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# FOAMING EXTRUSION OF THERMOPLASTIC POLYURETHANE MODIFIED BY POSS NANOFILLERS

**Thermoplastic polyurethane elastomers (TPU), having mechanical properties similar to chemically crosslinked rubbers, can be processed using extrusion or injection molding techniques. Combining extrusion with a foaming process leads to the fabrication of porous lightweight materials with novel properties. These properties can be further modified by applying additives, such as polyhedral oligomeric silsesquioxanes (POSS). POSS are organic-inorganic hybrid nanofillers that could enhance polymer-based composites properties, e.g. mechanical properties or thermal stability. In this work, the foaming extrusion process of TPU, utilizing azodicarboxamide (ADC), sodium bicarbonate (SC) and citric acid monohydrate (CA) as blowing agents (or their mixtures) was described. TPU was modified with two kinds of POSS nanofillers: TMP DiolIsobutyl POSS (TMP POSS) and trans-Cyclohexanediol Isobutyl POSS (TC POSS) to intensify the nucleation of the foaming process and to improve the thermal properties of the TPU matrix. A suitable processing window was determined by means of differential scanning calorimetry (DSC) and thermogravimetric analysis (TG). The relations between the type of blowing agent mixture, POSS nanofillers and microstructure/thermal properties of TPU porous composites were evaluated using DSC and scanning electron microscopy (SEM). The blowing agent mixtures, which produce solid residue after decomposition (ADC-CA and CA-SC), influence the nucleation process in the crystalline domains of TPU. The addition of POSS nanofillers strengthens the abovementioned effect and additionally increases the amount of pores in the extrudates, as well as enhances their shape stability.**

**Keywords:** thermoplastic polyurethanes, chemical blowing agents, polyhedral oligosilsesquioxanes, POSS, extrusion

## WYTŁACZANIE PORUJĄCE TERMOPLASTYCZNEGO POLIURETANU MODYFIKOWANEGO NANONAPEŁNIACZAMI POSS

**Termoplastyczne elastomery poliuretanowe (TPU), o własnościach mechanicznych podobnych do chemicznie usieciowanych kauczuków, mogą być przetwarzane za pomocą technik wytłaczania lub formowania wtryskowego. Połączenie wytłaczania z procesem spieniania prowadzi do wytworzenia porowatych lekkich materiałów o nowych właściwościach. Te właściwości można dalej modyfikować przez zastosowanie dodatków, takich jak wielościenne oligomeryczne silseskwioksany (POSS). POSS są organiczno-nieorganicznymi hybrydowymi nanowypełniaczami, które mogą polepszyć właściwości kompozytów polimerowych, np. właściwości mechaniczne lub stabilność termiczną. W pracy opisano proces wytłaczania porującego TPU z użyciem azodikarboksyamidu (ADC), wodorowęglanu sodu (SC) i monohydratu kwasu cytrynowego (CA) jako środków porotwórczych (lub ich mieszanin). TPU zmodyfikowano dwoma rodzajami nanowypełniaczy POSS: TMP DiolIsobutyl POSS (TMP POSS) i trans-Cyclohexanediol Isobutyl POSS (TC POSS) w celu zintensyfikowania procesu nukleacji podczas porowania i poprawy właściwości termicznych matrycy TPU. Wyznaczenie odpowiedniego okna przetwórczego przeprowadzono za pomocą różnicowej kalorymetrii skaningowej (DSC) i analizy termograwimetrycznej (TG). Zależność między rodzajem mieszaniny środków porotwórczych, nanowypełniaczami POSS a właściwościami mikrostrukturalnymi/termicznymi porowatych kompozytów TPU oceniano za pomocą DSC i skaningowej mikroskopii elektronowej (SEM). Mieszaniny środków porujących, które wytwarzają stałą pozostałość po rozpadzie (ADC-CA i CA-SC), wpływają na proces nukleacji w krystalicznych domenach TPU. Dodanie nanowypełniaczy POSS wzmacnia wyżej wspomniany efekt i dodatkowo zwiększa ilość porów w wytłoczynach, a także zwiększa ich stabilność kształtu.**

**Słowa kluczowe:** termoplastyczne poliuretany, chemiczne środki spieniające, poliedryczne oligosilseskwioksany, POSS, wytłaczanie

## INTRODUCTION

Thermoplastic polyurethane elastomers (TPU) combine the ability to be processed using traditional techniques for thermoplastic polymers with mechanical properties similar to chemically crosslinked rubbers. Lacking chemical networks, TPU can be repeatedly melted and processed, maintaining excellent tensility and good elastic resilience. TPU owe their unique properties to their segmented structure. The hard segments, derived from diisocyanate, act as both as physical crosslinks and reinforcing fillers, while the soft segments consisting of long flexible polyether or polyester chains account for the elastic properties of TPU. The domain structure of TPU is a consequence of the incompatibility between the hard and soft segments. Upon heating, the soft segments melt first. When the composition is further heated above the melting temperature of the hard segments, the polymer forms a homogeneous viscous melt, which can be processed by standard methods for thermoplastics [1-3].

The obvious reason for using foamed materials is to reduce the weight and amount of material used. The most widespread method to produce extruded or injection molded foamed items is to use blowing agents. Such a solution leads to cost savings, enhancement of the thermal insulation effect and improvement of the surface texture. Foamed materials are used in many industries. Blowing agents can be divided into two groups: physical blowing agents (PBAs) are incorporated into the molten polymer matrix as liquids or gases, whereas chemical blowing agents (CBAs) decompose due to chemical reactions and heat to generate gases such as carbon dioxide. The most commonly used inorganic chemical blowing agents include ammonium, sodium and potassium carbonates and bicarbonates (hydrogen carbonates). These compounds decompose yielding $CO_2$ and water under the action of heat and acids. Among numerous acids, the use of citric acid is particularly suitable because it gives off $CO_2$ and water upon its own decomposition. The physiologically harmless nature of inorganic chemical blowing agents and the products of their decomposition is their important advantage over other compounds used for this role. All the abovementioned inorganic blowing agents decompose endothermically, which leads to their gradual rather than sudden decomposition. Among organic chemical blowing agents, one of the most widely employed is azodicarbonamide (ADC or ADCA). In a complex exothermic cascade reaction, ADC decomposes liberating $N_2$, CO and $NH_3$ (in the presence of $H_2O$) and leaving some solid residue [2, 4-6].

Polyhedral oligomeric silsesquioxanes (POSS), with a chemical composition intermediate between that of silica and silicone, are an interesting class of hybrid nanofillers for modifying polymer matrices. Incorporating POSS offers new ways to enhance polymer-based composites properties such as the mechanical properties, thermal stability, water tolerance, fire resistance and dielectric properties [7-10]. In this study, POSS were added to intensify the nucleation of the foaming process and to improve the thermal properties of the TPU matrix.

## EXPERIMENTAL PROCEDURE

### Materials

TPU, manufactured by RAVAGO KİMYA Plastik San. ve Tic. A.S., Turkey, under the trade name RAVATHANE R130A65, was used in this study. It is based on standard grade saturated polyester and has strong resilience and tear resistance, excellent abrasion resistance, higher resistance to hydrolysis failure and oxidation, as well as good stability towards solvents and light.

As blowing agents, three compounds were used. Azodicarboxamide (ADC) (Fig. 1) is a solid powder, colored yellow to orange and has a molecular weight of 116.08 g/mol. Sodium bicarbonate (SC) is a solid powder, colored white and has a molecular weight of 84.01 g/mol. Citric acid monohydrate (CA) comes in the form of white, fine crystals and has a molecular weight of 210.1 g/mol. All of the abovementioned blowing agents were supplied by Sigma-Aldrich.

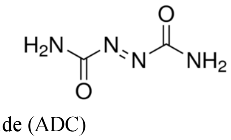

Fig. 1. Azodicarboxamide (ADC)
Rys. 1. Azodikarbonamid (ADC)

POSS - TMP DiolIsobutyl POSS (TMP POSS) (Fig. 2) and trans-Cyclohexanediol Isobutyl POSS (TC POSS) (Fig. 3), were obtained from Hybrid Plastics Inc., Hattiesburg, USA.

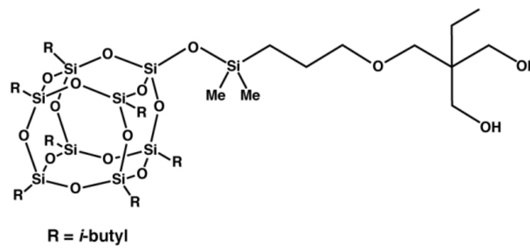


Fig. 2. AL0104 - TMP DiolIsobutyl POSS (TMP POSS)
Rys. 2. AL0104 - TMP DiolIsobutyl POSS (TMP POSS)

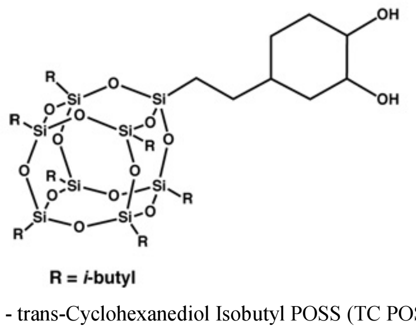


Fig. 3. AL0125 - trans-Cyclohexanediol Isobutyl POSS (TC POSS)
Rys. 3. AL0125 - trans-Cyclohexanediol Isobutyl POSS (TC POSS)

### Analysis methods

Differential scanning calorimetry was conducted using a Mettler Toledo 822$^e$ calorimeter, in the temperature range from −60 to 240°C, with 10°C/min heating rate in air atmosphere, using a standard aluminum sample holder and samples weighing approximately 5 mg.

Thermogravimetric analysis was conducted using a Netzsch TG 209 thermal analyzer, in the temperature range from 30 to 800°C, with a 10°C/min heating rate in air atmosphere, using an open α-$Al_2O_3$ crucible and samples weighing approximately 5 mg.

Microphotography was conducted using a Jeol JSM-6010LA scanning electron microscope, under low vacuum conditions. The samples were frozen in liquid nitrogen, fractured, mounted on holders and sputter coated with Au.

### Composite preparation

All of the obtained samples were prepared using a HAAKE Mini CTV, conical type laboratory twin screw extruder (Thermo Electron Corporation). The processing conditions and procedure for all of the samples were unified: TPU granulate was fed into the extruder barrel and mixed for 7 minutes at 140°C using by-pass to recycle the material, blowing agent mixtures as well as POSS nanofillers were then added within a 4-minute period gradually increasing the temperature from 140 to 225°C, then the mixture was recycled in the extruder for another 3 minutes and then extruded. The rotation speed of the screws of 50 rpm was used. The amount of blowing agent mixture used was 0.5 wt.% in each of the samples and the amount of POSS nanofillers used was 2 wt.%. The choice of the processing conditions was based on our previous studies [6, 10], ensuring full repeatability of the process. The designations and compositions of each sample are given in Table 1.

TABLE 1. **Designations and compositions of obtained samples**
TABELA 1. **Oznaczenia i składy otrzymanych próbek**

| Sample designation | Description |
|---|---|
| TPU ref | Pure TPU, after being processed as reference material |
| TPU/ADC | TPU with azodicarboxamide |
| TPU/ADC-SC | TPU with azodicarboxamide and sodium bicarbonate, mixed in 3 to 7 weight ratio |
| TPU/CA | TPU with citric acid monohydrate |
| TPU/CA-SC | TPU with citric acid monohydrate and sodium bicarbonate, mixed in 1 to 3 mol ratio |
| TPU/ADC-SC/ TMP POSS | TPU with azodicarboxamide and sodium bicarbonate, mixed in 3 to 7 weight ratio, modified with AL0104 - TMP DiolIsobutyl POSS |
| TPU/ADC-SC/ TC POSS | TPU with azodicarboxamide and sodium bicarbonate, mixed in 3 to 7 weight ratio, modified with AL0125 - trans-Cyclohexanediol Isobutyl POSS |
| TPU/CA-SC/ TMP POSS | TPU with citric acid monohydrate and sodium bicarbonate, mixed in 1 to 3 mol ratio, modified with AL0104 - TMP DiolIsobutyl POSS |
| TPU/CA-SC/ TC POSS | TPU with citric acid monohydrate and sodium bicarbonate, mixed in 1 to 3 mol ratio, modified with AL0125 - trans-Cyclohexanediol Isobutyl POSS |

## RESULTS AND DISCUSSION

### Determining the processing window

To determine the processing window, DSC analysis of the TPU and TG analysis of the blowing agents and POSS were performed (Figs. 4 and 5). Three requirements should be met to choose the processing window properly. Firstly, the processing temperature must be high enough to melt the hard segments in the TPU matrix and thus enable the molten material to homogenize and be mixed with the other additives properly. Secondly, the blowing agent mixtures must decompose, giving off volatile gases, and such phenomenon starts to occur at appropriately high temperatures. Finally, POSS nanofillers are susceptible to thermal degradation, thus the temperatures used in the extrusion process must not exceed the onset temperatures of POSS degradation.

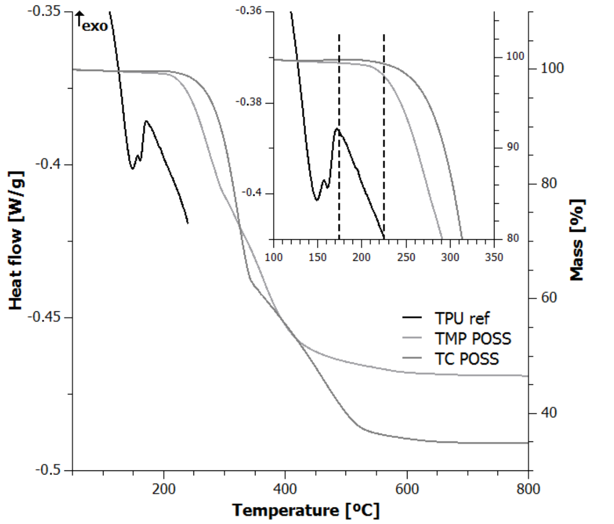


Fig. 4. DSC profile of TPU (second heating) and TG profiles of POSS used

Rys. 4. Krzywa DSC drugiego ogrzewania TPU oraz krzywe termograwimetryczne użytych POSS

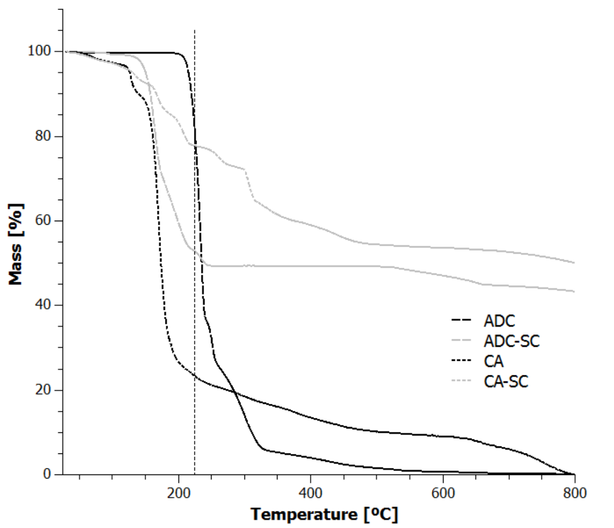


Fig. 5. TG profiles of blowing agent mixtures

Rys. 5. Krzywe termograwimetryczne użytych mieszanin porujących

 

Melting of the hard TPU segments starts at 122°C and finishes around 175°C, while the temperature of TMP POSS decomposition, which is the lower of the two POSS nanofillers used in this study, is 238°C (Fig. 4). The blowing agent mixtures considered in this study show differences in the course of decomposition routes as well as in the temperatures of the onset of the decomposition processes. Taking this into consideration, the temperature of 222°C (which is the onset of ADC degradation, Fig. 5) was chosen as the preferred one since it is the highest among all of the blowing agent mixtures used. Having in mind the abovementioned aspects: good TPU homogenization, proper decomposition of the blowing agents mixture and avoiding POSS degradation, the temperature of 140°C was chosen as the start of the homogenization process for the TPU matrix, and the temperature of 225°C was selected as the temperature of mixing and extrusion of the composites.

## Selection of the foamed TPU for POSS modification

The most suitable foamed TPU materials to be later modified with POSS nanofillers were determined on the basis of DSC studies as well as macroscopic observations of the obtained extrudates. For the TPU reference and TPU/ADC samples, some problems collecting the extrudates occurred. Both compositions exhibited a low melt viscosity and for the TPU/ADC sample a small number of pores was observed. Although the shape of the TPU/CA extrudate was preserved, it exhibited a small number pores, similar to the TPU/ADC sample. However, the compositions with mixed the blowing agents - TPU/ADC-SC and TPU/CA-SC, maintained their shapes after leaving the extruder and a large number small pores was observed in their structure. The results of the DSC study revealed that while the addition of blowing agents mixtures did not have a significant influence on the process of melting of obtained samples (Fig. 6, Tab. 2), observable changes occurred during the crystallization process (Fig. 7, Tab. 2). Besides the TPU/CA sample, the crystallization temperature of all the other samples increased (by around 26°C for the TPU/ADC and TPU/ADC-SC samples and around 18°C for the TPU/CA-SC sample). The presence of solid residues of the blowing agent mixtures may have contributed to this phenomenon, acting as nucleating sites during crystallization of the TPU matrix.

TABLE 2. **Results of DSC analysis of obtained samples**
TABELA 2. **Wyniki badań DSC dla otrzymanych próbek**

| Sample | $\Delta H_c$ [J/g] | $T_c$ [°C] | $\Delta H_m$ [J/g] | $T_m$ [°C] |
|---|---|---|---|---|
| TPU ref | −8.18 | 82.6 | 5.89 | 145.8 |
| TPU/ADC | −5.77 | 109.4 | 5.19 | 141.3 |
| TPU/ADC-SC | −8.13 | 108.8 | 5.01 | 144.7 |
| TPU/CA | −8.42 | 83.2 | 5.72 | 146.2 |
| TPU/CA-SC | −9.48 | 100.6 | 6.21 | 145.7 |

Bearing in mind the results of visual evaluation and the results of the DSC study, the most promising foamed TPU materials chosen to be modified with POSS nanofillers were TPU/ADC-SC and TPU/CA-SC.

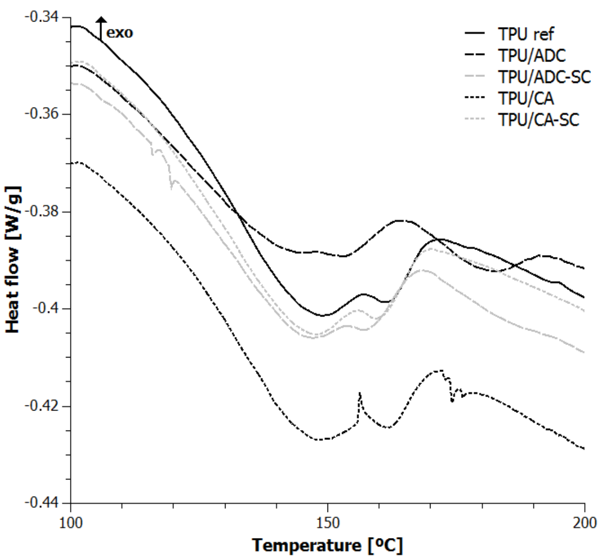


Fig. 6. DSC profiles of obtained samples before POSS modification (second heating)

Rys. 6. Krzywe DSC drugiego ogrzewania dla otrzymanych próbek przed modyfikacją POSS

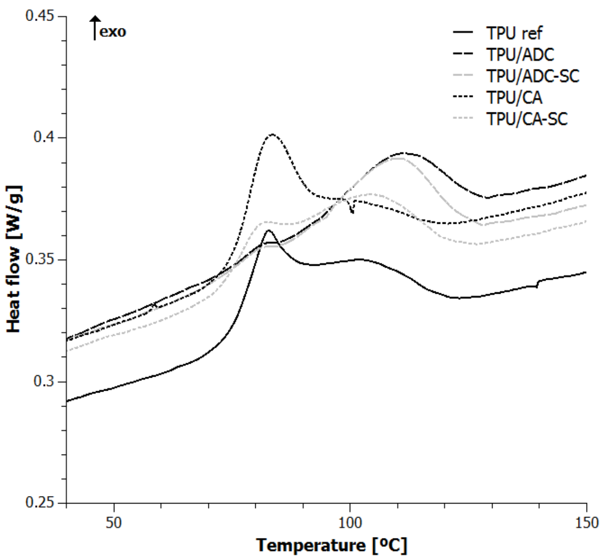


Fig. 7. DSC profiles of obtained samples before POSS modification (cooling)

Rys. 7. Krzywe DSC chłodzenia dla otrzymanych próbek przed modyfikacją POSS

 

## Determining POSS influence on foamed TPU composites

After modification with POSS, the obtained composites were examined by DSC. The results are presented in Figures 8 and 9 as well as in Tables 3 and 4. The results of the DSC study of the POSS-modified samples show similar trends to those presented by the compositions modified solely by the blowing agent mixtures. The process of melting the obtained samples does not undergo significant changes, while the process of crystallization starts to occur at even higher temperatures. The influence of a particular type of POSS nanofillers shows the same trend in the case of both blowing agent mixtures: the TMP POSS particles cause a greater increase in the crystallization temperature, while the TC POSS particles also cause a significant rise in the crystallization temperature. Yet, the effect of the increase in the crystallization temperature is exhibited to a greater extent by the sample with the CA-SC blowing agent mixture.

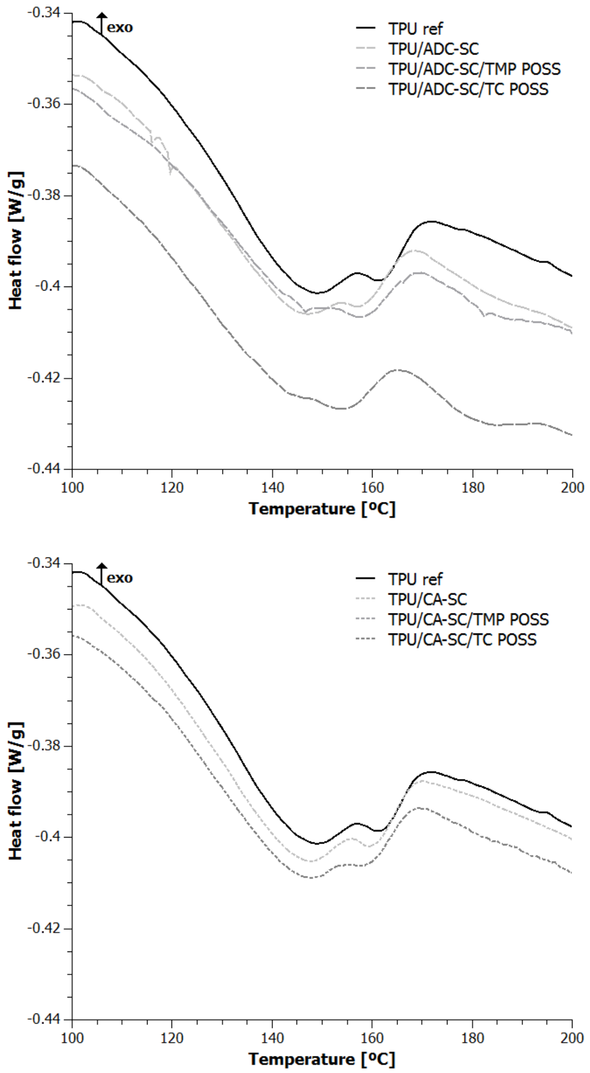


Fig. 8. DSC curves of obtained samples after POSS modification (second heating)

Rys. 8. Krzywe DSC drugiego ogrzewania dla otrzymanych próbek po modyfikacji POSS

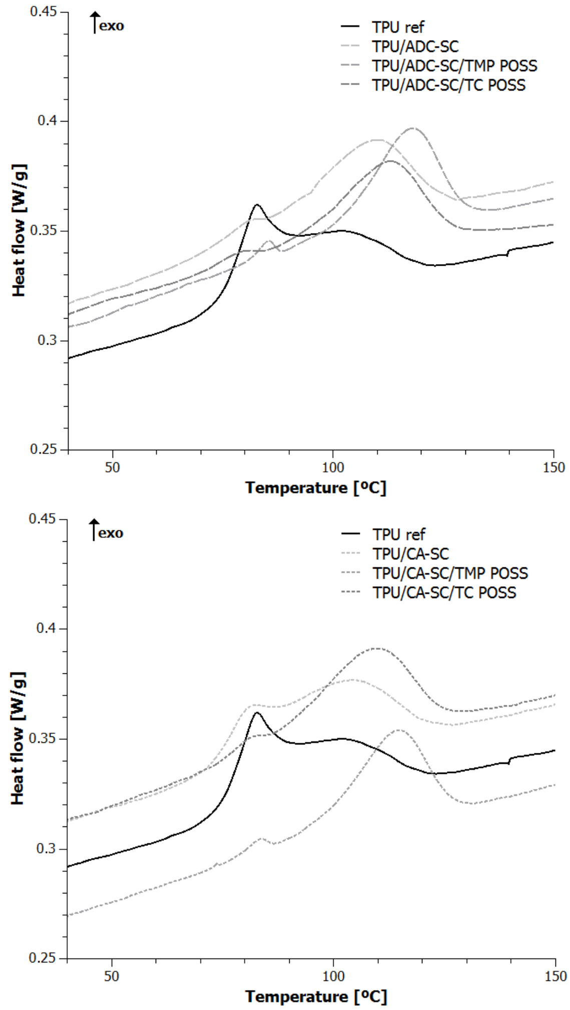


Fig. 9. DSC curves of obtained samples after POSS modification (cooling)

Rys. 9. Krzywe DSC chłodzenia dla otrzymanych próbek po modyfikacji POSS

TABLE 3. **Results of DSC analysis of samples with ADC-SC blowing agent mixture after POSS modification**

TABELA 3. **Wyniki badań DSC dla próbek z mieszaniną porującą ADC-SC po modyfikacji POSS**

| Sample | $\Delta H_c$ [J/g] | $T_c$ [°C] | $\Delta H_m$ [J/g] | $T_m$ [°C] |
|---|---|---|---|---|
| TPU ref | −8.18 | 82.6 | 5.89 | 145.8 |
| TPU/ADC-SC | −8.13 | 108.8 | 5.01 | 144.7 |
| TPU/ADC-SC/ TMP POSS | −8.94 | 117.6 | 4.02 | 146.6 |
| TPU/ADC-SC/ TC POSS | −10.51 | 112.1 | 4.77 | 143.1 |

TABLE 4. **Results of DSC analysis of samples with CA-SC blowing agent mixture after POSS modification**

TABELA 4. **Wyniki badań DSC dla próbek z mieszaniną porującą CA-SC po modyfikacji POSS**

| Sample | $\Delta H_c$ [J/g] | $T_c$ [°C] | $\Delta H_m$ [J/g] | $T_m$ [°C] |
|---|---|---|---|---|
| TPU ref | −8.18 | 82.6 | 5.89 | 145.8 |
| TPU/CA-SC | −9.48 | 100.6 | 6.21 | 145.7 |
| TPU/CA-SC/ TMP POSS | −7.81 | 114.2 | 4.98 | 145.9 |
| TPU/CA-SC/ TC POSS | −8.11 | 108.6 | 5.71 | 145.8 |

 

As for visual evaluation of the POSS modified samples, it was observed that the addition of both types of POSS nanofillers (TMP and TC) improved the shape stability of the obtained extrudates for both of the blowing agent mixtures used (ADC-SC and CA-SC) - all of the samples preserved their shape after leaving the extruder, yet for the compositions modified with the TC POSS nanofiller, the extrudate exhibited some degree of expansion in comparison to the sample modified with the TMP POSS nanofiller, as well as the samples without any POSS nanoadditive. The amount of pores present in all of the obtained composites was also observed to be significantly greater than for the samples without added POSS nanofillers.

For the samples modified with POSS moieties, SEM analysis was performed. The results are presented in Figures 10-15 (the TPU/ADC-SC and TPU/CA-SC samples were used as references).

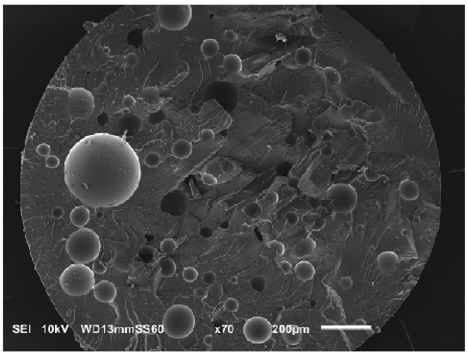


Fig. 10. SEM micrograph of TPU/ADC-SC sample
Rys. 10. Mikrofotografia SEM próbki TPU/ADC-SC

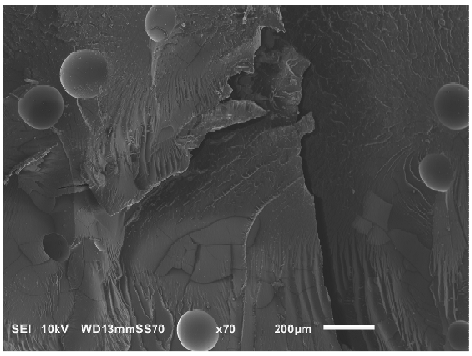


Fig. 11. SEM micrograph of TPU/CA-SC sample
Rys. 11. Mikrofotografia SEM próbki TPU/CA-SC

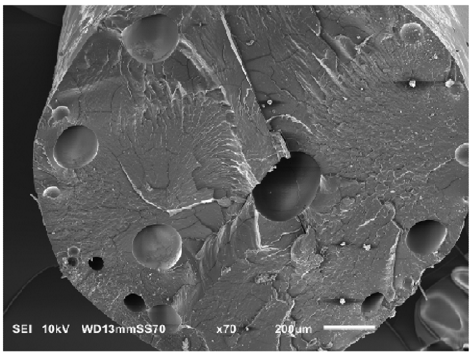


Fig. 12. SEM micrograph of TPU/ADC-SC/TMP POSS sample
Rys. 12. Mikrofotografia SEM próbki TPU/ADC-SC/TMP POSS

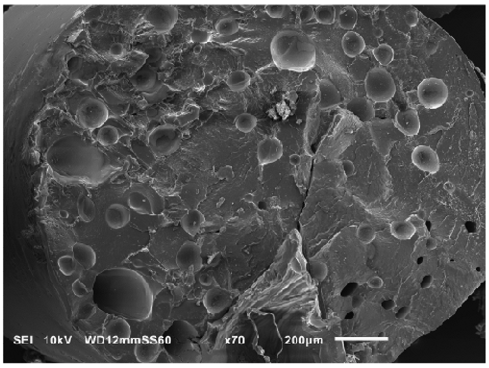


Fig. 13. SEM micrograph of TPU/CA-SC/TMP POSS sample
Rys. 13. Mikrofotografia SEM próbki TPU/CA-SC/TMP POSS

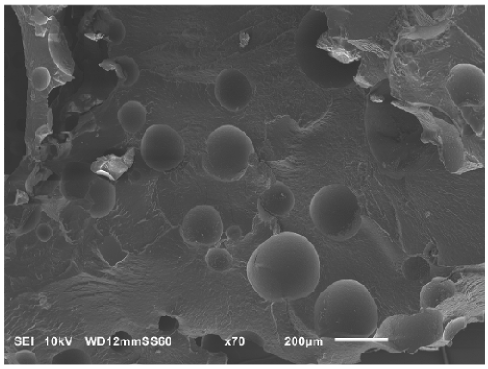


Fig. 14. SEM micrograph of TPU/ADC-SC/TC POSS sample
Rys. 14. Mikrofotografia SEM próbki TPU/ADC-SC/TC POSS

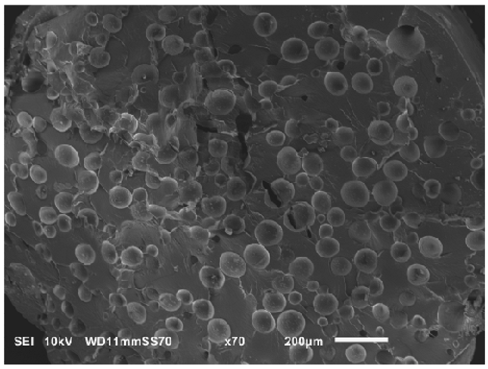


Fig. 15. SEM micrograph of TPU/CA-SC/TC POSS sample
Rys. 15. Mikrofotografia SEM próbki TPU/CA-SC/TC POSS

The results that can be seen on the SEM micrographs are in accordance with the visual observations. While the pore formation effect is less profound for the materials with the ADC-SC blowing agent mixture, the effect of POSS modification is exhibited to a great extent in the samples with the CA-SC blowing agent mixture. The number of pores present in the extrudates increased significantly with the addition of the TMP POSS nanofiller and the appearance of even more pores was observed with the addition of the TC POSS nanofiller. It confirms that the cage-like structure of silsesquioxanes and their organic functionalities facilitate pore formation during the foaming extrusion of thermoplastic polyurethane elastomers in the presence of traditional blowing agents.

 

## CONCLUSIONS

In this work, the foaming extrusion of TPU with different blowing agents was presented. The influence of the type of blowing agent mixture used, as well as the type of POSS nanofiller on the microstructure and thermal properties of TPU porous composites was evaluated. When choosing the processing window, three aspects have to be taken into account: suitable homogenization of the polymer matrix, proper decomposition of the blowing agent mixtures and avoiding the degradation of other additives (fillers). The use of blowing agent mixtures, which leave solid residues after their degradation has been completed, improves the nucleation process in the crystalline domains of thermoplastic polyurethane. The addition of POSS nanofillers further increases the temperature of crystallization, strengthening the abovementioned effect. The number of pores in the extrudates increases with the addition of POSS nanofillers and at the same time their shape stability improves, which can be effectively evaluated by SEM.

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