticed that all the composites, especially those with a 1% filler content, have a greater degree of flammability compared to the input polymer.

**Keywords:** sol-gel, silica filler, Stöber, thermal properties, composite, polypropylene

## WŁAŚCIWOŚCI TERMICZNE KOMPOZYTÓW PP-SiO<sub>2</sub> NAPEŁNIANYCH KRZEMIONKĄ TYPU STÖBERA

Kompozytem nazywamy materiał składający się z dwóch lub większej liczby różnych materiałów możliwych do wyodrębnienia metodami mechanicznymi, rozłożonych w kontrolowany sposób w celu nadania optymalnych właściwości danego kompozytu oraz posiadających właściwości wyjątkowe i lepsze niż jego indywidualne składniki. Składnik ciągły kompozytu, który często występuje w większej ilości, nazywany jest osnową. W niniejszej pracy analizie poddano wpływ cząstek ceramicznych na właściwości cieplne oraz palność kompozytów polimerowych. Przedmiot badań stanowiły kompozyty na bazie polipropylenu modyfikowanego krzemionką handlową Aerosil 200 oraz krzemionką Innosilica, otrzymywaną modyfikowaną metodą Stöbera. Materiał wejściowy o zmiennej zawartości SiO<sub>2</sub>: 1, 5 i 10% wytworzono w procesie wtryskiwania. Określono odporność cieplną wytworzonych kompozytów poprzez oznaczenie temperatury mięknięcia wg Vicata (VST), temperatury ugięcia pod obciążeniem (HDT) oraz na podstawie: pomiarów różnicowej kalorymetrii skaningowej (DSC), analizy termogravimetrycznej (TG) oraz dyfuzyjności cieplnej (D<sub>f</sub>). Przeprowadzono również próbę odporności ogniowej badanych kompozytów. Stwierdzono, że dodatek krzemionki do osnowy polipropylenowej wpływa korzystnie lub nie pogarsza odporności cieplnej badanych kompozytów. Zauważono ponadto, że wszystkie kompozyty w porównaniu do wejściowego polimeru charakteryzują się większą stabilnością procesu palenia, w szczególności kompozyty zawierające dodatek napelnacza w postaci Innosilica. Podkreślić należy także, że poza liniową szybkością palenia każdorazowo lepsze właściwości charakteryzują materiały kompozytowe wytworzone na bazie krzemionki Innosilica.

**Słowa kluczowe:** sol-gel, napelniacz krzemionkowy, Stöber, właściwości termiczne, kompozyt, polipropylen

## INTRODUCTION

Polymer composites have relatively low thermal stability and combustion, which, in turn, depend on the physical and chemical changes occurring in the polymer at a high temperature [1]. Silicon dioxide, in turn, is characterised by high thermal stability and favourable strength parameters, properties that make it suitable for being used as a filler to improve the thermal resistance

and strength of the polymers that contain it. For this reason, a variety of silicas are increasingly being used as active polymer fillers. In the literature on the subject, there are numerous references that confirm that pyrogenic and precipitated SiO<sub>2</sub> are used to form state-of-the-art polymer composites based on polypropylene because of their thermoplasticity and low price [2-5],

as well as polystyrene, polyethylene terephthalate thermoplastic polyesters, epoxy resins and polyacrylics [6-13].

The aim of the research was to study the influence of Aerosil 200 and Innosilica silica fillers on the thermal properties and flammability of polypropylene composites with 1, 5 and 10 weight percent filler (corresponding to 0.5, 2.5, 5 volume percent) compared to polypropylene that constituted the composite matrix.

## EXPERIMENTAL PROCEDURE

The following materials were used during the study: HP 456J polypropylene (Lyondell Basell, MFR<sub>(230/2.16)</sub> = 3.4 g/10 min), commercial hydrophilic Aerosil 200 silica (pyrogenic, with a specific weight of 200 m<sup>2</sup>/g, a density of 50 g/l and pH 3.7-4.7) as well as amorphous, spheroid, monodispersion Innosilica silica obtained using a modified Stöber method and with an average size of single particles amounting to about 500 nm.

Innosilica was synthesized in a thermostated glass reactor with a working volume of 10 dm<sup>3</sup>. A 3.3 dm<sup>3</sup> isopropyl solution (Sigma-Aldrich, p.), a 2 dm<sup>3</sup> methyl alcohol solution (POCH, p.), 0.3 dm<sup>3</sup> distilled water, a 0.3 dm<sup>3</sup> 25% (w/w) ammonium hydroxide solution (POCH, p.a. grade) were used as the reaction environment. Ethyl silicate (Aldrich, d = 1.05 kg/dm<sup>3</sup>) was added to the working solution at a steady temperature of 2°C to slow the precursor's hydrolysis reaction down. Ethyl silicate is a hydrolyzed and oligomerized form of silicate. It is a mixture of monomers, dimers, trimers and cyclic polysiloxanes. Ethyl silicate is a transparent liquid containing 40% silica by mass, but in practice, in addition to chain condensates, it also contains branch-shaped and ring-shaped condensates. Ethyl silicate was added at a flow rate of 0.15 dm<sup>3</sup>/h for the first 12 hours (speed being extremely significant because of the final product morphology) and at 0.2 dm<sup>3</sup>/h for a subsequent 6 hours. The total amount of ethyl silicate added stood at 3 dm<sup>3</sup>. After that, the product suspension was stirred at the temperature of 20°C for 24 hours. The suspension was evaporated in a vacuum evaporator and 1182 g of white powder was obtained, which was then dried at the temperature of 200°C for 24 h. After it was dried, a total amount of 1093 g of filler was obtained, which was then stored away from moisture.

During the first research stage, polypropylene/filler concentrates were produced with a 50/50 weight ratio from the two kinds of fillers used in the study. A ZAMAK MERCATOR rolling mill was used for this purpose. The obtained concentrates were ground in a SHINI SG-1417 slow motion mill and then dried (2h, 900°C). The raw materials (PP/Aerosil 200; PP/Innosilica; 50/50) prepared in this way were then diluted using a ZAMAK EH16.2D extruder ( $L = 16$  mm,  $L/D = 40$ ) during twin-screw extrusion. The studied concentrates were diluted to concentrations amounting

to 1, 5 and 10 weight percent filler, a process that resulted in the following composites (Table 1).

TABLE 1. Acronyms for prepared and characterized composites

TABELA 1. Akronimy przygotowanych i poddawanych charakterystyce kompozytów

Acronyms for composites	Description of composites
A1	1% Aerosil 200, 99% PP
A5	5% Aerosil 200, 95% PP
A10	10% Aerosil 200, 90% PP
I1	1% Innosilica, 99% PP
I5	5% Innosilica, 95% PP
I10	10% Innosilica, 90% PP

A BATTENFELD PLUS 35/37 hydraulic injection mould was used to produce test samples in their final form necessary for thermal testing. The moulder was a two-stage machine to create standardised dumbbells conforming to PN-EN ISO 527-2 (1A type).

Pure polypropylene was used as the reference material.

The morphology of the obtained research materials was analysed using a high-resolution electron microscope (Quanta 250 FEG, FEI) during scanning electron microscopy.

The thermal properties of the composites and the input material were determined using differential scanning calorimetry, thermogravimetric analysis, Vicat softening temperature, heat deflection temperature, thermal diffusivity and flammability tests.

Differential scanning calorimetry (DSC) and a DSC1 Mettler Toledo apparatus were used to determine the melting point ( $T_p$ ), crystallization temperature ( $T_c$ ) and the difference between them ( $\Delta T$ ). The measurements were carried out in an atmosphere of nitrogen according to the following temperature programme: 25÷230°C (10°C/min) - 230°C 2 min - 230÷25°C (5°C/min). Research samples with a weight of approx. 7 mg were taken from the internal central part of the 1A previously injected measurement dumbbell.

Thermogravimetric analysis (TG) of the studied materials was conducted in an atmosphere of nitrogen, using a NETSCH TG 209 F3 apparatus. The following measurement parameters were employed: the flow rate of inert gas amounted to 0.03 dm<sup>3</sup>/min, the specimen heating rate stood at 10°C/min, and the temperature ranged from 30 to 700°C. As with DSC, the test samples were taken from the internal central part of the sampling section of the 1A dumbbell.

An Instron CEAST HV3 was used to determine the Vicat softening temperature (VST) and heat deflection temperature (HDT) of the input materials and all the composites created with powder fillers.

The Vicat softening temperature (VST) was determined in accordance with the ISO 306 standard - method B, using a heating rate of 120°C/h and a force of 50 N. Test samples with a size of 10x10x4 mm cut

out from the sampling section of the 1A dumbbell were used in the experiment.

The heat deflection temperature (HDT) was determined according to ISO 75 - Method B, using a heating rate of 120°C/h and a tension of 0.46 MPa. Test samples measuring 40x10x4 mm cut out from the sampling section of the 1A dumbbell were used in the experiment.

The thermal diffusivity of the studied materials was measured using a modified Angstrom method described in detail in [14]. Test samples with a size of 40x10x4 mm cut out from the sampling section of the 1A dumbbell were used in the experiment.

Flammability tests were performed in accordance with PN-EN 60695-11-10 - Method A (the sample was placed horizontally).

## RESULTS AND DISCUSSION

Images obtained by means of scanning electron microscopy (SEM) proved that particular grains of Innosilica were spherical and their diameter amounted to about 500 nm (Fig. 1a). The topographic structure of particular composites was uniform, as confirmed by images of the surface of the tested samples. Figure 1b shows an example of an image of the composite structure that revealed the high degree of filler distribution homogeneity compared with the remaining tested systems.

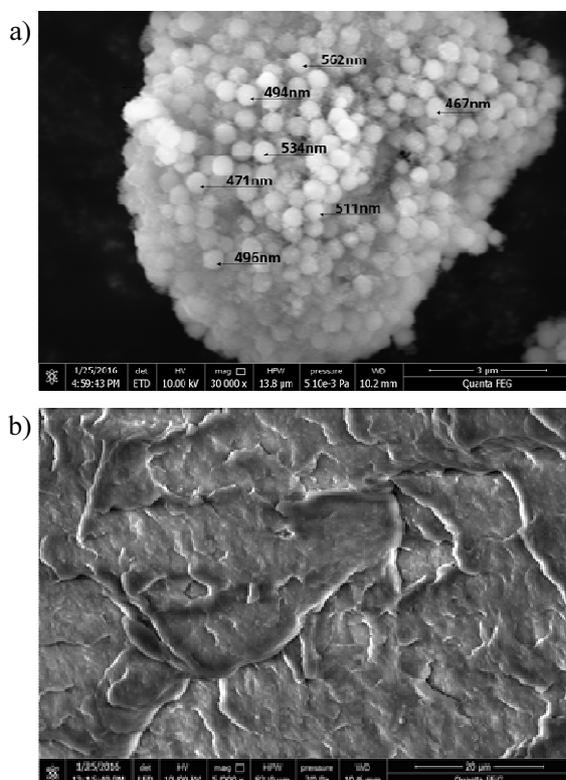


Fig. 1. a) Distribution, geometry and size of Innosilica spheroid grains. b) Topographic structure of 15 composite surface in a fracture

Rys. 1. a) Dystrybucja, geometria i wielkości ziaren krzemionki sferoidalnej Innosilica. b) Struktura topograficzna powierzchni kompozytu 15 w przełomie

All the studied composites were subjected to thermogravimetric analysis (TG) and differential scanning calorimetry (DSC). Since there were negligible differences between the results for particular composites, the paper presents the outcomes for the composites with the 5% filler content (A5, I5).

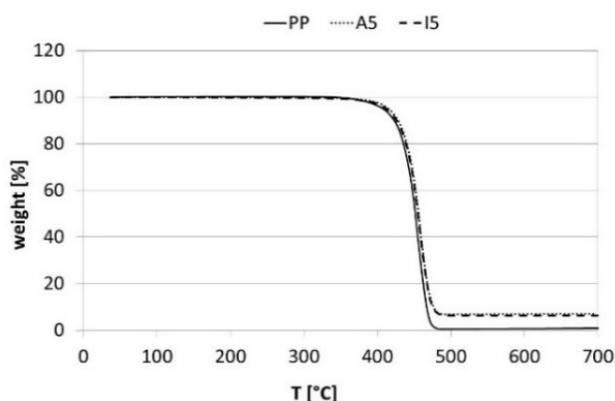
Thermogram thermogravimetric analysis makes it possible to determine the impact of a silica filler on the melting point and crystallization of the composites. When the obtained data were analysed, there were small changes in the  $T_m$  and  $T_c$  values of the A5 and I5 composites compared with PP (Table 2). Despite the negligible changes in both the temperature values, it was noticed that the difference ( $\Delta T$ ) between them decreased after the filler had been introduced to the polypropylene matrix. The noted phenomenon is extremely favourable from the viewpoint of the processing of the discussed materials. The lower  $\Delta T$  confirmed that it was possible to shorten the processing period (or injection cycles as discussed here) of the composites compared with the reference materials, which improves the cost, energy and time efficiency of the process.

TABLE 2. Temperatures of phase changes determined under DSC:  $T_m$  - melting point,  $T_c$  - crystallization temperature,  $\Delta T$  - difference between temperatures

TABELA 2. Temperatury przemian fazowych wyznaczonych metodą DSC:  $T_m$  - temperatura topnienia,  $T_c$  - temperatura krystalizacji,  $\Delta T$  - różnica temperatur

Sample	$T_m$ [°C]	$T_c$ [°C]	$\Delta T$ [°C]
PP	166.88	120.8	46.08
A5	165.42	121.98	43.44
I5	167.14	124.45	42.69

As part of the characteristics of thermal stability of the A5 and I5 composites, TG curves of the pure polypropylene and polypropylene composites with the 5% filler content (Fig. 2) were obtained, whose trajectories did not differ as to the temperature range of 25÷400°C, and their mass remains more or less the same.



Rys. 2. Analiza termogravimetryczna materiałów kompozytowych z 5% zawartością napelniacza

Fig. 2. Thermogravimetric analysis of composite materials with 5% filler content

When the temperature was over 400°C, it was noticed that there was a considerable decrease in the mass of the analysed systems because the polypropylene had reached the ignition temperature. In-depth analysis of the obtained thermograms showed that the temperature value determining the safe use of the specified material based on a 5% drop in the mass of the composites with the 5% silica filler content ranges from 416 to 412°C and is slightly higher, almost equal to that measured for the pure PP, as is the case for a 50% fall in mass, in the case of which the temperature rose by about 4-5°C (Table 3).

TABLE 3. Temperature of 5 and 10% fall in mass of researched composites constituting measure of thermal stability

TABELA 3. Temperatura 5 i 10% ubytku masy dla badanych kompozytów stanowiąca miarę stabilności termicznej

Fall in mass [%]	T [°C]		
	PP	A5	I5
5	407.8	416.2	412.4
50	451.5	456.1	455.3

The wide range of applications for plastics mean that they are faced with increasingly more demanding challenges, also as far as thermal resistance is concerned. From the viewpoint of applications for plastics and composites in various industries, quite significant thermal properties include Vicat softening temperature (VST) (Fig. 3) and heat deflection temperature (HDT) (Fig. 4). It is known that when it comes to thermoplastics and their composites, it is not possible to determine the accurate melting point that would mark the transition from a solid to a liquid state. As the temperature rises, they tend to soften slowly. When the obtained results are analysed, it is possible to state that adding a filler raises the VST values by a negligible extent. For the composites with the 1% filler content (A1, I1), the difference of the temperatures compared to the VST of pure PP amounts to approximately 3°C. As for the composites with the 10% filler content (A10, I10), the figure stands at about 6°C.

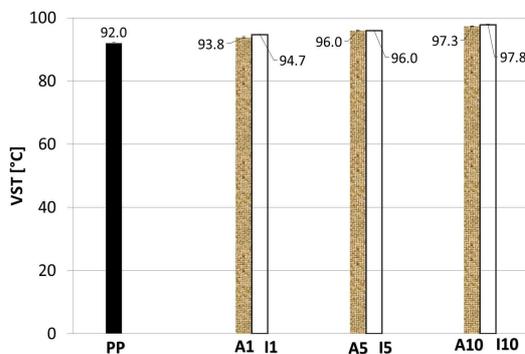


Fig. 3. Dependence of Vicat softening temperature on amount and kind of filler in a given composite

Rys. 3. Zależność temperatury mięknięcia wg Vicata od zawartości i rodzaju napełniacza w kompozycie

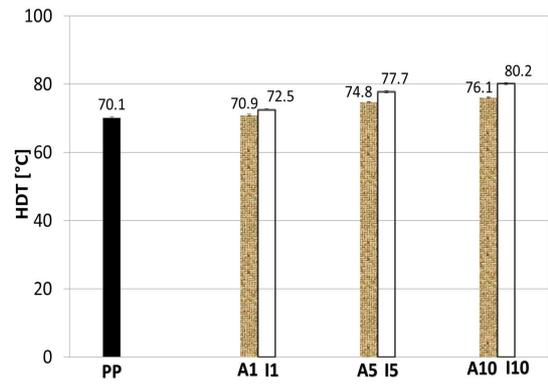


Fig. 4. Dependence of heat deflection temperature under load on amount and kind of filler in given composite

Rys. 4. Zależność temperatury ugięcia pod obciążeniem od zawartości i rodzaju napełniacza w kompozycie

Similar dependencies are demonstrated by the heat deflection temperature values under a load of selected composites (Fig. 4). As the silica filler content in the composite rises, there is also a growth in its heat deflection temperature. The highest HDT values are demonstrated by the I10 composite and the temperature amounts to 80°C, i.e. 10°C higher than the HDT of the reference material being pure polypropylene.

The thermal diffusivity of polymer materials is usually specified to determine their ability to transfer heat. Thermal diffusivity helps determine the ability of a ready product made of a specific plastic to heat or cool, that being an important parameter in the choice of applications for plastics.

The dependence of thermal diffusivity ( $D_f$ ) on the kind and amount of filler in a composite is shown in Figure 5. For the reference material (PP), the  $D_f$  value stands at  $9.87 \times 10^{-7} \text{ m}^2/\text{s}$ . There is a visible growth in the  $D_f$  value as the filler content in the composite goes up. The Innosilica composites show significantly higher  $D_f$  values compared to the Aerosil 200 ones. The highest  $D_f$  values are demonstrated for the composites with the filler content of 10 wt. % For the A10 composite,  $D_f = 1.46 \times 10^{-6} \text{ m}^2/\text{s}$  and for the I10 composite,  $D_f = 1.68 \times 10^{-6} \text{ m}^2/\text{s}$ .

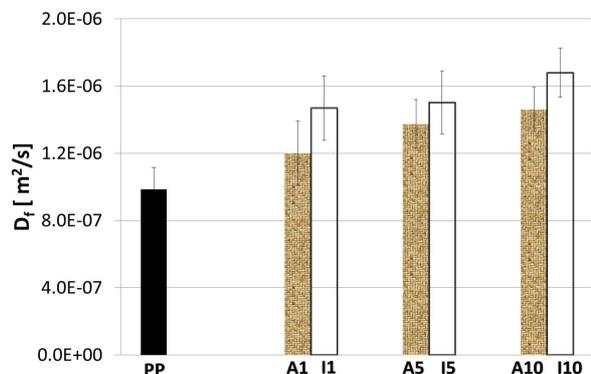


Fig. 5. Dependence of temperature diffusivity on amount and kind of filler in composite

Rys. 5. Zależność dyfuzyjności temperaturowej od zawartości i rodzaju napełniacza w kompozycie

The higher thermal diffusivity values found for the composites containing the studied silicas (especially Innosilica) are another favourable effect of polypropylene having been modified. This is because higher  $D_f$  values mean that composite materials transport heat more rapidly causing them to cool more quickly; in other words, the processing time cycles become shorter, as was observed in the discussion of the DSC results.

The linear burning rate was also specified for the studied materials in order to fully characterize their thermal properties (Fig. 6). It can be inferred from the collected measurement data that the flammability of the composites is lowered if they contain silicas - both Aerosil 200 and Innosilica. Both the reference material in the form of PP and all the composites researched burn at a rate lower than 75 mm/min, which classifies them as plastics with the HB75 flammability class. The composites with 1 and 5% filler content demonstrate a linear burning rate below 20 mm/min. As for the composites with the 10% filler content, the linear burning rate was only about 2 mm/min lower than that determined for pure PP and stood at approximately 21 mm/min.

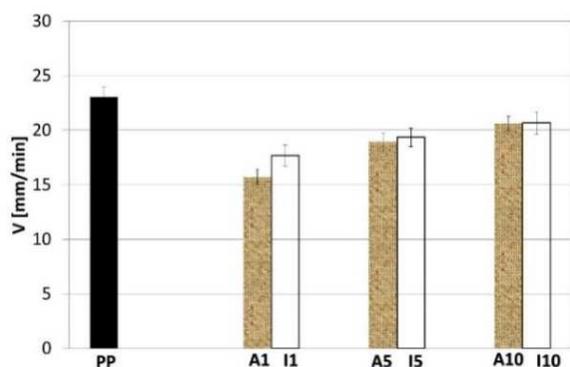


Fig. 6. Dependence of linear burning rate on amount and kind of filler in given composite

Rys. 6. Zależność liniowej szybkości palenia od zawartości i rodzaju napełniacza w kompozycie

## CONCLUSIONS

The obtained research results confirm the use of a modified Stöber method as a technique of creating amorphous, spheroid silica. Moreover, the results of the study show that even a small amount of a silica filler such as Aerosil 200 or Innosilica added to polypropylene composites has a favourable effect on their thermal properties and, above all, flammability. Nanosilica added as a filler does not influence the crystallinity of polypropylene composites, but has only a negligible impact on the value of the temperature that determines the safe use of the composite. Analysis of the Vicat softening temperature and temperatures of heat deflection under the load of the composites allows one to conclude that the addition of fillers such as Aerosil 200 and Innosilica has a favourable influence on raising the values of these parameters. The recorded rise in tem-

perature diffusivity values and the difference between the melting temperature and crystallinity of the composites compared to the reference material constitutes a positive processing aspect. Based on the tests that were carried out, it was also found that a filler such as Aerosil 200 and Innosilica added to the polypropylene matrix of the composites lowers their flammability, a phenomenon that raises the number of their applications.

It also needs to be stressed that apart from the linear burning rate, Innosilica-based composite materials have better properties.

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