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COMPOSITES THEORY AND PRACTICE

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THE EFFECT OF POLYHEDRAL OLIGOMERIC SILSESQUIOXANE (POSS) ON MORPHOLOGY AND MECHANICAL PROPERTIES OF POLYOXYMETHYLENE (POM)

Polyoxymethylene nanocomposites with octakis (*dimethylsiloxy, ethyl epoxycyclohexy*) octasilsesquioxanes (POSS) were obtained during melt blending. The influence of the POSS nanoparticles on the morphology and mechanical properties of polyoxymethylene (POM) nanocomposites properties was investigated. POM/POSS nanocomposites were produced by means of melt mixing of POM with POSS; with a POSS content of 0.5, and 1 wt.%. The uniaxial elongation test of polyoxymethylene has been performed to determine the influence of POSS on the mechanical properties of the new hybrid material. The dispersion of POSS in the POM nanocomposites was studied by scanning electron microscopy (SEM). According to the mechanical investigation, it was found that the process of polyhedral oligomeric silsesquioxane (POSS) addition leads to an enhancement of both the tensile strength and stiffness, where the most encouraging results were achieved for the POM/POSS nanocomposites with 0.5 wt.% POSS. The SEM studies allowed us to provide direct evidence of better interfacial adhesion between the POSS particles and POM matrix, which may lead to better mechanical properties, specially tensile strength, elongation and stiffness. The obtained polymer composites POM/POSS are an interesting group of materials of construction, showing very good performance.

Keywords: **polyoxymethylene, polyhedral oligomeric silsesquioxanes (POSS), nanocomposites, morphology, mechanical properties**

WPŁYW POLISILSESKWIOKSANU (POSS) NA STRUKTURĘ I WŁAŚCIWOŚCI MECHANICZNE POLIOKSYMETYLENU (POM)

Nanokompozyty polioksymetylenu z oktakis (dimetylosiloksy, etyloepoksycykloheksylo) oktasilseskwioksanem (POSS) otrzymano w procesie przetwórstwa. Określono wpływ nanocząstek POSS na strukturę i właściwości mechaniczne nanokompozytów na bazie polioksymetylenu (POM). Badaniom poddano kompozyty POM z POSS wytworzone poprzez homogenizację w stanie stopionym, dodawanymi w ilościach 0,5 i 1% wag. W próbie jednoosiowego rozciągania dokonano oceny wpływu POSS na właściwości mechaniczne nowego materiału hybrydowego. Stopień zdyspergowania POSS w matrycy POM określono metodą skaningowej mikroskopii elektronowej (SEM). Na podstawie badań mechanicznych stwierdzono, że proces modyfikacji polioksymetylenu nanocząstkami POSS prowadzi do poprawy zarówno wytrzymałości na rozciąganie, jak i sztywności, gdzie najbardziej zadowalające wyniki uzyskano dla nanokompozytów POM/POSS z 0,5% wag. zawartością POSS. Badania SEM okazały się bezpośrednim dowodem występowania lepszych oddziaływań międzyfazowych pomiędzy nanocząstkami POSS a matrycą polioksymetylenową, co może prowadzić do poprawy właściwości mechanicznych, w tym w szczególności wytrzymałości na rozciąganie, wydłużenie i sztywność. Uzyskane kompozyty polimerowe POM/POSS stanowią interesującą grupę materiałów konstrukcyjnych, wykazujących wyjątkowo korzystne właściwości użytkowe.

Słowa kluczowe: **polioksymetylen, polisilseskwioksan (POSS), nanokompozyty, struktura, właściwości mechaniczne**

INTRODUCTION

Polyoxymethylene (POM) belongs to major thermoplastic engineering materials, commonly used to replace metal or alloy products, due to its high stiffness, corrosion resistance, dimensional stability and processing ability [1, 2]. On the other hand, its low impact toughness, notch sensitivity and especially low heat-resistance displays a certain limit of POM applications in industries such as cams, bearings, springs, gear shafts and gear wheels production. The incorporation of a low quantity of polyhedral oligomeric silsesquioxane (POSS), in the form of a nanoclaster cage into polymeric materials may lead to an improvement of the polymer properties, like temperature and oxidation resistance, surface hardening and reduction in flammability [3, 4].

Nowadays, considerable interest is devoted to nanocomposites due to their appealing properties, which may be obtained by additional nanoscaled fillers, including montmorillonite, aluminium oxide, and calcium carbonate, carbon nanotubes (CNTs), carbon nanofibers and silica or titanium oxide [5, 6, 16, 17]. The composites of polyhedral oligomeric silsesquioxane reagents, monomers, and polymers are emerging as a new class of organic-inorganic nanocomposites [7-9]. It is known that the final properties of nanocomposites depend on the particle size and shape, contents and distribution of fillers in the matrix of the polymer and on the adhesion at the interface surface [10, 16, 17].

Silsesquioxanes are compounds with an empirical formula $RSiO_{1,5}$, where R is hydrogen and belongs to an organic group [6, 9, 11, 12], which has aroused great interest among researchers in recent years. . Silsesquioxanes may reveal an enclosed ladder or random structures, and partial cage structures or cage structures, as illustrated in Figure 1 [11]. Today POSSs are readily available and can be functionalized with various functional groups such as: epoxy, vinyl, alkyl or methacryloylin in order to achieve interfacial coupling or copolymerization and/or cross linking [11-13]. In certain cases, very low POSS contents - i.e. a few percent, may be sufficient to improve stiffness, strength, dimensional stability and toughness, to enhance barrier resistance and to improve thermal stability as well as halogen-free flame retardancy [5, 6].

The aim of this study is to determine the effect of the octakis (*dimethylsiloxy, ethyl epoxycyclohexy*) octasilsesquioxane (POSS) nanofiller on the morphology and thermo-mechanical properties of the POM/epoxy POSS nanocomposites.

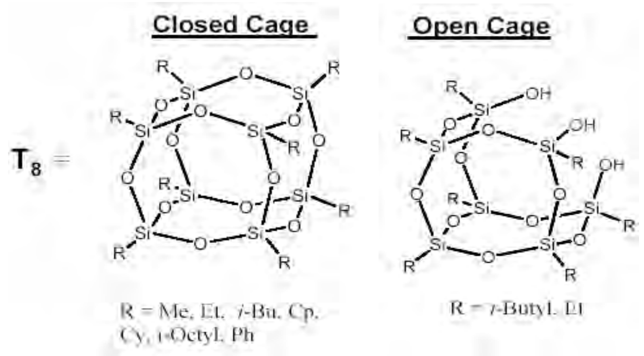

Fig. 1. General cage structure (closed and open) of polyhedral oligomeric silsesquioxanes (POSS)

Rys. 1. Ogólna struktura klatkowa polisilseskwioksanu (POSS) [11]

MATERIALS AND INVESTGATION METHODS

As the matrix of the composite, poly(oxymethylene) (POM), a copolymer Tarnoform 300 (density, ρ = = 1.41 g/cm^3, T_m =167°C) provided by the Nitrogen Works in Tarnow (Poland) was used in our investigations. The POM pellets were characterized by a melt flow index (MFI) of 9 g/10 min, at 190°C and load of 2.16 kg. Before compounding, the polymer pellets were dried for at least 4 hours, at 120°C. The POSSs were manufactured by the laboratory at the Faculty of Chemistry at the Adam Mickiewicz University of Poznan [14, 15]. The chemical structure of the octakis (*dimethylsiloxy, ethyl epoxycyclohexy*) octasilsesquioxane (POSS) [8] used in this work is shown in Figure 2.

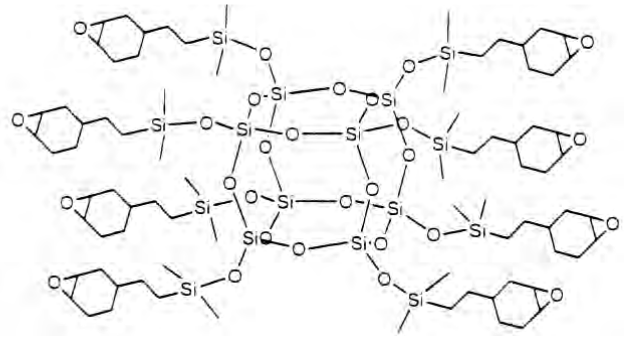

Fig. 2. Chemical structure of octakis (*dimethylsiloxy, ethyl epoxycyclohexy*) octasilsesquioxane (POSS)

Rys. 2. Budowa chemiczna oktakis(*dimetylosiloksy, etyloepoksycykloheksylo*)oktasilseskwioksanu (POSS)

PREPARATION OF POM/POSS NANOCOMPOSITES

The POM/POSS nanocomposites were produced by means of melt mixing POM with POSS; with a POSS content of 0.5, and 1 wt.%. The POSS powder and POM pellets were mixed in a solid state during 15 minutes, followed by melt mixing with a single screw extruder, equipped with a zone of intensive mixing, operating at the temperature of 180°C. The L/D ratio of the screw was 34 and the rotating speed of the screw was kept at 10 rpm. To achieve a high homogeneity of the composites, the POM/POSS blends were processed twice. The extruded rods were cooled and palletised. Before further processing, the granulates were dried at 120°C for 4 hours in a Shini - CD 5 dryer (Shini Plastics Technologies, Inc., Taiwan). Dumbbell-shaped samples were produced (sample geometry according to ISO 527-2, type 1A). The injection molding machine ENGEL ES 80/20 HLS with a Twente Mixing Ring was used. All the samples were produced in accordance to the processing conditions recommended by the producer (nozzle temperature 190°C, mould temperature 60°C, injection pressure 76 MPa).

The mechanical properties were determined by means of tensile tests performed with a universal testing machine, Instron model 4481 (Canton, MA, UK), operating at room temperature, with a ν = 50 mm/min crosshead speed, and the stress-strain curves σ = f(ε) were registered.

The dispersion of POSS in the POM nanocomposites was studied by scanning electron microscopy (SEM). The fracture surfaces of the tensile loaded specimens, coated with a carbon layer were subjected to

SEM inspection in a Vega Tescan model TS 5135 (TESCAN, Brno, Czech Republic), at an acceleration voltage of 3 kV.

RESULTS AND ANALYSIS

The uniaxial elongation test of polyoxymethylene has been performed to determine the influence of POSS on the mechanical properties of the new hybrid material. In Figure 3, a comparison of the stress-strain curves of neat POM and nanocomposites of 0.5 and 1 wt.% POSS can be seen.

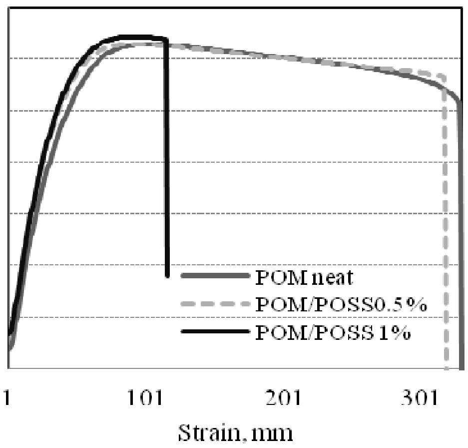

Fig. 3. Comparison of stress-strain curves of POM neat and POM/POSS composites with different POSS content

Rys. 3. Porównanie krzywych naprężenie-odkształcenie czystego POM i kompozytów POM/ POSS z różną zawartością POSS

The mechanical properties of the neat polyoxymethylene (POM) and POM/epoxy-POSS, for e.g. tensile strength, elongation at yield, and Young's modulus were evaluated on the basis of a stress-strain curve, as an average value determined for five samples in each case. The corresponding results are presented in Figures 4, 5 and 6.

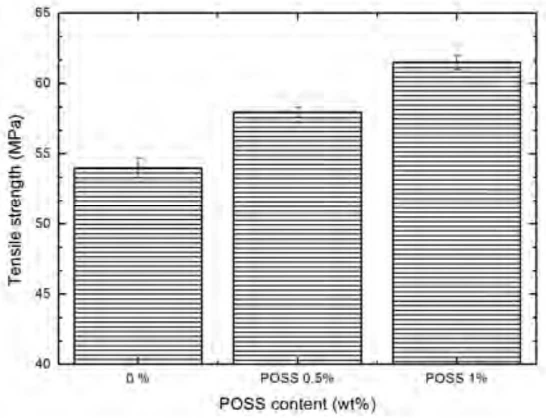

Fig. 4. Tensile strength of neat POM and POM/POSS composites with different POSS content

Rys. 4. Naprężenie zrywające dla czystego POM i kompozytów POM/POSS z różną zawartością POSS

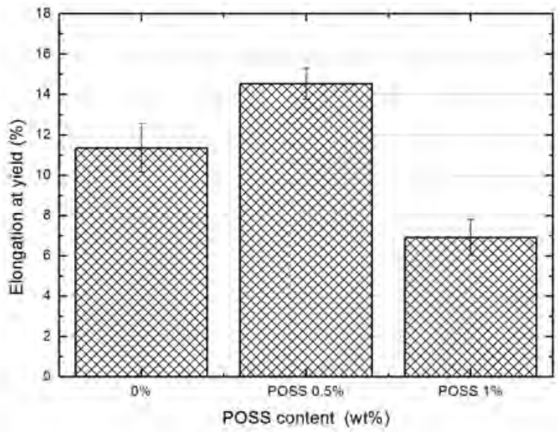

Fig. 5. Elongation at yield of neat POM and POM/POSS composites with different POSS content

Rys. 5. Wydłużenie na granicy plastyczności dla czystego POM i kompozytów POM/POSS z różną zawartością POSS

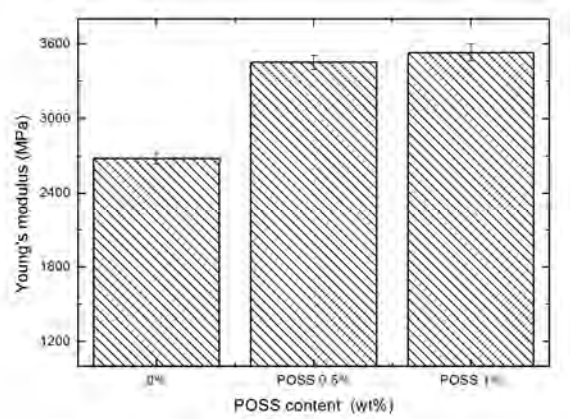

Fig. 6. Young's modulus of neat POM and POM/POSS composites with different POSS content

Rys. 6. Moduł sprężystości wzdłużnej dla czystego POM i kompozytów POM/ POSS z różną zawartością POSS

As follows from Figure 4, the tensile strength of POM/POSS nanocomoposites increases continuously with an increasing POSS content up to 1 wt.%, where a tensile strength value of 61.5 MPa was noted, compared to 54 MPa for pure POM (increase of about 14%). A significant increase in stiffness and stress at break observed in nanocomposites may be due to an increase in the degree of crystallinity with an increasing POSS content in the matrix polymer.

The highest value of elongation at the yield point of the POM/POSS nanocomposites (Fig. 5) was observed for the addition of 0.5 wt.% POSS (an increase of about 28%). Also a higher value of Young's modulus (about 28%, Fig. 6), comparing to the neat POM, was found, an effect which may be caused by the increased interfacial area in the nanocomposite with the nanofiller.

Further, from the results of the mechanical tests, the incorporation of 0.5 wt.% POSS leads to a satisfactory interfacial interaction with POM, where also a homogeneous dispersion of POSS in the POM matrix was observed (Fig. 8). A certain decrease in the elongation at yield, as observed for the POSS content of 1 wt.%

may probably be explained by the stress concentration, due to the agglomeration of POSS particles in the polymeric matrix. In general, it may be stated that the sample of POM/POSS with 0.5 wt.% POSS, reveals better mechanical properties comparing to non-modified POMs.

To determine the microstructure of the nanocomposites, especially the dispersion of polyhedral oligomeric silsesquioxanes (POSS) in the polyoxymethylene matrix, the fracture surfaces of neat POM and POM/POSS nanocomposites were studied by means of SEM, as shown in Figures 7, 8 and 9.

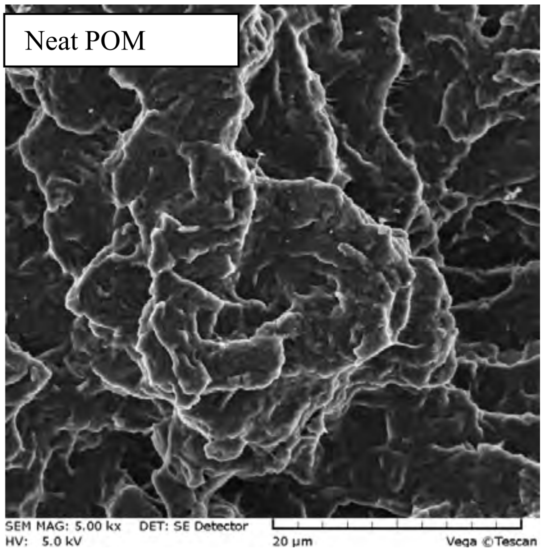

Fig. 7. SEM micrograph of neat polyoxymethylene (POM)

Rys. 7. Obraz SEM powierzchni przełomów pierwotnego polioksymetylenu (POM)

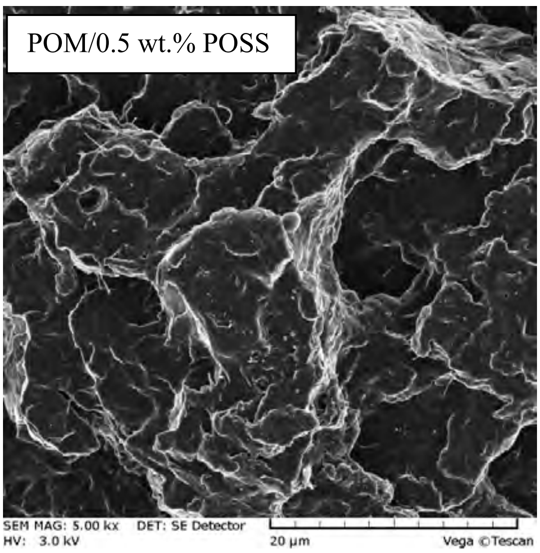

Fig. 8. SEM micrograph of POM/POSS composites with 0.5 wt.% POSS

Rys. 8. Obraz SEM powierzchni przełomów nanokompozytów POM/POSS z 0,5% zawartością POSS

In Figure 7, the fractured surfaces of neat polyoxymethylene are shown, and in Figures 8 and 9, the surface of the POM/POSS nanocomposites with 0.5 wt.% and 1 wt.%, are presented. As can be seen on the SEM micrographs, the dispersion of the POSS particles in the polyoxymethylene matrix was homogeneous, only a few so called aggregates appeared with an average dimension less than 5 µm, may be seen in Figure 9. As POSS cage molecules are characterized with a dimension between 1.5 and 3 nm [1], the sub particles can be observed on the micrographs, due to the development of nanospherical aggregates [10].

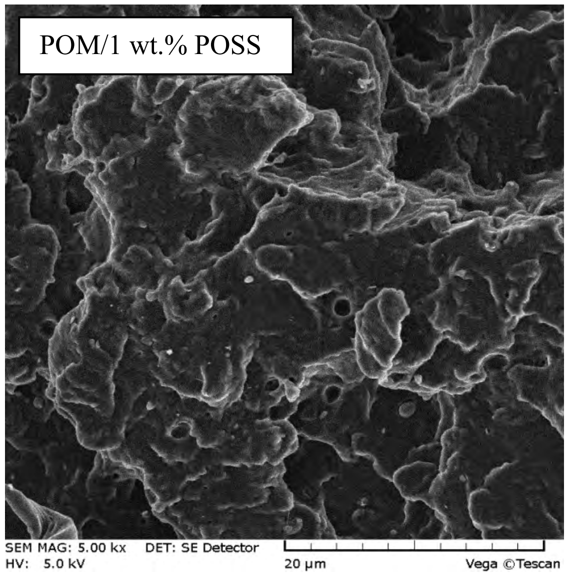

Fig .9. SEM micrograph of POM/POSS composites with 1 wt.% POSS

Rys. 9. Obraz SEM powierzchni przełomów nanokompozytów POM/POSS z 1% zawartością POSS

CONCLUSIONS

According to the mechanical investigation, it was found that the process of polyhedral oligomeric silsesquioxane (POSS) addition leads to an enhancement of both the tensile strength and Young's modulus, where the most encouraging results were achieved for the POM/POSS nanocomposites with 0.5 wt.% POSS. The SEM studies allowed us to provide direct evidence of better interfacial adhesion between the POSS particles and POM matrix, which may lead to better mechanical properties, especially tensile strength, elongation and stiffness. Further determination of the POM/POSS characteristic properties, such as thermal and rheological properties, will be published.

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R & D projects for companies, carried out by scientific bodies," Sub-measure 1.3.1 "Development projects".

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