The effect of nanosilica filler on the foaming process and properties of flexible polyurethane foams obtained with rapeseed oil-based polyol

Elżbieta Malewska[1)], **Aleksander Prociak**[1), *)]

DOI: dx.doi.org/10.14314/polimery.2015.472

Abstract: In this paper, the analysis of the foaming process of flexible polyurethane modified with the addition of silica nanoparticles is presented. Flexible polyurethane foams (FPURF) were obtained using petrochemical components and a rapeseed-oil-based polyol (used in an amount of 20 wt %). Nanosilica was added to the polyurethane system in the amount of 0.5, 1.0 and 1.5 php (parts per hundred polyols). The characteristic parameters of the foaming process, such as the growth velocity of foamed materials, the core temperature and dielectric polarization, were measured using a Foamat device. It was observed that polyurethane-forming reactions slowed down as an effect of the increase of nanosilica content in the polyurethane composition. Consequently, the temperature in the core of the reaction mixture containing 1.5 php nanosilica was lower by approx. 35 °C compared to the reference material. Moreover, the influence of the method of homogenization of the nanofiller with polyols on the selected properties of prepared foams was analyzed. The following properties of flexible polyurethane foams were determined: apparent density, resilience, compressive strength, hardness, hysteresis and support factor. The introduction of nanosilica filler to the polyurethane formulation caused an increase in the apparent density from 24.6 kg/m^3 for the reference foam to 28.5 kg/m^3 for the foam containing 1.5 php of nanosilica. However, this nanofiller did not significantly affect the cell structure of foamed materials. The foams obtained with the nanosilica additive of 1.0 php had the most preferred properties, such as a slightly higher value of resilience, lower hardness and higher support factor than the reference foam without nanosilica.

Keywords: nanosilica, polyurethane, foaming process, flexible foam, physical-mechanical properties.

Wpływ dodatku nanokrzemionki na proces spieniania oraz właściwości elastycznych pianek poliuretanowych otrzymywanych z zastosowaniem poliolu z oleju rzepakowego

Streszczenie: Analizowano proces spieniania elastycznych poliuretanów modyfikowanych dodatkiem nanokrzemionki. Elastyczne pianki poliuretanowe (FPURF) otrzymywano z zastosowaniem poliolu pochodzenia petrochemicznego oraz poliolu wytworzonego z udziałem 20 % mas. oleju rzepakowego. Nanokrzemionka była dodawana do kompozycji poliuretanowej w ilości 0,5, 1,0 i 1,5 php [masa napełniacza (g) na 100 g mieszaniny polioli]. Charakterystyczne parametry procesu spieniania, takie jak: szybkość wzrostu pianki, temperatura w rdzeniu mieszaniny reakcyjnej oraz polaryzacja dielektryczna, mierzono za pomocą urządzenia Foamat. Zaobserwowano, że reakcje tworzenia poliuretanu ulegały spowolnieniu wraz ze wzrostem udziału masowego krzemionki w kompozycji poliuretanowej. Konsekwencją tego była niższa o ok. 35 °C temperatura w rdzeniu materiału zawierającego 1,5 php nanokrzemionki, w porównaniu z temperaturą w rdzeniu pianki referencyjnej. Określono też wpływ sposobu homogenizacji nanonapełniacza z poliolem na wybrane właściwości otrzymywanych pianek. Analizowano następujące właściwości fizyko-mechaniczne: gęstość pozorną, odbojność, wytrzymałość na ściskanie, twardość, histerezę i współczynnik komfortu. Dodatek krzemionki do kompozycji poliuretanowej spowodował wzrost gęstości pozornej z 24,6 kg/m^3 pianki referencyjnej do 28,5 kg/m^3 pianki zawierającej 1,5 php nanokrzemionki. Dodatek nanokrzemionki nie wpłynął w istotnym stopniu na strukturę komórkową pianek, jednak materiały wytworzone z udziałem nanokrzemionki w ilości 1,0 php charakteryzowały się najkorzystniejszymi właściwościami, m.in. nieznacznie większą odbojnością, mniejszą twardością i większym współczynnikiem komfortu niż pianki niezawierające nanokrzemionki.

Słowa kluczowe: nanokrzemionka, poliuretan, proces spieniania, pianki elastyczne, właściwości fizyko-mechaniczne.

[1)] Cracow University of Technology, Department of Chemistry and Technology of Polymers, Warszawska 24, 31-155 Cracow, Poland.

[*)] Author for correspondence; e-mail: aprociak@pk.edu.pl

The basic components used in the synthesis of polyurethanes (PUR) are polyols and isocyanates, which have petrochemical origins. Rising oil prices and limited resources have caused the industry to look for new ideas, among others, the use of renewable raw materials such as polyols from natural oils (NOPs) [1—3]. NOPs can be obtained from vegetable oils such as palm, rapeseed, sunflower or soya using different methods described in the literature. These methods are mostly based on the conversion of the double bond to the hydroxyl groups [4—6] or transesterification and transamidization reactions [7—9].

NOPs synthesized from rapeseed oil can be used for the preparation of flexible polyurethane foams (FPURF). Components obtained from renewable raw materials of plant origin are environmentally friendly and their application can be commercially reasonable. The addition of such polyols in the synthesis of FPURF affects its properties, mostly causing an increase in apparent density, reduction in the surface tension and thereby an increase of cell numbers in the foam structure and different mechanical properties [10—13].

Changes of polyurethane compositions and production parameters can significantly influence the foaming process and properties of the final foams. The addition of fillers complicates the manufacturing process, but it can have a positive impact on the final physical and mechanical properties of the foams. Powder and fibrous fillers of nano- and micro- sizes are more and more often added to composites obtained in the form of foamed materials. Mostly, they are added to one of two basic polyurethane components (polyol or isocyanate) before their mixing or placed in the mold before pouring the polyurethane reaction mixture. The main purpose of fillers is to improve the mechanical properties of the final products and their dimensional stability [14]. The distribution and size of the fillers affect the mechanical properties of the modified foams. The level of changes depends on the proportion of filler and its interaction with the polyurethane matrix [15].

In recent years, polyurethane nanocomposites with silica nanoparticles have attracted much attention due to significant improvements in the properties of such materials [16]. Nanosilica can affect the chemical reaction of the PUR formation and cell geometry of foams. At higher concentrations, nanosilica increases the viscosity of the reaction mixture and affects cell growth [17]. Small size, well-dispersed nanoadditives simplify the process of bubble nucleation during the foaming of polyurethanes [18]. However, due to their high surface area, nanoparticles tend to agglomerate and it is very difficult to disperse them in polymer matrices. High-intensity ultrasonic waves may be useful to produce homogenous dispersions [19]. The introduction of nanosilica to polymer materials influences their properties, among others, sound absorption, thermal stability and fire retardancy [20—22].

In this paper, different contents (0.5, 1.0 and 1.5 php) of nanosilica, as well as polyol based on rapeseed oil (20 wt % in polyols premix), were used in the synthesis of FPURFs. Additionally, various methods for mixing nanosilica with the polyol premix were applied. The aim of the work was to determine the influence of the method of nanosilica introduction to the polyol premix, and the nanosilica content in polyurethane formulation, on the cell structure and mechanical properties of the final flexible foams.

EXPERIMENTAL PART

Materials

PUR foams were prepared using a petrochemical polyether polyol F3600, having a hydroxyl number (L_{OH}) 48 mg KOH/g and water content of 0.10 wt % (PCC Rokita S.A.); rapeseed oil-based polyol Rz/iP having L_{OH} = 84 mg KOH/g and water content of 0.02 wt % (Zakład Doświadczalny Organika in Nowa Sarzyna); toluene diisocyanate (TDI) supplied by Ciech Pianki S.A.; additives like catalysts (Dabco T-9, Dabco BLV) supplied by Air Products and surfactant (Niax L-618) supplied by Momentive Performance Materials, hydrophilic fumed silica Aerosil 200 with a specific surface area of 200 m^2/g and an average particle size of 12 nm (Evonik Industries AG). The blowing agent was carbon dioxide obtained as a result of the polyisocyanate reaction with water.

Preparation of foams

All foams were prepared at room temperature using a one-shot method. The formulations used to prepare FPURF are shown in Table 1. In all formulations, rapeseed oil-based polyol was applied at 20 wt % of the polyols mixture. Formulations differed in the amount of nanosilica content, which was added from 0 to 1.5 php. The same amounts of catalysts (like in the case of reference formulation) were also applied in the case of all formulations with nanosilica to analyze the foaming process. However, in order to obtain foam materials with good quality of physical and mechanical properties it was necessary to increase the amount of catalysts in the formulations modified with nanosilica (Table 1).

Three homogenization methods of polyols with nanosilica were used in order to estimate the effect of the mixing method of the raw materials on the properties of prepared foams:

A — mechanical mixing for 30 s;

B — mechanical mixing for 5 min;

C — mechanical mixing for 5 min + ultrasonic homogenization (OMNI Sonic Ruptor 400) for 20 min using a power of 200 W.

Catalysts, water and surfactant were added to the dispersion of nanosilica in polyols and mixed together for 30 s. Then, a suitable amount of TDI was introduced to the polyol premix. Both components were mixed for 10 s and the reaction mixture was poured into a mold (120 × 120 ×

100 mm). The free growth of foams was carried out in the vertical direction.

T a b l e 1. Formulations of flexible polyurethane foams

Raw materials, g	Foam symbol			
	P0	P05	P10	P15
Petrochemical polyol — F3600	80.0	80.0	80.0	80.0
Rapeseed oil-based polyol — Rz/iP	20.0	20.0	20.0	20.0
Catalysts and surfactant	2.0	3.0	3.0	3.0
H_2O	4.2	4.2	4.2	4.2
Nanosilica — Aerosil 200	0.0	0.5	1.0	1.5
Isocyanate — TDI	46.6	46.6	46.6	46.6

Methods of testing

— Measurement of foaming process characteristic parameters

In order to analyze the process of PUR foam formation, a Foamat device (produced by Format Messtechnik GmbH) was used. This device allows the determination of the foaming process parameters such as: temperature, growth velocity and dielectric polarization of the reaction mixture.

— Cell structure analysis

The cellular structure of the foamed materials was analyzed using an optical microscope (produced by PZO Warszawa) coupled to an Oscar Color Camera CCD (supplied by Centrum Mikroskopii Warszawa). The foams were cut into 8 monolayers in perpendicular and parallel directions to the foam growth direction. ImageJ software was used for analyzing images of cell structure and to determine cell size and the anisotropy index.

— Physical and mechanical properties

The apparent density of the foams was determined using the standard ISO 845: 2006. Compressive strength was measured using a Zwick Z005 TH Allround-Line in accordance with ISO 3386-1:1997. Each sample was compressed four times to 25 % of its height. Between compressions, a 5 min interval was introduced so that samples had time to return to their original size. Compressive strength values were recorded during both loading and unloading of foam samples. On the basis of these data, hysteresis, support factor, hardness at 40 % strain and strength at 75 % strain were determined. Foam resilience in a parallel direction to the foam growth direction was measured in accordance to ISO 8307:2007 using the steel ball method.

The support factor and hysteresis were calculated using the following formulas (1), (2) respectively [23]:

$$\text{Support} \cdot \text{factor} = \frac{F_{65\,\%}}{F_{25\,\%}} \tag{1}$$

where: $F_{65\,\%}$ — the stress at 65 % deformation (kPa), $F_{25\,\%}$ — the stress at 25 % deformation (kPa).

$$\text{Hysteresis} = \frac{W_{load} - W_{unload}}{W_{load}} \tag{2}$$

where: W_{load} — the work on loading sample (J), W_{unload} — the work on unloading sample (J).

RESULTS AND DISCUSSION

Foaming process analysis

Firstly, three formulations differing only in the content of nanosilica (0, 1.0, 3.0 php) were used in the foaming process analysis. The reference foam did not contain any nanoadditive. In the case of all analyzed formulations (with and without nanosilica), the same concentration of catalyst was applied. The results of this study showed that the introduction of nanosilica to the PUR formulation has considerable influence on the foaming process. The foaming process of material containing 3.0 php of nanosilica significantly differed from the other two. The reaction mixture with 3.0 php of nanosilica hardly grew, the temperature in the foam core reached only approx. 70 °C, and the reactions were slower, which was confirmed by a slow decrease in the dielectric polarization during the foaming process. Such an additive of silica nanoparticles (3.0 php) in the case of the analyzed formulations was too large and caused technological difficulties, which made it impossible to obtain FPURF of good quality [24]. Therefore, in further studies, foams were prepared with 0.0, 0.5, 1.0 and 1.5 php of nanosilica content. Even such small additions of nanosilica resulted in a decreased temperature of the core of the foamed mixture (Fig. 1) and, as a consequence, decreased growth velocity of foams (Fig. 2). Moreover, the changes of the dielectric polarization of reaction mixtures were slower (Fig. 3).

The introduction of 0.5 php nanosilica to the PUR formulation caused a significant decrease of the highest temperature of the reaction mixture. In the case of the reference formulation, the highest temperature reached 108.4 °C, whereas only 93.2 °C was reached for the formu-

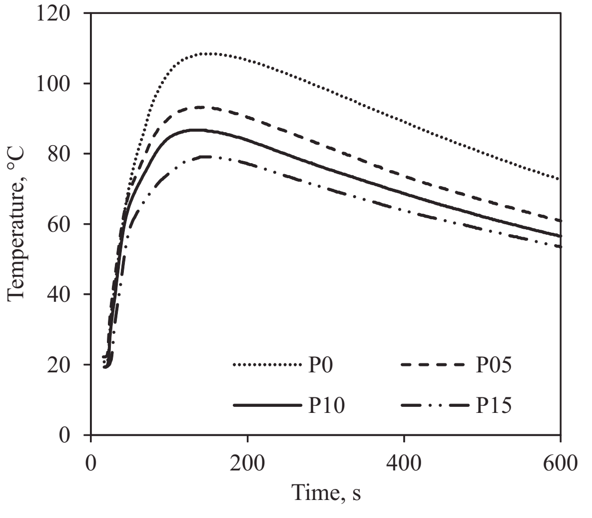

Fig. 1. Temperature of reaction mixture depending on the nanosilica content in the polyurethane formulation

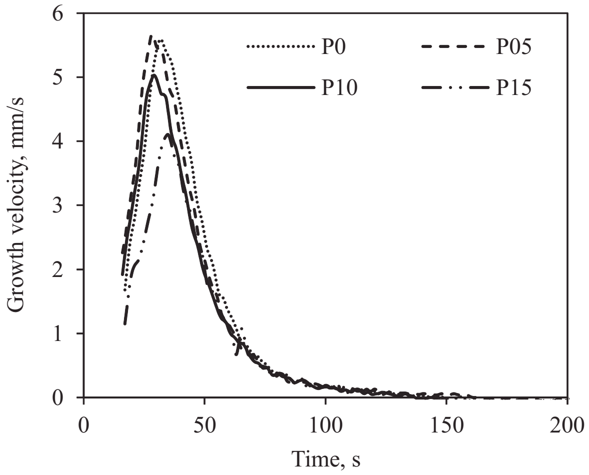

Fig. 2. Velocity of growth of reaction mixture depending on the nanosilica content in the polyurethane formulation

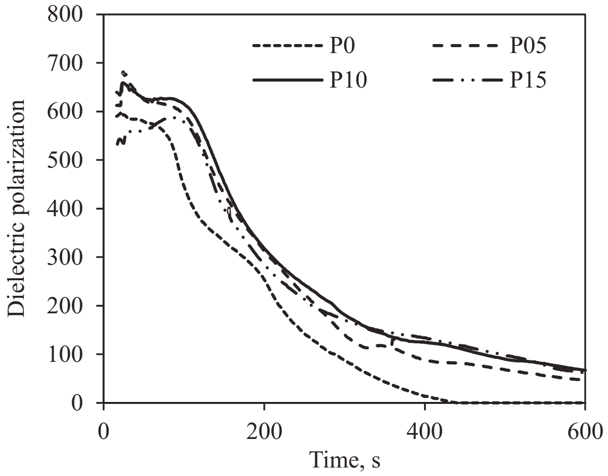

Fig. 3. Dielectric polarization changes depending on the nanosilica content in the polyurethane formulation

lation with 0.5 php of nanosilica (Fig. 1). In the case of foams modified with 1.0 and 1.5 php of nanosilica, the highest temperature reached a level of approx. 80—85 °C.

Likewise, in the case of dielectric polarization, the important difference in the values of this parameter (Fig. 3) was noticed as an effect of the nanosilica additive to reference formulation in the amount of 0.5 php, which confirms the slow-down of polyurethane-forming reactions.

However, considerable changes of growth velocity (Fig. 2) were noted for the FPURF formulation containing 1.5 php of nanosilica compared to the reference material. The curves reflected the changes of growth velocity during the foaming process of reference formulation and modified with 0.5 php of nanosilica are similar.

Cell structure and apparent density of foams

The physical-mechanical properties of polyurethane foams considerably depend on their apparent density and cell structure. Generally, flexible foams must have open cells in order to avoid shrinkage phenomena. On the other hand, such foams should be characterized by a low apparent density. Therefore, on the basis of the analysis of the foaming process, the catalysts content in the formulations with nanosilica was modified (Table 1) in order to obtain foams with good quality cell structures. Before the modification at the catalysts level, the foams obtained with nanosilica contained the defects in the form of holes (so called pockets). These defects were created due to the low reactivity of the system, as confirmed by analysis of the foaming process.

The increase of catalyst content in the formulations with nanosilica allows us to obtain two foams (reference and modified with 0.5 php of nanosilica) with similar apparent density (Fig. 4a). It was found that the increase of nanosilica content from 0.5 to 1.5 php resulted in an increase in the foam apparent density from 25.1 to 28.5 kg/m^3. The introductory method of the nanofiller to polyol premix did not clearly affect the apparent density of the final foams. However, it was observed that the foams obtained with the polyol premix prepared using the ultrasonic homogenizer had a lower spread of apparent density results, which means

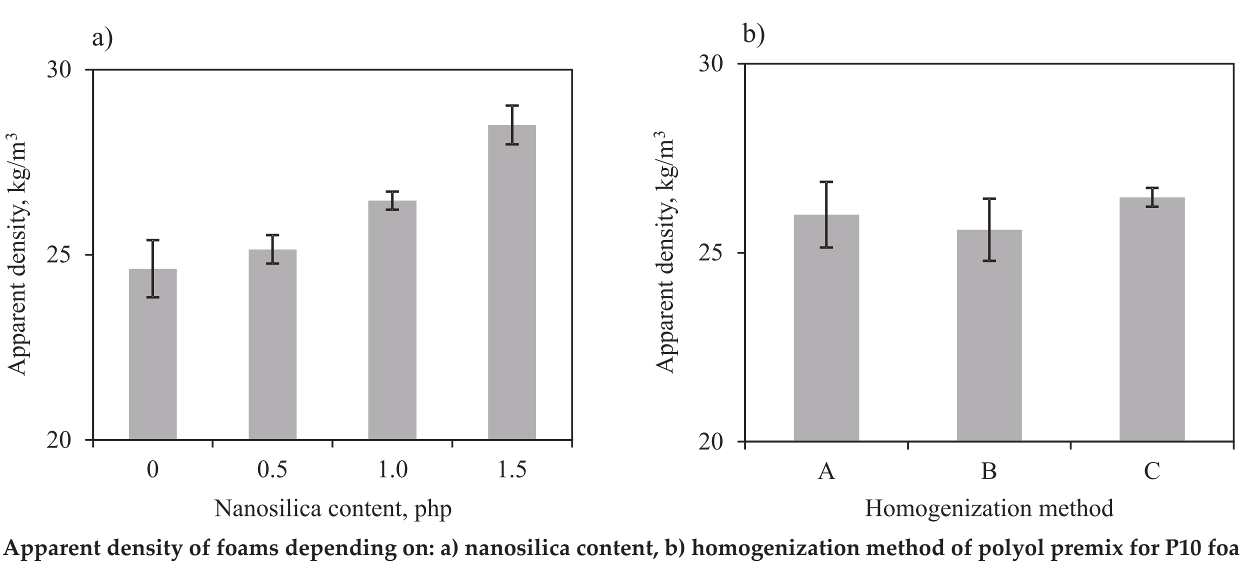

Fig. 4. Apparent density of foams depending on: a) nanosilica content, b) homogenization method of polyol premix for P10 foam

that it makes the synthesis more reproducible (Fig. 4b). These observations can be explained by the fact that, due to their large surface area, nanoparticles tend to agglomerate. Therefore, it is difficult to uniformly disperse them in the PUR matrix. Agglomerated nanoparticles can cause defects and negatively affect the structure of the obtained material [10]. Using an ultrasonic homogenizer, it was possible to obtain a more uniform dispersion of nanosilica in the polyol premixes, and to prevent defect formation in foamed materials, but not to prepare the foams with a lower apparent density.

Nanofillers including nanosilica are attributed as the nucleating agents in the foaming processes so they have an impact on the cell structure of the obtained foams. The influence of the applied additives of nanosilica on the structural characteristics of the prepared porous materials is shown in Table 2 (nanosilica content) and Table 3 (homogenization method).

Table 2. Cell structure characteristic of foams depending on nanosilica content

	Foam symbol							
	Perpendicular				Parallel			
	P0	P05	P10	P15	P0	P05	P10	P15
Cells area, 10^{-2} mm^2	1.59	1.46	1.54	1.63	2.07	1.95	2.15	2.12
Cell height, mm	0.13	0.13	0.14	0.14	0.13	0.13	0.13	0.13
Cell width, mm	0.13	0.12	0.12	0.13	0.16	0.16	0.16	0.15
Anisotropy index	0.95	0.92	0.90	0.91	0.79	0.83	0.78	0.84

Table 3. Cell structure characteristic of foams depending on homogenization method

	Foam symbol					
	Perpendicular			Parallel		
	P10A	P10B	P10C	P10A	P10B	P10C
Cells area, 10^{-2} mm^2	1.69	1.58	1.54	2.70	2.32	2.15
Cell height, mm	0.14	0.14	0.14	0.14	0,13	0.13
Cell width, mm	0.13	0.13	0.12	0.19	0.17	0.16
Anisotropy index	0.91	0.91	0.90	0.77	0.76	0.78

The cell structure of all obtained foams also depends on the cut direction of the material slices. The cells were more fine in the cross-section, which is perpendicular to the direction of foam growth. The cells, in the cross-sections perpendicular to foam growth, have lower cross-section areas and are more spherical (anisotropy index approx. 0.90—0.95) in contrast to the cells in the cross-section parallel to the growth direction of foam, which are larger and have an elongated shape (anisotropy index in the range of 0.76—0.84). Generally, the cellular structure analysis shows that the nanosilica content in the range of 0.5 to 1.5 php did not significantly affect the cell structure of the obtained materials. It was found that the homogenization method of nanosilica with polyols premix affected the cellular structure of the obtained foams. By extending the mixing time and the application of ultrasonic homogenizer (method C), the cells were smaller in the obtained materials (which is confirmed by the average cell cross-section areas shown in Table 3) than in the mixing methods A and B.

Mechanical properties of foams

There are many different methods of measuring mechanical properties that can be helpful to determine the foams' suitability for various applications. The compressive test allows us to assess the influence of nanosilica additive and its homogenization method with polyol on such properties as hardness, support factor and ability for absorbing energy (hysteresis). The hysteresis loops of the foams with different nanosilica content are shown in Fig. 5. It was found that when more nanofiller was applied, the material was characterized by a hysteresis loop of smaller surface area. This means that modified foams have a smaller ability to absorb energy. These changes correlate with higher values of resiliency, which is presented in Fig. 6a. The values of resilience increases from 33 % for the reference foam to more than 35 % for foam modified with 1.0 php of nanosilica.

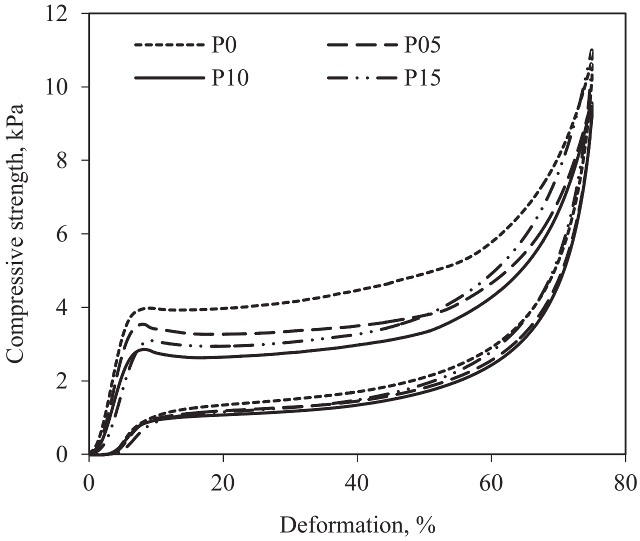

Fig. 5. Hysteresis loops of foams with different nanosilica content

A similar correlation between the foams' properties and the amount of nanosilica was found when analyzing the hysteresis (Fig. 7a), support factor (Fig. 8a), hardness at 40 % strain and compressive strength at 75 % strain (Fig. 9a). The results shown in Fig. 7 and Fig. 8 confirm that the increase of nanosilica content caused an improvement in the useful properties of modified foams (higher support factor, lower hardness) taking into account their potential application in the furniture industry.

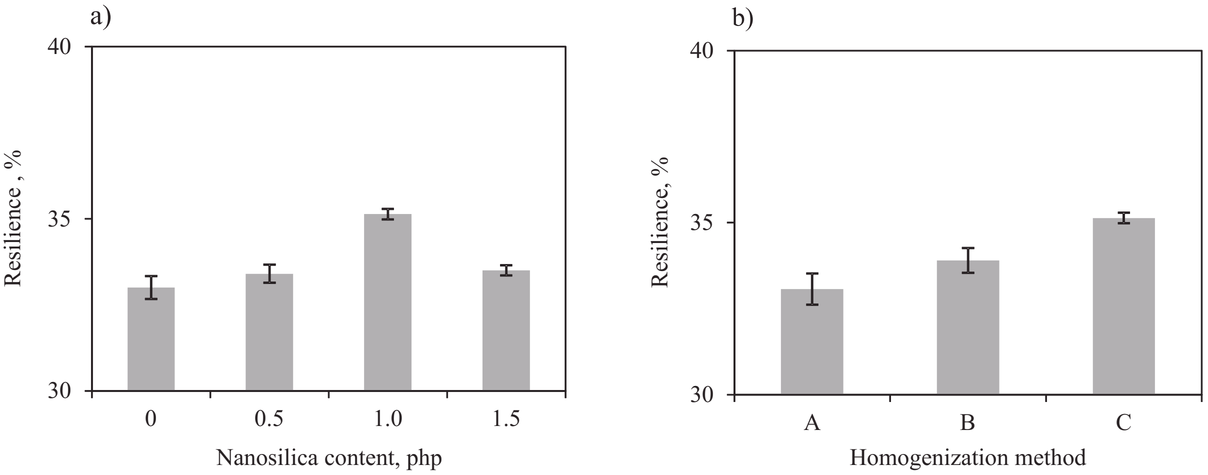

Fig. 6. Resilience of foams depending on: a) nanosilica content, b) homogenization method of polyol premix for P10 foam

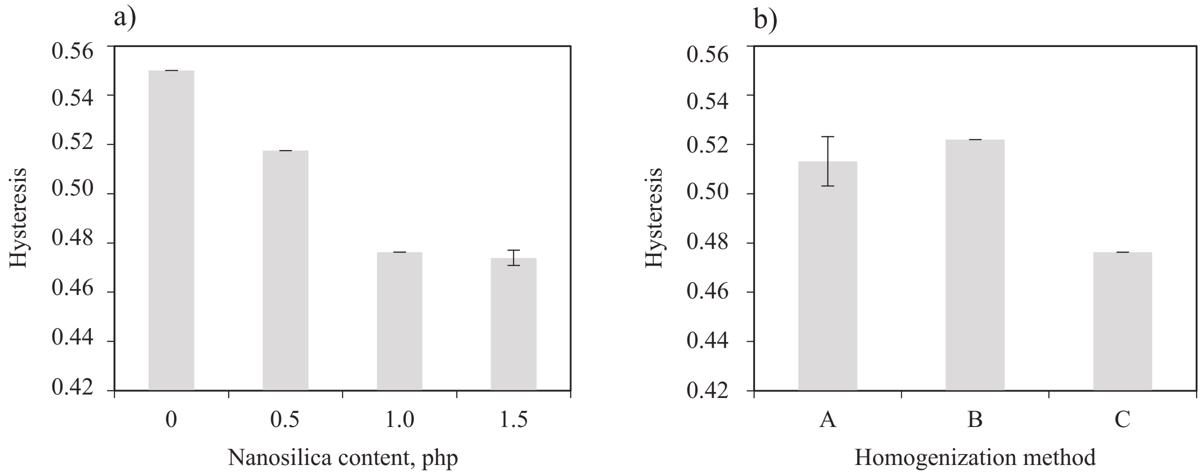

Fig. 7. Hysteresis value depending on: a) nanosilica content, b) homogenization method of polyol premix for P10 foam

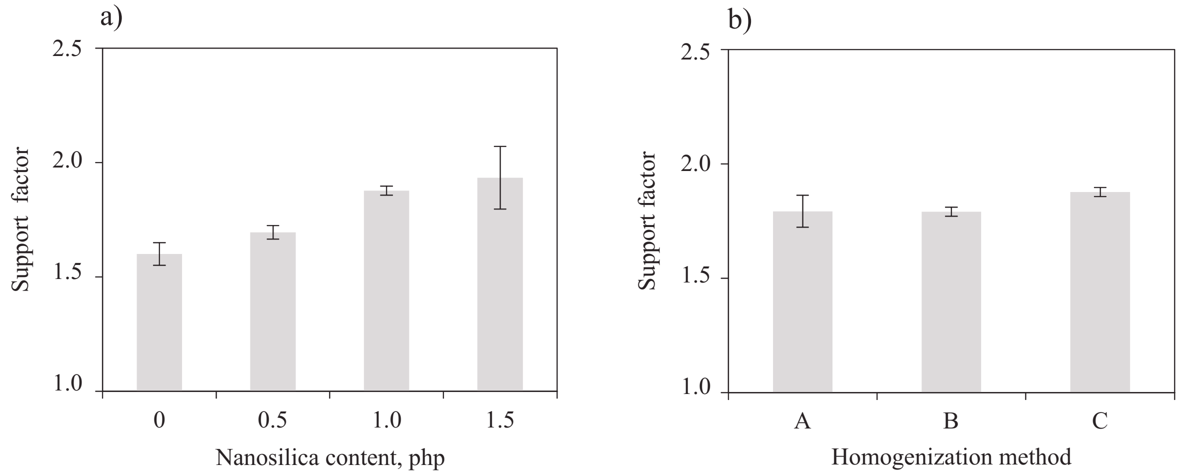

Fig. 8. Support factor of foams depending on: a) nanosilica content, b) homogenization method of polyol premix for P10 foam

The unexpected higher values of compressive strength, as well as lower resiliency, of the foams with 1.5 php of nanosilica versus the foams with 1.0 php of nanosilica can be an effect of the difference in the apparent densities of the compared materials.

Interesting dependencies were noted when analyzing the properties of foams obtained using different homogenization methods of nanosilica with polyols. Extension of the time of mixing and applying an ultrasonic homogenizer resulted in a greater reproducibility of the mechanical

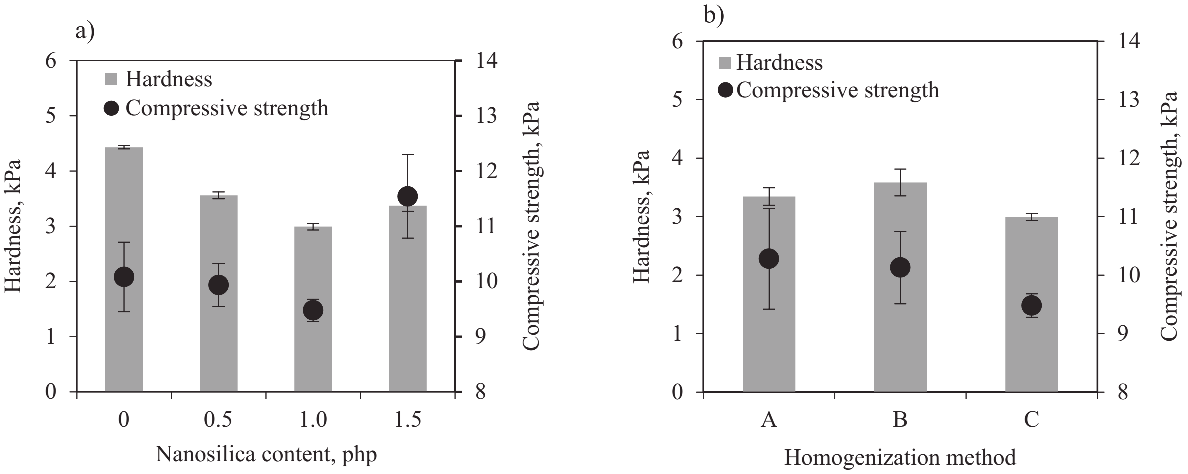

Fig. 9. Hardness and compressive strength at 75 % deformation of foams depending on: a) nanosilica content, b) homogenization method of polyol premix for P10 foam

properties of the obtained materials, as evidenced by the smaller standard deviations of the analyzed results. In addition, better homogenization of the investigated mixtures resulted in foams with a lower hardness and a higher support factor (Fig. 8b and 9b). The resilience (Fig. 6b) of foams increased from 33 % for the foam in which the nanosilica was mixed with a polyol only 30 s to more than 35 % for the foam, in which the raw materials were mixed using a sonicator.

CONCLUSIONS

The application of silica nanoparticles in the synthesis of flexible polyurethane foams incorporating polyols based on rapeseed oils significantly influences the foaming process.

A small additive of this nanofiller causes a considerable slow-down of the polyurethane-forming reaction as evidenced by the decrease of reaction mixture temperatures and a slowing-down of the dielectric polarization changes during the foaming process.

Polyurethane formulations containing nanosilica require higher concentration of catalysts in comparison to the reference formulation without this nanofiller.

The mixing method of polyol with nanosilica is a very important factor in the reproducibility of the preparation process of polyurethane foams and influences the properties of the final porous products.

Cell structure analysis of the obtained materials demonstrated that the addition of silica nanoparticles in amounts up to 1.0 php does not significantly affect pore size and shape in the investigated foams. However, prolonged mixing of the polyol premix with nanofiller and the application of an ultrasonic homogenizer allows us to obtain materials with finer cells.

The application of nanosilica in polyurethane formulation can be a beneficial influence on the physical and mechanical properties of flexible foams causing a greater support factor, lower hardness and higher resilience.

ACKNOWLEDGMENTS

This research was supported by The National Center of Research and Development in the project NCBiR/ERA-NET MATERA/05/2011, titled: Bio-Based Polyurethane Materials (BBPM).

REFERENCES

[1] Prociak A., Rojek P., Pawlik H.: *Journal of Cellular Plastics* **2012**, *48*, 489. http://dx.doi.org/10.1177/0021955X12446210
[2] Zlatanić A., Lava C., Zhang W., Petrović Z.S.: *Journal of Polymer Science Part B: Polymer Physics* **2004**, *42*, 809. http://dx.doi.org/10.1002/polb.10737
[3] Desroches M, Escouvois M., Auvergne R., Caillol S.: *Polymer Reviews* **2012**, *52*, 38. http://dx.doi.org/10.1080/15583724.2011.640443
[4] Kirpluks M., Cabulis U., Kurańska M., Prociak A.: *Key Engineering Materials* **2013**, *559*, 69. http://dx.doi.org/10.4028/www.scientific.net/KEM.559.69
[5] Prociak A.: *Cellular Polymers* **2007**, *26*, 381.
[6] Lubguban A.A., Tu Y.-C., Lozada Z.R. *et al.*: *Journal of Applied Polymer Science* **2009**, *112*, 19. http://dx.doi.org/10.1002/app.29382
[7] Stirna U., Fridrihsone A., Misane M., Vlsone Dz.: *Scientific Journal of Riga Technical University* **2011**, *6*, 85. http://dx.doi.org/10.2478/v10145-011-0012-4
[8] Petrovic Z.S.: *Polymer Reviews* 2008, *48*, 109. http://dx.doi.org/10.1080/15583720701834224
[9] Ionescu M.: "Chemistry and Technology of Polyols for Polyurethanes", Rapra Technology Ltd, Shawbury 2005.
[10] Prociak A., Rokicki G., Ryszkowska J.: „Materiały poliuretanowe", PWN, Warszawa 2014.
[11] Palanisamy A., Rao B.S., Mehazabeen S.: *Journal of Polymers and the Environment* **2011**, *19*, 698. http://dx.doi.org/10.1007/s10924-011-0316-2
[12] Singh P., Bhattacharya M.: *Polymer Engineering & Science* **2004**, *44*, 1977. http://dx.doi.org/10.1002/pen.20201
[13] Pawlik H., Prociak A.: *Journal of Polymers and the Environment* **2012**, *20*, 438. http://dx.doi.org/10.1007/s10924-011-0393-2

[14] Lee W.H., Lee S.W., Kang T.J.: *Fibers and Polymers* **2002**, *3 (4)*, 159. http://dx.doi.org/10.1007/BF02912661

[15] Saint-Michel F., Chazeau L., Cavaille J.: *Composites Science and Technology* **2006**, *66*, 2709. http://dx.doi.org/10.1016/j.compscitech.2006.03.008

[16] Lee J., Kim G-H., Ha Ch-S.: *Journal of Applied Polymer Science* **2012**, *123*, 2384. http://dx.doi.org/10.1002/app.34755

[17] Javni I., Zhang W., Karajkov V., Petrovic Z.S.: *Journal of Cellular Plastics* **2002**, *38*, 229. http://dx.doi.org/10.1177/0021955X02038003139

[18] Ibeh C.C., Bubacz M.: *Journal of Cellular Plastics* **2008**, *44*, 493. http://dx.doi.org/10.1177/0021955X08097707

[19] Kabir M.E., Saga M.C., Jeelani S.: *Materials Science and Engineering: A* **2007**, *459*, 111. http://dx.doi.org/10.1016/j.msea.2007.01.031

[20] Gayathri R., Vasanthakumari R., Padmanabhan C.: *International Journal of Scientific and Engineering Research* **2013**, 4, 301.

[21] Francés A.B., Navarro Bańón M.V.: *IOP Conf. Series: Materials Science and Engineering* **2014**, *64*, 1.

[22] Liu T., Liangliang M., Fuwei L. *et al*.: *Wuhan University Journal of Natural Science* **2011**, *16*, 29. http://dx.doi.org/10.1007/s11859-011-0706-2

[23] Ni H., Chee K.Y., Yan J.: *Journal of Applied Polymer Science* **2007**, *104*, 1679. http://dx.doi.org/10.1002/app.25798

[24] Malewska E., Prociak A.: „Flexible polyurethane bio-foams modified with nanosilica", Materiały konferencyjne XIII Międzynarodowej Konferencji Naukowej MAT-ECO-SHOES 2014, Kraków 20—21 listopada 2014.

Received 2 X 2014.