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Thermoplastic polyurethane foamed under microwave irradiation

Summary — Microwave heating has a number of advantages over the conventional method. However, most thermoplastics are relatively transparent for microwave irradiation. In the case of polyurethanes, these materials absorb microwaves to a sufficient extent to be heated. This effect can be enhanced by the use of fillers such as carbon black. In this paper, the ability of thermoplastic polyurethane and its composite with carbon black to be heated by microwave irradiation and to be foamed using chemical blowing agents are discussed. The temperature changes in different parts of samples as the heating effect under microwave irradiation with 500 W power were analyzed. Selected porous products were obtained under microwave irradiation using azodicarbonamide as a chemical blowing agent. The influence of foaming conditions on cell structure, apparent density and mechanical properties of porous products was estimated.
Keywords: thermoplastic polyurethane, foaming, microwave irradiation.

POLIURETAN TERMOPLASTYCZNY SPIENIANY ZA POMOCĄ PROMIENIOWANIA MIKROFALOWEGO
Streszczenie — Ogrzewanie mikrofalowe ma wiele zalet w stosunku do ogrzewania konwencjonalnego. Jednak większość materiałów polimerowych jest transparentna dla promieniowania mikrofalowego. Inaczej jest w przypadku poliuretanów, które absorbują mikrofale wystarczająco, aby można było je efektywnie ogrzewać. Efekt ten może być jeszcze wzmocniony poprzez wprowadzenie do poliuretanu napełniaczy takich jak sadza. W niniejszej pracy analizowano zdolność termoplastycznego poliuretanu i jego kompozytu z dodatkiem sadzy do ogrzewania się w polu promieniowania mikrofalowego i do spieniania w obecności poroforu chemicznego. W różnych miejscach próbki mierzono zmiany temperatury badanych materiałów, jako skutek ogrzewania mikrofalowego z mocą 500 W. Wybrane produkty porowate otrzymano w procesie spieniania prowadzonym w reaktorze mikrofalowym, stosując azodikarbonamid jako czynnik spieniający. Określono wpływ warunków spieniania na strukturę komórkową, gęstość pozorną i właściwości mechaniczne wytworzonych materiałów porowatych.
Słowa kluczowe: poliuretan termoplastyczny, spienianie, promieniowanie mikrofalowe.

In recent years, development of foaming technology allowed manufacturing cellular polymers with designed structures and properties. Foaming of different polymers using innovative solutions gives the possibility to improve physical and mechanical properties and to reduce the weight and costs of such materials [1—5]. Among the thermoplastics the most popular polymers applied for manufacturing of cellular products are polyethylene, polypropylene, poly(vinyl chloride), polystyrene and polyurethane. These materials are foamed using physical and chemical blowing agents. The type of used blowing agent depends on many different factors including the character of foamed polymer and processing method [4, 6].

Thermoplastic polyurethanes (TPURs) are a class of thermoplastic elastomers used in a large number of various applications, due to good processing characteristics and interesting properties like high tensile strength, low temperature flexibility and excellent abrasion resistance [7].

A few methods were proposed for preparation of microporous elastomers on the base of thermoplastic polyurethanes. Ito *et al*. [8] examined the formation of microcellular foam in a TPUR with supercritical carbon dioxide. The results showed that the saturation pressure and foaming temperature affected the cell structure. Michaeli and Heinz [9] carried out the extrusion process with CO_2 as a physical blowing agent. They showed the influence of carbon dioxide solubility in the polymer melt and the screw geometry on the extrusion process and cell structure of examined TPUR. In order to obtain TPUR with improved material properties for new applications Nema *et al.* [10] applied the injection molding process

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with the mixture of exo- and endothermic blowing agents. The effectiveness of the use of exo- and endothermic blowing agents is characterized with uniform and consistent cell structure with 40 % density reduction in the foam.

A non-toxic production process of scaffolds for medical applications was developed by Hougen *et al.* [11] to manufacture a porous structure on the base of a thermoplastic polyether-polyurethane. The process enabled mass production of samples with adjustable pore size and porosity. This study tried to develop novel processing methods for scaffolds with controlled moisture content in TPUR. Water was used as a foaming agent and NaCl was applied as a porogen to achieve an open cell structure. The polyether-polyurethane samples with the porosity of 64 % were processed in a heated press. In contrast to solvent casting method, processing of the samples was not limited by its thickness [11].

The mechanism of formation of microporous films using the liquid-liquid phase inversion process is discussed by Khorasani and Shorgashti [12]. Polyurethane films prepared in an alcoholic coagulant had uniform porous structure compared to films obtained in water coagulant. Authors stated that increase in the polymer concentration and coagulant temperature over 23 °C allows decreasing the macro-void formation and enhancing the tensile modulus of cellular products. Such process allows fabrication of microporous TPUR to be used as small diameter vascular grafts.

Typical processing of thermoplastics with injection molding, pressing or extrusion needs heating to allow the polymer liquefaction. Microwave irradiation can be one of heating methods that has many advantages, compared to conventional heating. Among the main advantages of microwave processes are volumetric heating that allows a very rapid energy transfer into the heated material and selective heating. The material ability to be heated by electromagnetic energy depends on its dielectric properties, what means that in a mixture containing a number of different constituents, the heating of each will vary [13].

In this paper, the results of heating and microwave enhanced foaming of TPUR and its composite with carbon black are discussed. The effects of different processing conditions on the ability of these materials to be heated, on the cell structure and selected physical and mechanical properties of final porous products were analyzed.

EXPERIMENTAL

Materials

In this paper only the one type of thermoplastic polyurethane was used. It was Jelur S75A, delivered by Jelchem S.A. It is standard thermoplastic polyurethane elastomer with the hardness 75 °ShA. This basic polymer was blended with a chemical blowing agent, which was azodicarbonamide (ADC) from Lehmann & Voss & Co. and with carbon black Corax 339 (CB) with the specific surface area 92 m^2/g, delivered by Evonik.

Methods of sample preparation

Samples of different type materials were prepared in the form of granulated products. The first extrusion process was performed to obtain six compositions of TPUR with 1 wt. % of chemical blowing agent (ADC) and three of them additionally with 3 wt. % of carbon black (CB).

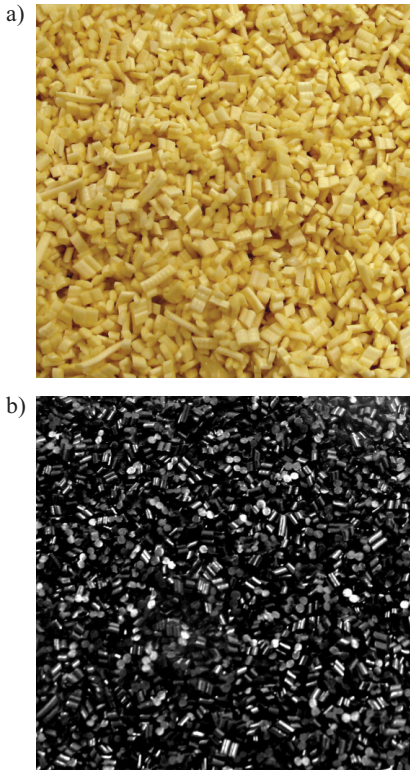

Fig. 1. Granulated compositions of TPUR: a) with ADC (yellow), b) with CB and ADC (black)

Fig. 2. Mold for foaming of TPUR and composites with CB

This first compounding process was performed on the twin screw extruder (Leistritz MICRO 27 GL/GG-44D). The extruded wire was quenched and pelletized. The temperature of extrusion was lower than the decomposition temperature of the applied chemical blowing agents. The granulated compositions of TPUR with ADC only (yellow) and additionally with CB filled TPUR with ADC (black) are shown in Figure 1. Such prepared materials were irradiated and foamed in poly(tetrafluoroethylene) mold shown in Figure 2 using microwave reactor Nova 2004.

Methods of testing

First, the ability of prepared materials to be heated by microwave irradiation was analyzed. The measurements of material temperatures during the heating of samples of different mass were carried out at microwave irradiation power equal to 500 W. The TPUR samples were heated in microwave reactor Nova 2004. The samples of granulated TPUR and its composite with carbon black filler in the amount of 100 g were heated in a glass batch 5 cm in diameter. Two different devices and two various methods of temperature measurement were used. The first device was a pyrometer, which is a non-contact, infrared thermometer. It is equipped with a laser pointer to pinpoint the exact measurement spot on the material. As it is shown in Figure 3, surface (level 0) temperature was measured with a pyrometer. The second device was a glass optical fiber detector with a Fabry-Perot's temperature sensor. It was put inside a glass capillary tube and pushed down into the material to a certain depth. Temperature measurements were taken at 1, 2, 3 and 4 cm below the surface (levels 1—4, respectively) of the TPUR sample.

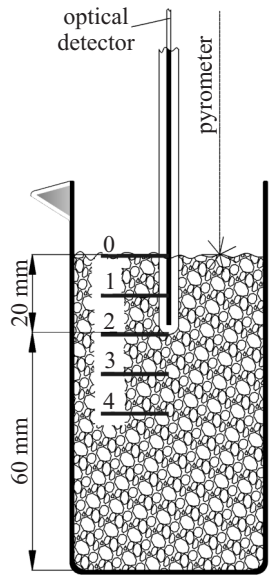

Fig. 3. Procedure of temperature measurements using a pyrometer and an optical detector

The foamed materials were conditioned at 22 °C and 50 % relative humidity for 24 hours, before being cut to analyze the cell structure and to measure their physical and mechanical properties. The slices of TPUR foam samples were cut using a microtome blades. Several photos of each TPUR foam structure were taken using optical and scanning electron microscope (SEM) in order to estimate the cell parameters (cross-section area and anisotropy index of cells). Foam morphology in each photo was analyzed using the same procedure of Aphelion software. The anisotropy index expresses circularity of the cells. It is set as the ratio of the height and width of the rectangle, in which a cell is inscribed. Moreover, SEM was applied to prepare the images of materials cross-sections.

The apparent density (kg/m^3) was measured in accordance with standard test ISO 845. Tensile strength, elongations at maximal strength and at break were estimated according to ISO 527.

RESULTS AND DISCUSSION

Measurements of heating ability

TPUR and its composite have to be able to absorb microwaves in order to be efficiently heated under irradiation and to give porous products with the thermoplastic matrix. Therefore, the measurements of temperature profiles of TPURs under different conditions were carried out. The trials realized in the microwave reactor Nova 2004 have confirmed the ability of both TPUR materials and its CB filled composite to achieve a high temperature in a short time, when the power of 500 W was applied. The heating time effects on the shape of temperature increase curves for TPUR sample are shown in Figure 4.

First, the temperatures inside the materials and on the surface were similar but after *ca.* 45—60 s a higher increase of temperature was noticed inside the material due to the heat transport from the sample surface to surrounding air, that was not heated by microwaves. It was found that the temperature rise rate at various places of materials during the TPUR samples heating was different (Fig. 4). However, the temperature changes are not proportional to the distance from the sample surface. The temperature of TPUR at the level 1 (1 cm from the surface) and on the surface are similar during the whole 90 s of heating.

As it is shown in Figure 5, in the case of TPUR samples filled with CB the temperature changes in analyzed places were similar as for TPUR without this additive. It indicates that the additive of 3 wt. % of CB does not change significantly the ability of TPUR to absorb microwaves.

On the second hand, the rate of temperature increase considerably depends on the sample arrangement in microwave reactor. Applying the multimode microwave reactor it was achieved that TPUR absorbed microwaves and be heated equally in whole volume. While, as it was presented in Figure 6, the change of mold arrangement in

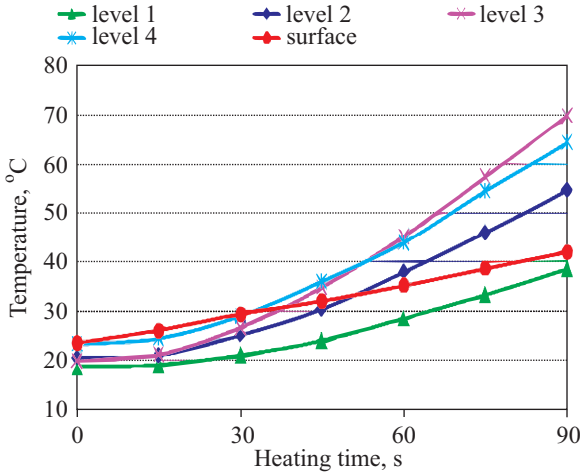

Fig. 4. Temperature profiles of the TPUR sample versus distance from its surface

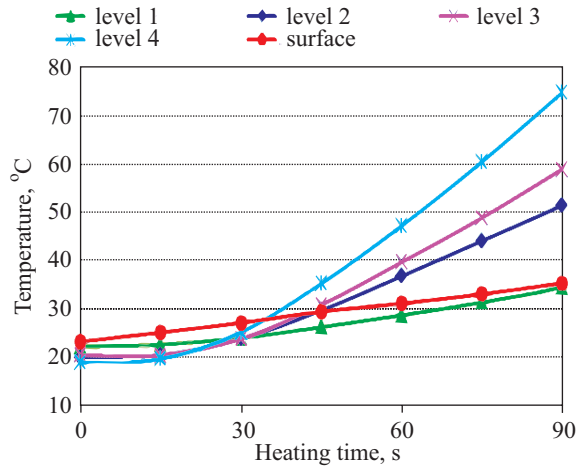

Fig. 5. Temperature profiles of the carbon black filled TPUR sample versus distance from its surface

the microwave reactor from perpendicular to parallel position of the mold side with the highest area in relation to the reactor doors allows heating the TPUR (for 480 s) to the temperature *ca.* 60 °C higher.

Cell structure and selected properties of foamed materials

The samples of TPUR materials with or without CB additive were blown under microwave irradiation. The

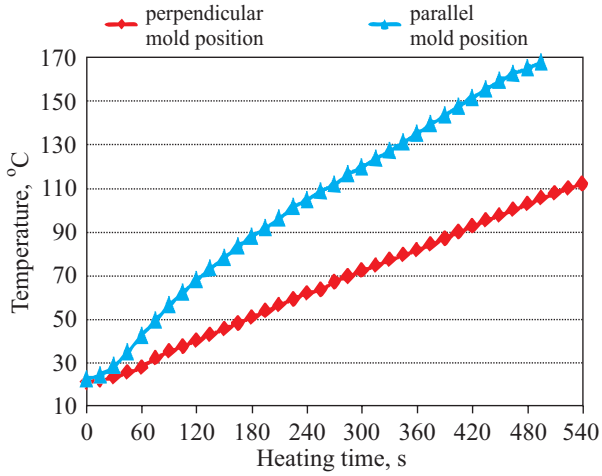

Fig. 6. Temperature profiles of TPUR versus mold arrangement

influence of CB fillers on the cell structure of obtained products is shown in Table 1 and Figure 7. The application of carbon black additive allowed obtaining cellular materials with large number of fine cells that are evenly distributed throughout the whole cross-section (Fig. 7b). In the case of TPUR without CB fine cells are only close to the walls and the core contains big pores, what is shown in Fig. 7a. However, the average values of cross-section area importantly depend on the foaming conditions. Both, the smallest and the biggest cells were found in samples with the additive of CB, respectively in sample 5 and 6 (Table 1). Anisotropy index for all investigated samples is close to 1, what indicates that cells are generally isotropic.

The foaming process of TPUR and its carbon black composite was carried out. Probably, a little bit more effective heating of TPUR composites with than without CB and higher viscosity of melted materials as a consequence of microwave absorbing gave the benefit like fine cells of these composites with CB, excluding the sample 6. Selected physical and mechanical properties of prepared materials are shown in Table 2. The average apparent density of CB filled samples are *ca.* 12—36 % higher than in the case of TPUR samples without CB.

Different effects of heating time on apparent density of final porous product were noticed for reference TPUR samples and CB filled TPUR. In the case of TPURs without CB the lowest apparent density had the samples

T a b l e 1. Parameters of cells structure of prepared porous materials

Number of sample	Material	Heating conditions	Mean area of cells, mm^2	Anisotropy index
1	TPUR+ADC	4 cycles, each 2.5 min long, 500 W	0.33	1.07
2	TPUR+ADC	4 cycles, each 3 min long, 500 W	0.31	1.18
3	TPUR+ADC	5 cycles, each 3 min long, 500 W	0.43	0.96
4	TPUR+ADC+CB	4 cycles, each 2.5 min long, 500 W	0.27	0.85
5	TPUR+ADC+CB	4 cycles, each 3 min long, 500 W	0.17	0.90
6	TPUR+ADC+CB	5 cycles, each 3 min long, 500 W	0.37	1.04

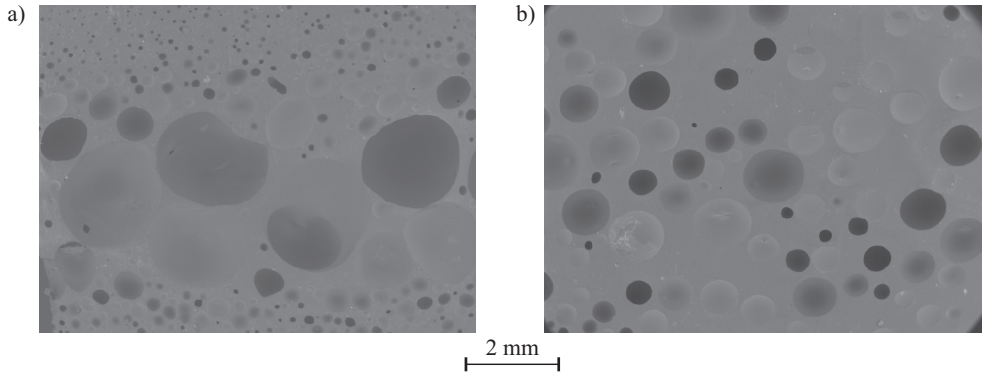

Fig. 7. SEM images of cross-section for TPUR material samples: a) without CB (sample 2), b) with CB (sample 5)

T a b l e 2. Foaming conditions and selected properties of cellular products

Number of sample	Apparent density, kg/m^3		Tensile strength, kPa		Elongation at maximal strength, %		Elongation at break, %	
	mean	standard deviation	mean	standard deviation	mean	standard deviation	mean	standard deviation
1	664.0	95.6	1589.7	1113.0	331.37	44.91	365.42	10.02
2	564.9	25.8	800.1	392.3	328.98	141.13	371.10	94.89
3	602.5	49.3	2216.9	103.9	391.22	17.58	391.22	17.58
4	778.4	32.0	942.8	141.5	68.83	23.08	69.58	23.03
5	770.5	50.1	500.0	106.5	46.82	16.57	97.18	59.15
6	673.1	52.2	254.4	113.5	44.33	24.75	98.22	23.60

heated for 12 min., while this property for samples with CB was the lowest for the sample 6 heated for 15 min.

First of all, the influence of CB additive on considerable decrease of tensile strength and elongation has been noticed. However, processing conditions as the power of microwave irradiation and the exposition time have also influence on the strength and elasticity of foamed products.

CONCLUSIONS

Microwave irradiation is an effective method to heat thermoplastic polyurethanes and their composites with carbon black filler. This heating method can be applied in order to prepare cellular thermoplastic materials "*in situ*" using chemical blowing agents.

Heating efficiency of polyurethanes depends on many different parameters and conditions such as the type and mass of polyurethane, the type and arrangement of the mold in microwave reactor.

The type and mass of additive have important influence on the character of foaming process and the quality of cells structure. The application of carbon black additive to thermoplastic polyurethane improves the cell structure, increases the apparent density and significantly worsens its mechanical properties.

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