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COMPOSITES THEORY AND PRACTICE

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THE INFLUENCE OF SPHERICAL SILICA PREPARED BY SOL-GEL METHOD ON MECHANICAL PROPERTIES OF POLYPROPYLENE-SiO_2 COMPOSITE

In the present paper the spherical silica material Innosilica was proposed to be used as filler for a composite with polypropylene. The spherical silica synthesis was based on a modified Stöber method. The aim of the study was to obtain a composite of better properties than those of pure polypropylene. The composite system with 1, 5, 10% of silica fillers were used. The characteristics of the obtained systems were defined by scanning microscopy. A universal fatigue testing machine Zwick Roell Z020 was employed to determine the tensile properties of the input material and composites under static extension and to the test of flexure resistance of the composites. The impact test with a composite notch and input material was determined using an Instron pendulum hammer type and the hardness property was measured with Shore hardness tester with a sharp conic indenter made by Zwick. As the reference material unmodified polypropylene and it's composite with market silica - Aerosil 200 were used. The results of our researches indicate that the presence of the silica fillers improved the polypropylene properties. Parameters change depending on the content of the fillers. Innosilica allowed to obtain better results than the commercial silica. The study showed that the mechanical properties of silica-filled polypropylene material depend on weight ratio of the individual components of their constituent and on the geometry also. The filler of a spherical construction has a greater influence on the increase in composite stiffness than a filler of an irregular shape (Aerosil 200). This suggests that the higher structural homogeneity of composites PP/Innosilica exhibits the better mechanical properties.

Keywords: **sol-gel, polypropylene, Stöber SiO_2, composite, mechanical properties**

WPŁYW SFERYCZNEJ KRZEMIONKI OTRZYMYWANEJ METODĄ ZOL-ŻEL NA WŁAŚCIWOŚCI MECHANICZNE KOMPOZYTU POLIPROPYLEN-SiO_2

W pracy zaproponowano materiał krzemionkowy w postaci sferycznej krzemionki - Innosilica do zastosowania jako wypełniacz w kompozycie polipropylenowym. Sferyczna krzemionka została otrzymana za pomocą zmodyfikowanej metody Stöbera. Celem badań było otrzymanie kompozytu o lepszych właściwościach w porównaniu z niemodyfikowanym polipropylenem. Zastosowano 1, 5, 10% dodatek wypełniaczy krzemionkowych. Charakterystykę struktury materiałów przeprowadzono z wykorzystaniem mikroskopii skaningowej. Badania właściwości wytrzymałościowych kompozytów i materiału wejściowego przy statycznym rozciąganiu oraz pomiar wytrzymałości na zginanie kompozytów przeprowadzono z użyciem uniwersalnej maszyny wytrzymałościowej Zwick Roell Z020. Udarność z karbem określono, stosując młot wahadłowy firmy Instron, model CEAST 9050, a pomiar twardości wykonano za pomocą analogowego twardościomierza Shore'a firmy Zwick. Jako materiał referencyjny zastosowano niemodyfikowany polipropylen oraz jego kompozyt z handlową krzemionką Aerosil 200 jako wypełniaczem. Przeprowadzone badania wykazały, że wprowadzenie do polipropylenu wypełniaczy krzemionkowych powoduje polepszenie jego właściwości mechanicznych. Parametry zmieniają się wraz z zawartością wypełniacza w kompozytach. Innosilica pozwoliła osiągnąć lepsze rezultaty niż handlowa krzemionka. Stąd można przypuszczać, że wpływ na właściwości kompozytu ma nie tylko zawartość wypełniacza (wyrażona w procentach wagowych), ale przede wszystkim jego kształt. Sferyczna krzemionka Innosilica wykazuje mniejsze powinowactwo do tworzenia aglomeratów w osnowie polimerowej w porównaniu do nieregularnych kształtów Aerosilu 200. Kompozyty PP/Innosilica wykazują wyższą jednorodność strukturalną, a wysoka homogeniczność układu skutkuje lepszymi właściwościami mechanicznymi.

Słowa kluczowe: **zol-żel, polipropylen, krzemionka Stöbera, kompozyt, właściwości mechaniczne**

INTRODUCTION

Polypropylene is one of the most popular polymers due to its properties and low manufacturing costs. Polypropylene is used in practice in the form of composites with inorganic fillers. Their presence changes the polypropylene properties: mechanical properties, increase in surface hydrophobicity, steric stabilization of nanoparticles in agglomeration or increase in compatibility between the surface and polymer matrix [1-6]. Among many fillers, special attention should be paid to SiO_2. Studies on PP-SiO_2 composites indicate that compared to PP without any modifications, the mechanical stability of PP improved [7-10] as well as the resistance to thermal deformations [11, 12]. New types of SiO_2 are very promising for the development of polymers. The present paper is focused on the PP-SiO_2 composite prepared with spherical Stöber silica. The composites were obtained by mechanical milling. The PP-SiO_2 systems were submitted to tensile properties tests, flexure resistance tests, impact testing and hardness measurements.

EXPERIMENTAL PROCEDURES

Material

The following input materials were used in the tests: polipropylene HP456J (*Lyondell Basell*, $MFR_{(230/2.16)}$ = = 3.4 g/10 min), Hydrophilic silica Aerosil 200 (pyrogenic with specific weight 200 m^2/g, density 50 g/l and pH 3.7÷4.7) and amorphous, spherical monodispersopnal silica Innosilica of the average particle size of 500 nm obtained by Stöber's method. The spherical silica synthesis was based on a modified Stöber method. The synthesis was performed in a thermostatic glass reactor (working capacity 10 dm^3). As the reaction solution, 3.3 dm^3 of isopropyl alcohol, 2 dm^3 of ethyl alcohol, 300 cm^3 of distilled water and 300 cm^3 of a 25% solution of aqueous ammonia were used. At the temperature of 2°C, ethyl silicate (d = 1.05 g/cm^3) was added to the working solution. Ethyl silicate is a hydrolyzed and oligomerized form. It is a mixture of monomers, dimers, trimers and cyclic polysiloxanes. Ethyl silicate is a transparent liquid containing 40% silica (SiO_2) by mass, but in practice, in addition to chain condensates, it also contains branch-shaped and ring-shaped condensates. The dosing rate of the ethyl silicate (very important parameter because of the morphology of the final product) was 150 cm^3/h in the first 12 hours of the process and 200 cm^3/h for a further 6 h process. The total amount of added ethyl silicate was 3000 cm^3. Once the dozing stage ended, the slurry was stirred for 24 h at 20°C and then evaporated using a vacuum evaporator to obtain 1182 g of white powder. Next, the powder was placed in a dryer and left to dry at 200°C for 24 h. After the drying process, the filler was weighed and was 1093 g, and eventually was stored under hermetic conditions.

The first stage consisted in preparing polypropylene/filler concentrates of a 50/50 weight ratio created from two types of fillers used in the study. The concentrates were prepared using a ZAMAK MERCATOR rolling mill. The concentrates were milled in a *SHINI SG-1417* slow motion mill and then were left to dry for 2 hours at 90°C. The thus prepared raw materials (PP/Aerosil 200; PP/Innosilica; 50/50) were diluted during a twin-screw extrusion process carried out using a ZAMAK EH16.2D (L = 16 mm, L/D = 40) extruder. The concentrates were diluted until concentrations of 1.5 and 10 wt.% filler were reached.

In order to obtain the final form of the test sample, essential in the mechanical tests, a hydraulic injection molder by *BATTENFELD*, model PLUS 35/75 (equipped with a double-seat mold to prepare normalized testing paddles in conformity with the PN-EN ISO 527-2 norm, type 1A) was used. Pure polypropylene was used as the reference material.

Methodology

For the cross-section observation, the microporous membrane was freeze-fractured in liquid nitrogen and then sputter coated. Imaging of the surface was performed by SEM electron microscopy (Quanta 250 FEG, FEI).

A universal fatigue testing machine Zwick Roell Z020 was employed to determine the tensile properties of the input material and composites under static extension. The measurement was performed according to the applicable norm PN-EN ISO 527-1. The test involved the use of measurement jaws of a 20 kN maximal load force and a crosshead motion speed rate of 100 mm/min.

The test of flexure resistance of the composites was carried out also using the fatigue testing machine Zwick Roell Z020 with a suitable element for 3-point bending. Determination of the flexure resistance was conducted according to the applicable norm PN-EN ISO 178 and bending was performed at a speed ratio of 1.5/min until the flexure reached the accorded arrow of 6 mm in length.

The impact test with a composite notch and input material was determined using an Instron pendulum hammer type CEAST 9050 with a maximal energy of 25 J for impact testing according to the Charpy method. The test was carried out in conformity with the applicable norm PN-EN ISO 179-1.

The hardness property was measured according to the PN-ISO 868:2005 norm using an analogous Shore hardness tester (D scale) with a sharp conic indenter made by Zwick.

Abbreviations

PP	- polypropylene,
PP/SiO_2	- polypropylene with SiO_2 composite,
E_t	- Young's modulus
σ_M	- extension strength
ε_B	- extension at rupture
E_f	- flexure modulus
F_{max}	- force registered at accorded flexure arrow
HS	- Shore's hardness
a_N	- Charpy's impact strength

RESULTS AND DISCUSSION

SEM photos of the PP/SiO_2 surface indicate the presence of a homogeneous composite material (Fig. 1). For all the systems, we obtained very good dispersion of the silica in the polypropylene matrix. We did not observe the presence of precipitated SiO_2 which indicates good distribution of the silica in the polypropylene matrix.

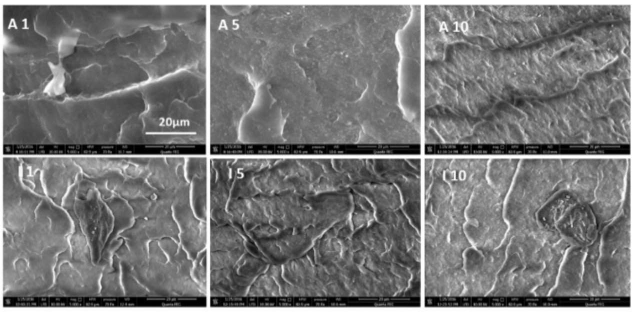

Fig. 1. SEM image of composite (A - aerosil 200, I - innosilica: A1-1%, A5-5%, A10-A10%, I1-I1%, I5-5%I, I10-I10%)

Rys. 1. Zdjęcia kompozytów (A - aerosil 200, I - innosilica: A1-1%, A5-5%, A10-A10%, I1-I1%, I5-5%I, I10-I10%)

Figure 2 displays a graph with particular values of the E modulus (E_t) for PP, materials with the referential silica Aerosil 200 and with silica Innosilica depending on the content of the composites.

While analyzing the obtained results, it was found that the incorporation of two types of silica to the polypropylene bulk influenced an increase in the Young's modulus of the composites, compared to the input material.

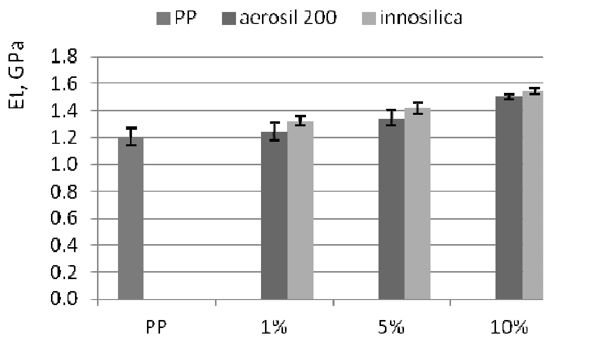

Fig. 2. Young's modulus dependence on filler content and type in PP/SiO_2 composite

Rys. 2. Zależność modułu Younga od zawartości i rodzaju napełniacza w kompozycie PP/SiO_2

The E modulus increased along with an increase in the amount of both types of SiO_2 fillers contained in the PP bulk. Each time higher values of E_t were registered for the materials obtained on the basis of Innosilica, which suggests that a filler of a spherical construction has a greater influence on the increase in composite stiffness than a filler of an irregular shape (Aerosil 200). The values of maximal tension were registered for all content configurations at rupture of the studied material and are shown in Figure 3. For both tested silica fillers, it was found that the increase in weight percent of filler in the PP/SiO_2 composite implied an increase in σ_M. It was also noticed that higher σ_M values were characteristic for the composites with the Innosilica filler.

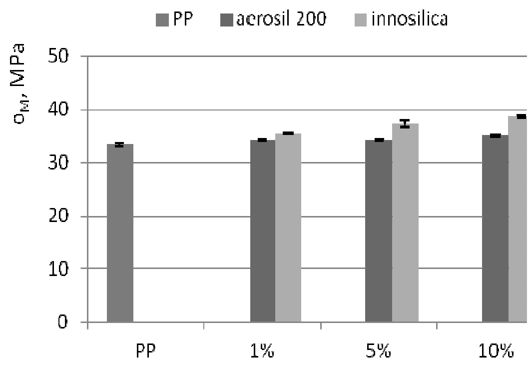

Fig. 3. Extension strength dependence on filler content and type in PP/SiO_2 composite

Rys. 3. Zależność wytrzymałości na rozciąganie od zawartości i rodzaju napełniacza w kompozycie PP/SiO_2

The obtained results suggests that in the case of the used fillers not only their content influences the tensile properties of the finished product but also their size, shape as well as adhesion at the polymer-filler interface. The higher values of tensile properties registered for the composites with Innosilica could arise from the fact that spherical silica shows a lower tendency to agglomerate in the polymer bulk than the irregular shapes of Aerosil 200. It suggests that the PP/Innosilica composites have a more homogenous structure.

The foregoing assumptions are confirmed by the received results from the extension-at-rupture test. The results are displayed in the graph below (Fig. 4). As it can be seen, the incorporation of a filler to the PP bulk provokes a decrease in the extension of the composite at rupture. Moreover, ε_B decreased with an increase in the silica content in the PP/SiO_2 material. The composites with the highest filler content demonstrated a drop in extension of over 50%, compared to pure polypropylene.

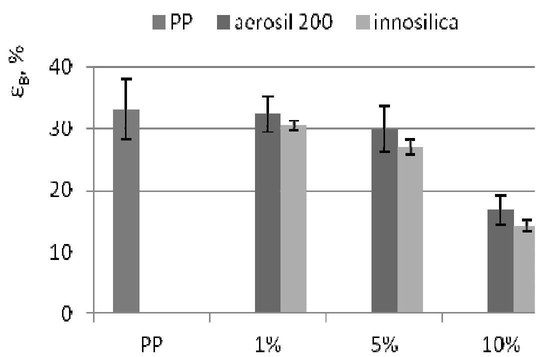

Fig. 4. Extension at rupture dependence on filler content and type in PP/SiO_2 composite

Rys. 4. Zależność wydłużenia przy zerwaniu od zawartości i rodzaju napełniacza w kompozycie PP/SiO_2

The registrated lower ε_B values for the composites with the Innosilica filler content suggest that probably the spherical silica grains show a lower adhesion at the polymer-filler interface compared to Aerosil 200. The lower values of the noted standard deviations also confirm the above-suggested higher homogeneity of the Innosilica-based materials.

The next graph (Fig. 5) presents the results of the flexure test carried out for the composites and input material. Analysis of the given results showed that similarly to E_t, E_f indicated higher values for the composites than for pure polypropylene.

The flexure modulus increases along with an increase in the amount of both types of used fillers in the PP carcass and each time the Innosilica-based composites reach higher values, which means that these composites are stiffer. The registered force values at the accorded flexure arrow are shown in Figure 6. It can be clearly seen that *Fmax* increased after the incorporation of both types of fillers to the PP bulk and this tendency was also maintained after an increase in filler content in the PP structure. However, each time higher *Fmax* values were noted for the composites with Aerosil 200.

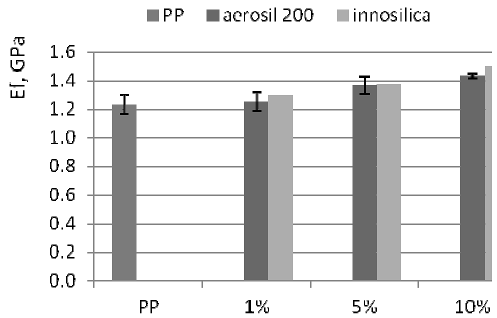

Fig. 5. Flexure modulus dependency on filler content and type in PP/SiO_2 composite

Rys. 5. Zależność modułu zginającego od zawartości i rodzaju napełniacza w kompozycie PP/SiO_2

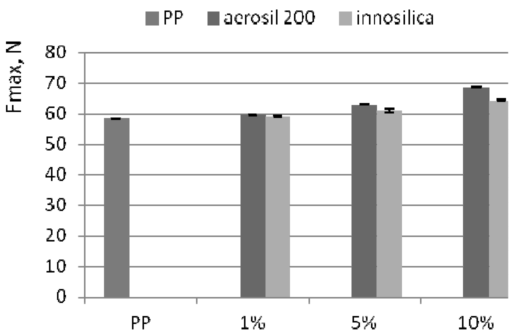

Fig. 6. Dependence of force registered at accorded flexure arrow on filler content and type in PP/SiO_2 composite

Rys. 6. Zależność siły zarejestrowanej przy umownej strzałce ugięcia od zawartości i rodzaju napełniacza w kompozycie PP/SiO_2

It should be emphasized that in the case of bending tests, the direction of forces affecting the sample are perpendicular towards it, and not longwise as during the elongation tests. The received results from flexure resistance are determined by the force of the filler - polymer bulk adhesion (impacts in impact tests are likewise). The results in the figure above (Fig. 6) indicate that adhesion of the spherical filler (Innosilica) to polypropylene is lower than that of the Aerosil 200 - a filler with irregular shapes.

Hardness is another mechanical property determined for all the tested composites and input material. The obtained results were arranged analogously to the tension tests and presented in Figure 7.

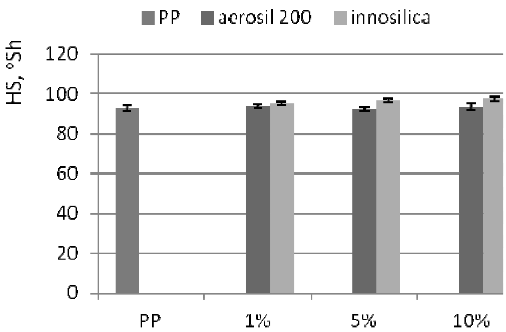

Fig. 7. Shore's hardness dependency on filler content and type in PP/SiO_2 composite

Rys. 7. Zależność twardości Shore'a od zawartości i rodzaju napełniacza w kompozycie PP/SiO_2

Analysis of the test results revealed that the incorporation of both types of fillers to the PP bulk provokes an increase in HS of the composites, compared to the polypropylene bulk. The increase grew along with an increase in filler content in the polymer structure. It was also found that the shape of the used filler (spherical, irregular) clearly affected the hardness of the finished product. The HS values recorded for the fillers with Innosilica were higher than those of the composites with Aerosil 200.

The last mechanical property determined for the tested composites was Charpy's impact strength. The received results as a function of content and type of filler are shown in Figure 8.

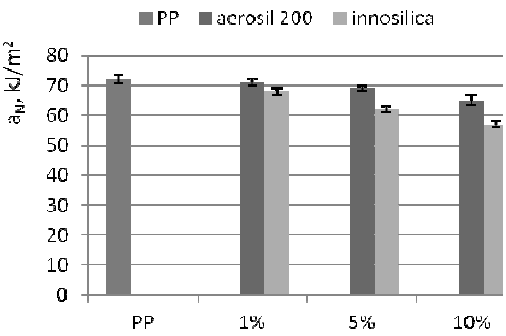

Fig. 8. Charpy's impact strength dependence on filler content and type in PP/SiO_2 composite

Rys. 8. Zależność udarności wg Charpy'ego od zawartości i rodzaju napełniacza w kompozycie PP/SiO_2

Analysis of the obtained results indicated that after introducing silica into the PP bulk the impact strength of the composites expectedly dropped, compared to pure polypropylene. Furthermore, it decreased along with an increasing content of filler in the polymer structure.

The test also revealed that significantly lower a_N values are characteristic of Innosilica-based composites. This observation confirms the earlier assumption that the spherical silica has a lower adhesion compared to a standard filler.

CONCLUSIONS

The influence of silica on polypropylene was studied using two different inorganic fillers. The study showed that the mechanical properties of silica-filled polypropylene material depend on the weight ratio of the individual components of their constituent and on the geometry as well (spherical, irregular). It has been shown that the shape of the filler which was used influences the tendency to agglomerate and the strength of adhesion on the polymer-filler border. In the cases of the investigated mechanical properties, higher values of the E_t, σ_M, E_f and HS parameters (expectation from the application point of view) were observed for the composite made with spherical Innosilica. This suggests that the filler with regular shapes has a lower affinity for forming agglomerates during processing and at the same time allows one to obtain a composite with structural homogeneity.

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