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COMPOSITES THEORY AND PRACTICE

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MODIFICATION OF POLYURETHANE VISCOELASTIC FOAMS BY FUNCTIONALIZED POLYHEDRAL OLIGOMERIC SILSESQUIOXANES (POSS)

The aim of this paper is to present synthesis and characterization routes of hybrid polyurethane viscoelastic foams reinforced by - inorganic nanoaddities. Recently, much attention has been given to polymer nanocomposites made with POSS (Polyhedral Oligomeric Silsesquioxanes) - a family of siloxane material consisting of inorganic silicon-oxygen core and organic functional groups. Functionalization of POSS enables formation of chemical linkages with polymer matrix and increases compatibility between the organic and inorganic components. Our research focused on the modification of polyurethane materials by functionalized POSS. Octa(3-hydroxy-3-methylbutyldimethylsiloxy) POSS containing eight hydroxyl groups and 1,2- propanediolisobutyl POSS with 2 hydroxyl groups were chosen as additional co-reagents which were mixed by ultrasound homogenizer in polyol phase. POSS was added in amounts 5, 10 and 15% by weight of polyol, and reacted with diisocyanate (TDI) to obtain PU/POSS composite. The effects of incorporation of POSS on the mechanical properties of PU-based hybrid composites were presented. Moreover, the morphology of PU/POSS hybrids was investigated by means of wide-angle X ray diffraction (WAXD) and scanning electron microscopy (SEM) techniques.

Keywords: PUR foams, POSS nanofiller, foam morphology, mechanical properties

MODYFIKACJA LEPKOSPRĘŻYSTYCH PIANEK POLIURETANOWYCH FUNKCJONALIZOWANYMI POLIEDRYCZNYMI OLIGOMERYCZNYMI SILSESKWIOKSANAMI (POSS)

Tematem niniejszej pracy jest zaprezentowanie syntezy i charakterystyki wiskoelastycznych pianek poliuretanowych wzmacnianych nanododatkami nieorganicznymi. W ostatnich czasach wiele uwagi poświęca się otrzymywaniu nanokompozytów poliuretanowych zawierających POSS (poliedrycznych oligomerycznych silseskwioksanów) - grupy związków silanowych zbudowanych z krzemowo-tlenowego, nieorganicznego rdzenia oraz organicznych grupy funkcyjnych. Funkcjonalizacja cząstek POSS pozwala na chemiczne łączenie z matrycą polimerową, zwiększając kompatybilność pomiędzy komponentami organicznymi i nieorganicznymi. Wprowadzenie POSS do matrycy polimerowej skutkuje poprawą właściwości mechanicznych i termicznych. Celem tej pracy była modyfikacja materiału poliuretanowego poprzez zastosowanie funkcjonalizowanych nanocząstek POSS. Octa(3-hydroxy-3-methylbutyldimethylsiloxy) POSS zawierający w swojej budowie osiem pierwszorzędowych grup hydroksylowych oraz 1,2- propanediolisobutyl POSS z jedną pierwszo- i jedną drugorzędową grupą hydroksylową zostały zastosowane jako reagenty i wraz z składnikiem poliolowym poddane działaniu homogenizacji ultradźwiękami. Wprowadzono POSS w ilościach 5, 10 i 15% w stosunku do ilości poliolu i poddano reakcji z diizocyjanianem TDI w celu otrzymania kompozytu piankowego PUR/POSS. Zbadano właściwości mechaniczne oraz morfologie otrzymanych materiałów przy użyciu techniki WAXD (szerokątowej dyfrakcji rentgenowskiej) oraz skaningowej mikroskopii elektronowej (SEM).

Słowa kluczowe: pianki poliuretanowe, nanonapełniacz POSS, morfologia pianek, właściwości mechaniczne

INTRODUCTION

Recently, novel composite materials based on polyurethanes have attracted an increasing attention in many fields of research. Interesting results were described for flexible polyurethane foams used as a matrix in nanocomposites based on nanosilica, nanoclays or carbon nanotubes [1-3]. Those works show numerous relationships between foam structure and the kind of nanosized materials. Furthermore unique types of polyurethane (PU) foams, such as viscoelastic foams that combine elastic and rigid phases considered as a useful matrices for further modification. Nanocomposites based on viscoelastic PUR foams and nanosilica or nanoclays have been already obtained [4-6]. However, viscoelastic PU foams modified by POSS nanoparticles are reported here - the first time. As modification of rigid polyurethane foam matrix by using POSS nanoparticles may results in better mechanical and thermal properties, as well as different cell structure [7, 8], it may be expected that silsequioxanes beneficially influence on the structure and properties of viscoelastic PU foams [9].

EXPERIMENTAL SECTION

Materials

As a reactive nanofiller octa(3-hydroxy-3-methylbutyldimethylsiloxy) POSS (octaPOSS) and 1,2-propanediolisobutyl POSS (PHIPOSS) from Hybrid Plastics USA have been used. 5, 10, and 15% of POSS by the weight of polyols were mixed with polyetherols Rokopol M6000 and V700. Next ultrasound homogenization was used to reduce the amount of POSS agglomerates. Then water, catalyst, surfactant and diisocyante TDI were added and vigorously mixed with POSS/polyols dispersions in order to obtain composites foams.

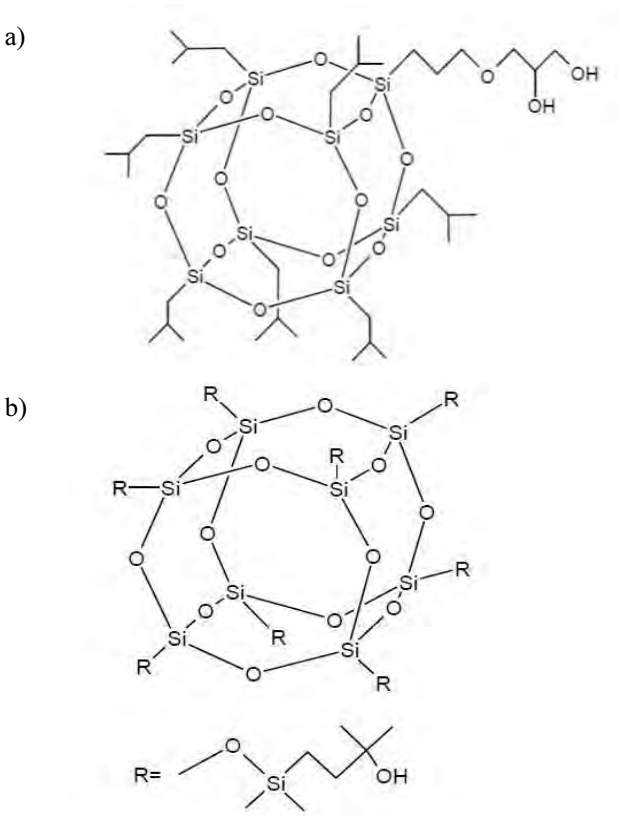

Fig. 1. PHIPOSS (a) and octaPOSS (b) structures
Rys. 1. Struktury PHIPOSS (a) oraz octaPOSS (b)

Methods and equipment

Apparent density [kg/m^3] measurement of the PU/POSS composites was performed according to ISO 845 standard. Mechanical properties were measured according to PN-EN ISO 2439:2000 standard by using Zwick Roell Z005 machine.

Infrared spectroscopy with Fourier transformation (FT-IR) measurements were performed using a Nicolet iS5 Thermo Scientific equipped with diamond ATR Slide-on iS7. The spectra were recorded with a resolution of 8 cm^{-1} from 4000 to 500 cm^{-1} with average of 16 scans.

Scanning electron microscopy (SEM) micrographs were taken using a microscope JEOL InTouchScope JSM-6010LV operating at 10 kV accelerating voltage. Wide angle X-ray diffraction (WAXD) data were collected by applying a Bruker D-Phaser diffractometer in the reflection mode. As an anode a standard Cu-K_α with wavelength λ = 1.54184 Å was used.

RESULTS AND DISCUSSION

Structure and morphology- FT-IR analysis

FT-IR spectroscopy was applied to analyse the structure of the obtained PU foams (Fig. 2). Several bonds characteristic for polyurethane were found. Amine stretching at ca. 3320 cm^{-1}, methylene stretching at ca. 2900÷3000 cm^{-1}, carbonyl stretching bonds at 1600cm^{-1}, amine bending and carbon-carbon at ca. 1500cm^{-1} and ether stretching 1050÷1150cm^{-1} are the most remarkable. POSS presence is shown by the characteristic bonds in the range of ca. 550 cm^{-1} of stretching Si-O linkage, as well as stretching Si-C for ca. 750 cm^{-1}. Weak signal from Si-O bending at ca. 850 cm^{-1} can be also seen.

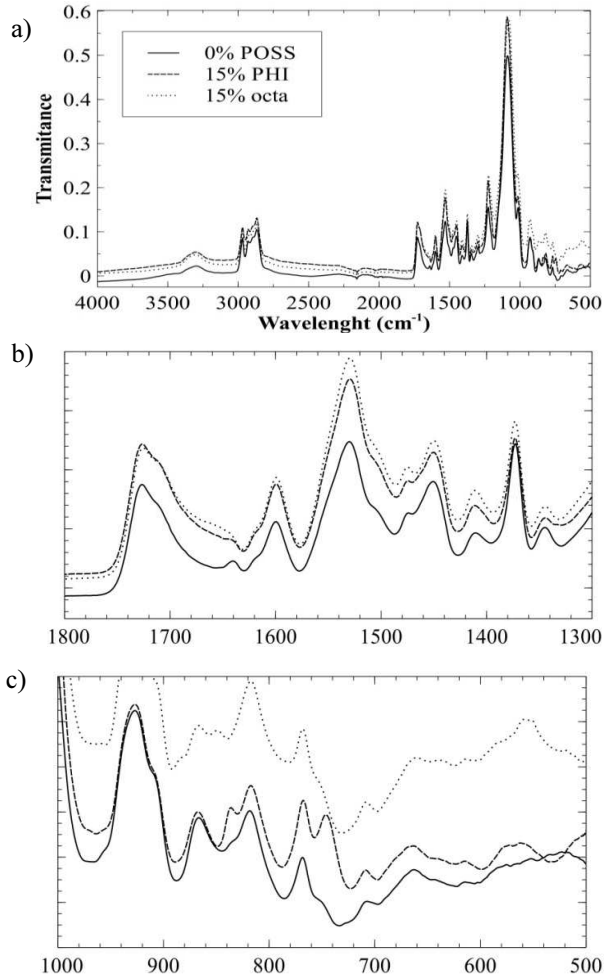

Fig. 2. FT-IR spectra of PU/POSS foams. Spectra in full range (top), spectra in range 1800÷1300 cm^{-1} (b), spectra in range 1000÷500 cm^{-1} (c)

Rys. 2. Widma FT-IR pianek PU/POSS. Widmo w pełnym zakresie (a), widma w zakresie 1800÷1300 cm^{-1} (b), widma w zakresie 1000÷500 cm^{-1} (c)

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Structure and morphology - SEM analysis

Morphology of PU viscoelastic foam and composites with POSS was studied by using SEM at different magnification. Presence of relatively similar amount of open and closed cells, characteristic for viscoelastic foams structure, can be clearly seen for the neat foam Figure 3.

Figure 4 presents morphology of the foam after addition of 15 wt.% of octaPOSS. Figure 4a image shows different size and structure of pores in comparison to the neat material. Cell shape become more irregular whereby size of pores is noticeably bigger. Apparently the addition of octaPOSS caused disorder during small cell formation leading to its agglomeration into bigger structures. However, at greater magnification (Fig. 4b) one cannot observe any distinct octaPOSS crystalline structures.

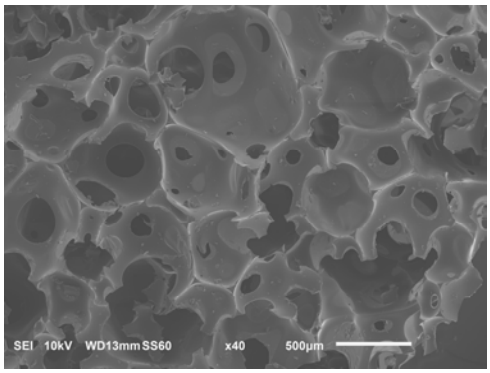

Fig. 3. SEM microphotography of reference foam

Rys. 3. Mikrofotografia SEM pianki referencyjnej

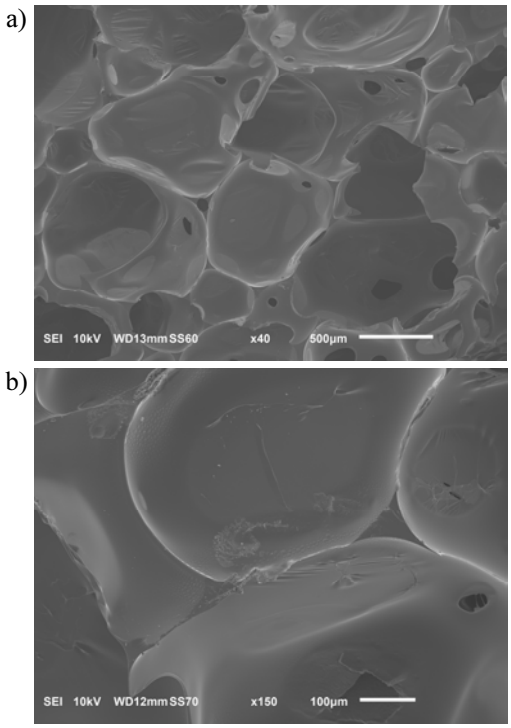

Fig. 4. SEM microphotographs of PUR/octaPOSS 15 wt.%: a) 500 µm, b) 100 µm

Rys. 4. Mikrofotografie SEM pianek PU/octaPOSS 15% mas.: a) 500 µm, b) 100 µm

Addition of 15 wt.% of PHIPOSS (Fig. 5) generated different effect on foam morphology. The microstructure was comparable to this of unfilled foam, although cell structure was more deformed. Higher magnification (Fig. 5b) enabled to detect PHIPOSS crystallites. One can assume that these crystalline arrangements can be responsible for the deformation of cells structures.

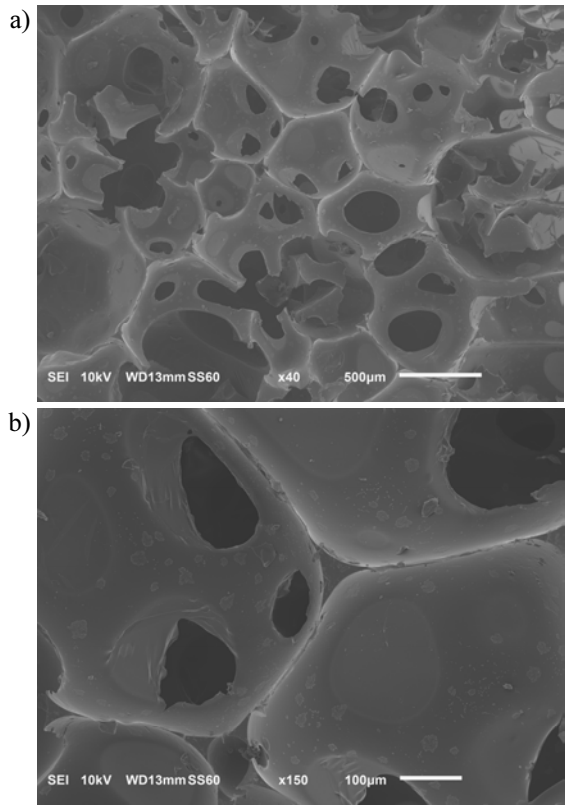

Fig. 5. SEM microphotography of PU/PHIPOSS 15 wt.%: a) 500 µm, b) 100 µm

Rys. 5. Mikrofotografie SEM pianek PU/PHIPOSS 15% mas.: a) 500 µm, b) 100 µm

Structure and morphology - WAXD studies

Crystalline structures were examined by WAXD technique and results were presented in Figure 6. The pure octaPOSS and PHIPOSS show well-arranged crystalline structures represented by sharp peaks in area starting from $2\theta = 5^{o}$. Presence of amorphous halo for $2\theta = 18.5^{o}$ from polyurethane matrix was reported previously [9]. However, despite of crystalline structure of octaPOSS, no crystalline peaks in modified PU foams were observed. This observation is confirmed by SEM analysis which does not show visible crystalline structures (Fig. 4). Noticeable changes in crystallinity were observed in PHIPOSS filled foams. Sharp peaks for $2\theta = 8^{o}$ correspond to crystallites originating from PHIPOSS. Moreover, greater amount of PHIPOSS leads to higher intensity of crystalline peaks. The crystallities evidenced by diffraction patterns were also found during SEM analysis as white flat structures located in cells walls (Fig. 5).

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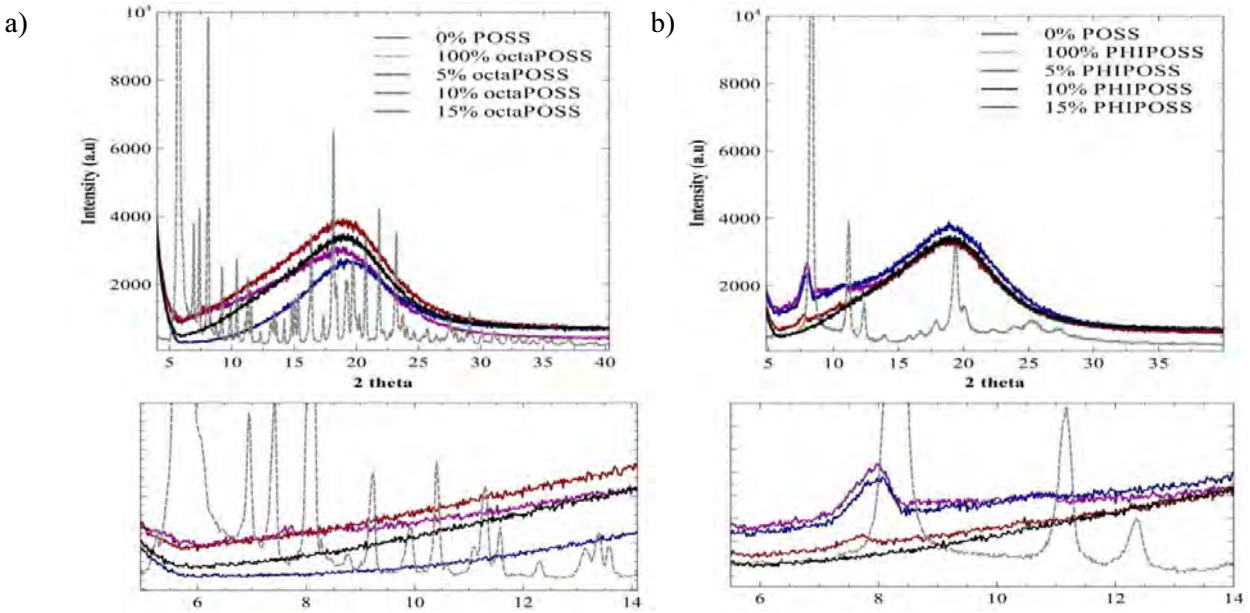

Fig. 6. WAXD patterns for PU/POSS composites: a) octaPOSS based composites, b) composites filled with PHIPOSS

Rys. 6. Dyfraktogramy WAXD pianek z dodatkiem POSS: a) kompozyt z dodatkiem octaPOSS, b) dodatek PHIPOSS

Physical and mechanical properties

Figure 7 shows the effects of incorporation of different POSS nanoparticles into viscoelastic foam matrix on apparent density and mechanical properties.

It can be observed that for all modified foams maximum applied force has increased. This phenomenon can be explained in such way that addition of likely rigid structure into cell walls what leads to greater material response. Some differences depending on the type of POSS particles were observed. Incorporation of octaPOSS, which is able to - crosslink PU chains, results in linear increase of F max towards maximum 22 kPa for 15 wt.% of POSS foams. PHIPOSS as a pendant group leads to similar result for maximum amount, however, the difference between 5 and 15 wt.% was slightly noticeable.

Different results were observed by measuring apparent density of composites foams. Apparent density is a main factor that characterizes foams and specify type of material. In octaPOSS containing material an increase was observed only for 5 wt.% of nanoparticles. Further addition of octaPOSS results in a decrease of apparent density in comparison to neat foam. For PHIPOSS containing foam composite a slight decrease was found for 5 and 10 wt.% of POSS addition. 15 wt.% of PHIPOSS leads to sharp reduction, similar as for 15 wt.% octaPOSS. Those effects can be explained by two opposing processes: nucleation and agglomeration which are characteristic for nanoparticles. Nucleation enhanced by nanoparticles exert an effect during first cells formations. Particles can cause an increase in porosity which might lead to higher apparent density (more cells higher mass in the same volume). In contrary large crystalline agglomerates can interrupt process of pores growth by opening cells through sharp crystalline structures. Disrupted structures tend to create bigger and deformed cells, and the apparent density decreases.

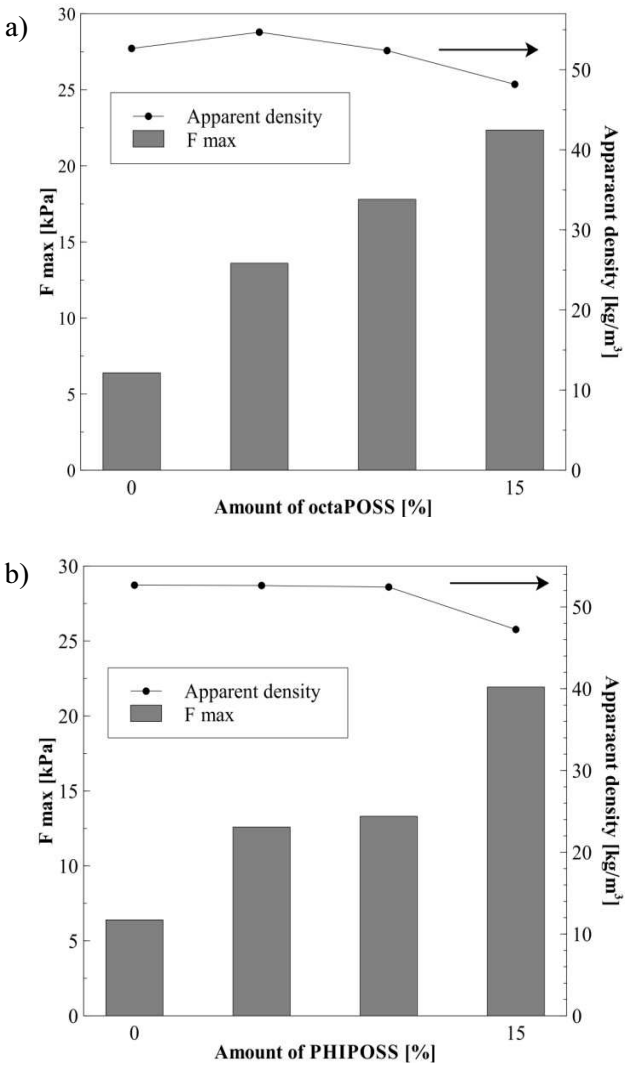

Fig. 7. Apparent density and maximum force value of PU/octaPOSS (a) and PU/PHIPOSS (b)

Rys. 7. Gęstość pozorna oraz wartość siły maksymalnej PU/octaPOSS (a), PU/PHIPOSS (b)

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CONCLUSIONS

Novel type of hybrid composite materials based on viscoelastic polyurethane foams and POSS particles were described in this work. The influence of different type of POSS particles on structure, morphology, crystallinity, apparent density and mechanical properties on PU foams was studied. Addition of crosslinking POSS particles leads to an increase of apparent density for 5 wt.% load, although larger contents lower it significantly. 15 wt.% of octaPOSS causes differences in cell structures towards bigger size and more irregular shape. Furthermore, on the WAXD patterns octaPOSS agglomerates are not visible, in contrary to the PHIPOSS filled foams. Crystalline structures are visible on diffraction patterns for $2\theta = 8^{o}$. Those crystallites are also clearly visible on SEM images as light flat structures. For all modified foams the mechanical properties have been improved, whereby changes in the apparent density arise from two opposing processes: nucleation and agglomeration which are characteristic for nanoparticles.

Acknowledgements

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