Microcellulose as a natural filler in polyurethane foams based on the biopolyol from rapeseed oil*)

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Abstract: Rigid polyurethane (PUR) foams based on biopolyols from rapeseed oil were modified with microcellulose in the amounts of 3, 6 and 9 wt % with respect to the mass of the foams. The biopolyol was synthesized using transesterification of rapeseed oil with triethanolamine. The content of the microcellulose in the PUR system was limited by the increased viscosity of the polyol premix. The viscosity of the polyol premix increased from 297 (for the unmodified system) to 1394 mPa · s (for the system modified with 9 wt % of microcellulose). The introduction of the microcellulose to the PUR systems slightly decreased their reactivity. The addition of the microcellulose caused an increase of the apparent density of the modified foams and the content of closed cells. The biofoams modified with microcellulose were characterized by a similar apparent density. It was found that the modification of the PUR systems with the microcellulose had a positive effect on the mechanical properties and reduced the brittleness of the obtained porous biocomposites in comparison to the reference, unmodified foam. The thermal properties and flammability of the obtained biocomposites were also analyzed. Unexpectedly, it was found that the addition of the microcellulose increased the oxygen index of the modified foams from 20.5 to 21.2 (for the material modified with 9 wt %).

Keywords: biopolyol, polyurethane, foams, biocomposites, microcellulose, mechanical properties.

Mikroceluloza jako napełniacz naturalny pianek poliuretanowych wytwarzanych z udziałem biopoliolu z oleju rzepakowego

Streszczenie: Biopoliol otrzymany w reakcji transestryfikacji oleju rzepakowego trietanoloaminą zastosowano do wytworzenia sztywnych pianek poliuretanowych modyfikowanych mikrocelulozą w ilości 3, 6 i 9 % mas. Zawartość mikrocelulozy w układzie była ograniczona ze względu na wzrost lepkości przedmieszki poliolowej (z 297 mPa · s – system niezawierający mikrocelulozy do 1394 mPa · s – system modyfikowany mikrocelulozą w ilości 9 % mas.). Modyfikacja układu mikrocelulozą wpłynęła nieznacznie na zmniejszenie jego reaktywności. Modyfikowane w ten sposób pianki PUR wykazywały większą gęstość pozorną oraz zawartość komórek zamkniętych niż pianki niemodyfikowane. Stwierdzono, że modyfikacja PUR mikrocelulozą wpływa korzystnie na właściwości mechaniczne oraz kruchość otrzymanych materiałów. Wykonano analizę termiczną oraz zbadano palność wytworzonych pianek. Stwierdzono, że dodatek do kompozycji PUR 9 % mas. mikrocelulozy zwiększył wskaźnik tlenowy otrzymanych pianek z 20,5 do 21,2 %.

Słowa kluczowe: biopoliol, poliuretany, pianki, biokompozyty, mikroceluloza, właściwości mechaniczne.

Polyurethanes (PURs) are polymers that contain urethane linkages formed by the reaction of organic isocyanates with components containing hydroxyl groups [1, 2]. In the literature, there is an increasing share of information on PURs derived from vegetable polyols. PURs based on biopolyols can be produced as fibers, flexible [3–6] and rigid foams [7–9], as well as elastomers [10]. This allows their use in a wide range of consumer and industrial applications, including medical applications [11].

Currently, the PUR industry is highly dependent on petrochemical raw materials. Global warming and the oil crisis have raised an interest in developing alternative substrates that are renewable and of plant origin. For this reason, efforts have been made to find solutions permit-

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T a b l e 1. Properties of the biopolyol and petrochemical polyol

Polyol	Hydroxyl value mg KOH/g	Number average molecular weight g/mol	Functionality	H_2O wt %	Viscosity mPa · s
RP	384	263	1.8	0.14	190
Lupranol 3422	464	485	4.0	0.10	22 750

ting PURs with a combination of biopolyols and natural fillers.

Composite materials formed by natural fillers and polymeric matrices are a current interest of many researchers. Modification of PURs with renewable, raw materials may lead not only to a reduction in the use of petrochemical raw materials but also in an improvement of some characteristics, such as a higher hydrophobicity of the polymer matrix [12, 13].

Rigid PUR foams are among the most important insulating materials used today in the construction and appliance (refrigerators, freezers, *etc.*) industries [14]. In the last years, many researchers have analyzed the influence of renewable raw materials on various properties of rigid PUR foams and composites of low density [15–17].

Silva *et al*. studied the influence of the cellulose fiber concentration on the structural, mechanical and thermal properties of PUR foams. They found that increasing the cellulose filler concentration up to 16 wt %, with the respect to the polyol mass, the cell size and thermal conductivity of the foams were decreased. Meanwhile, the thermooxidative stability and mechanical properties of the foams remained approximately constant [18].

The aim of the research described in this article is an investigation of the influence of microcellulose on the foaming process, as well as on the mechanical and thermal properties of rigid PUR foams synthesized with a rapeseed oil-based polyol.

EXPERIMENTAL PART

Materials

– A rapeseed oil-based polyol (RP) was prepared in the Latvian State Institute of Wood Chemistry. The biopolyol was synthesized on a base of rapeseed oil produced by Iecavnieks SIA using the transesterification method with triethanolamine in the molar ratio 1 : 2.9 [19]. The petrochemical polyol (Lupranol 3422) was supplied by BASF. Selected properties of the biopolyol and the petrochemical polyol used in the synthesis of the foams are shown in Table 1.
– Polymeric methylene diphenyldiisocyanate (PMDI) containing 31.5 wt % of free isocyanate groups was supplied by Minova Ekochem S.A.
– Polycat 5, produced by Air Products and Chemicals, and potassium acetate, produced by Performance Chemicals, were used as catalysts.
– A silicone surfactant with the trade name Niax Silicone L-6915 produced by Momentive Performance Mate-

rials Inc. was used as a stabilizer of the porous structure.
– Carbon dioxide generated by the reaction of water with isocyanate groups was used as a chemical blowing agent.
– Microcellulose Arbocel UFC100 with average fiber thickness and length of 2 and 8 μm, respectively, was supplied by Rettenmaier. The SEM microphotography of the microcellulose is shown in Fig. 1.
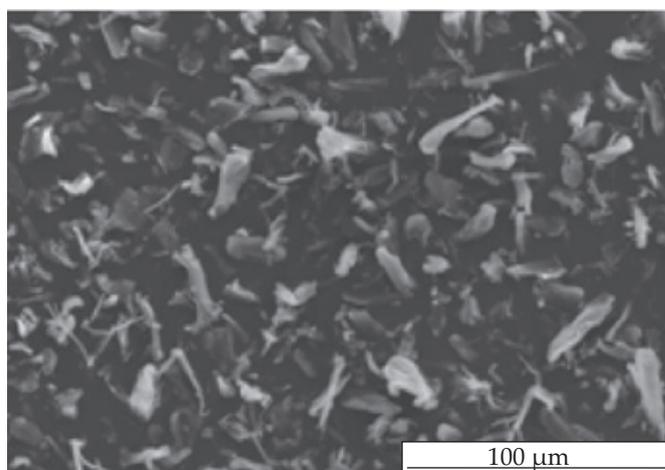

100 μm

Fig. 1. SEM microphotograph of the used microcellulose

Preparation of PUR foams

The PUR foams were obtained by mixing two – A and B – component systems. The chemical composition of component A consisted of the petrochemical and rapeseed oil-based polyols, catalysts Polycat 5 – 1 php (per hundred of polyols) and potassium acetate – 1 php, water 3.7 php and surfactant 1.5 php. This formulation was modified with the microcellulose (3, 6 and 9 wt % of PUR matrix mass).

The content of biopolyols in the prepared foams was 70 php. The isocyanate indices of foams were 150. The rigid PUR foams were marked with respect to the microcellulose content (*e.g.* RP3 – 3 wt %). The foams were obtained using the one-shot and free rise foaming method.

Methods of testing

– The viscosity of the polyol premix was determined using a rotational rheometer model Thermo Scientific Haake Mars III. The measurements were carried out using the controlled-rate mode (CR) in the plate/plate measuring geometry with a diameter of 60 mm and a speed of 10 rpm and 100 rpm. However, the flow curves were obtained using the same measuring system (plate-plate)

in the speed range from 10 to 300 rpm. The measurements were made at constant temp. 25 °C.

– The foaming process was analyzed using the Foamat device, which allows the determination of characteristic foaming parameters, such as the reaction mixture temperature, pressure and dielectric polarization during the foaming process of PUR systems. The temperature was measured with the use of thermocouples.

– The dielectric polarization was measured using a Curing Monitor Device (CMD), which gives an insight into the electrochemical processes occurring during foam formation.

– The following properties of the foams were measured in accordance with ISO Standard tests: ISO 845 – apparent density (kg/m^3); ISO 844 – compressive strength at 10 % deformation (kPa); ISO 4590 – closed cells content (%). The mechanical properties of the foams were estimated in two directions, parallel and perpendicular to the foam rise.

– The morphology of the cells was analyzed using a scanning electron microscope (Hitachi S-4700). The samples were sputter coated with graphite before testing to avoid charging.

– The brittleness of the examined materials was measured using the tumbling box technique in accordance with ASTM C421. For each material, twelve foam cubes (25 mm edge length) and twenty four oak cubes (20 mm edge length) were tumbled together for 10 min at 60 rpm. All samples were weighed to the nearest 0.001 g before and after tumbling. The resulting brittleness was calculated as the percentage of the total weight loss for all 12 cubes in relation to their initial weight.

– The oxygen index was determined according to ISO 4589-2:2006. The behavior of the rigid PUR foams under a heat flux of 35 kW/m^2 was tested using an FTT Dual Cone Calorimeter (Fire Testing Technology Ltd.). The tests were performed according to the ISO 5660-1 standard. The cone calorimeter test allowed the determination of parameters such as the heat release rate (*HRR*), total heat release (*THR*), peak of the heat release rate (p-*HRR*) and total smoke release (*TSR*).

– The thermal stability was tested *via* thermogravimetric analysis using a Mettler Toledo TGA/SDTA 851e under a nitrogen flow and at a heating rate of 10 °C/min from room temperature to 1000 °C.

RESULTS AND DISCUSSION

Nowadays, polymer composites are one of the most commonly used materials. This is related to their lightness and good mechanical properties at low apparent densities in the case of porous materials. The properties of polymeric materials can be improved by the use of different types of fillers. The introduction of plant/vegetable fillers, characterized by a low price, into the PUR matrix allows the improvement of selected properties of the foamed materials and decreases their final price,

as well as forms an environmentally-friendly product [15, 20].

When it comes to natural fillers, in recent years there has been a large interest in microcellulose [21, 22]. However, the use of natural fillers in PUR systems has some limitations including those resulting from an increase in the initial viscosity. This motivates the studies presented here involving systems that contain up to 9 wt % of the microcellulose per total weight of foam. In Table 2 and in Fig. 2, the influence of the microcellulose additive on the viscosity of polyol premixes is shown.

The rheological properties of the obtained polyol premixes are shown as the viscosity versus shear rate. The polyol premixes that contained microcellulose are characterized by an increase in their viscosity with an increasing filler content. The highest viscosity changes were observed for the polyol premix with 9 wt % of the microcellulose. The viscosity of this polyol premix increased more than 4 times compared to the reference polyol premix without microcellulose. In the systems containing microcellulose, one can see a strong impact of the shear rate on the viscosity of the obtained polyol premixes. The viscosity is generally reduced at increased shear rates. This is due to the fact that the polyol premixes containing the microcellulose, which form a dispersion of asymmetrical particles, are thinned at higher shear rates. Such a phenomenon is typical for non-Newtonian fluids with a pseudoplastic nature [23]. The foaming process is the most important stage in the synthesis of PUR foams. At this stage, the cellular structure is formed. The cellular structure has a decisive influence on the mechanical and heat insulating properties of the foams. Therefore, the influence of the microfiller on the foaming process of the PUR systems was determined. One of the most important parameters is the temperature of the reaction mixture during the foaming process. The influence of the microcellulose on the temperature changes of the PUR systems during the foaming process is shown in Fig. 3.

The modification of the PUR foams with microcellulose slightly decreased the maximum temperature during the foaming process. This effect is associated with a decrease of the reactivity of the PUR system. This was confirmed by a slower decrease of the dielectric polarization, which reflects the conversion degree of functional groups during PUR formation (Fig. 4) [20].

T a b l e 2. **Influence of the microcellulose on the viscosity of the polyol premixes**

Symbol of sample	Viscosity of polyol premix, mPa · s	
	Measured for shear rate, s^{-1}	
	10	100
RP0	350 ± 7	297 ± 4
RP3	522 ± 17	497 ± 4
RP6	784 ± 88	573 ± 31
RP9	2413 ± 8	1394 ± 5
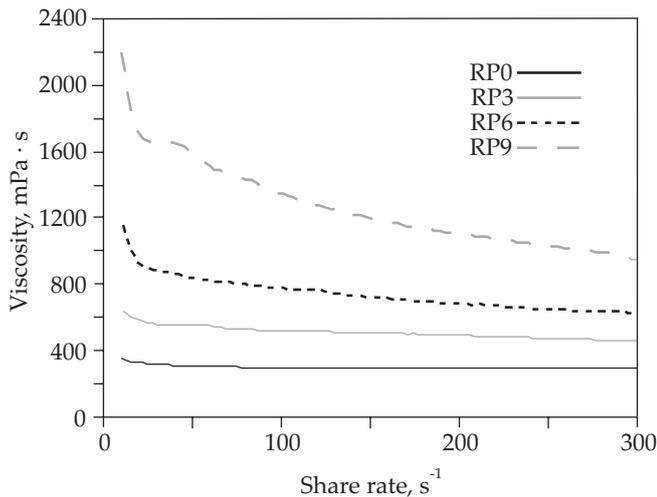
Fig. 2. The dependence of the polyol premix viscosity on the share rate

Fig. 3. The influence of the microcellulose on the temperature changes of the PUR systems during the foaming process

The modification of the PUR system with microcellulose affects the pressure of the reaction mixtures (Fig. 5) during the foaming process, which is related to the closed cell content in the final products. Such an effect can be valuable from the processing point of view of PUR foams, where low pressure is demanded.

The selected properties of PUR materials can be improved by the use of different types of fillers. Moreover, the introduction of plant/vegetable fillers into PUR systems may decrease the price of the final products, as well as allow the manufacturing of environmentally-friendly composites. The influence of the microcellulose on the physical properties of the rigid PUR foams modified with the biopolyol is shown in Table 3.

The addition of microcellulose into the PUR system caused an increase in the apparent density of the obtained foams, which is related to the high viscosity of the polyol premix after adding the filler. The obtained results were satisfactory because the water absorption of the modified foams was lower than 1 vol %. A decrease
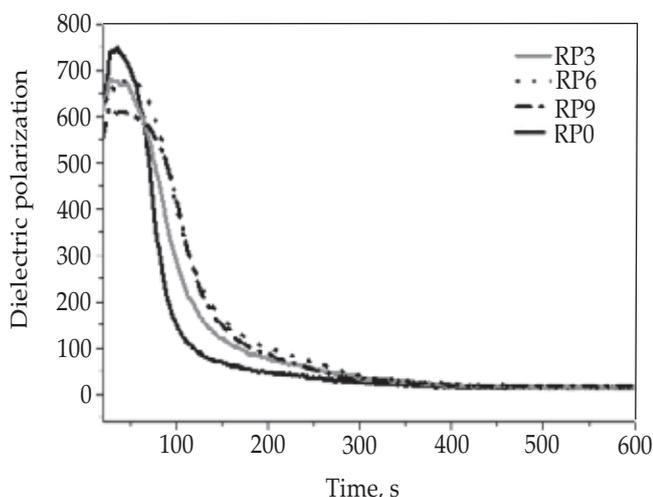
in the brittleness of *ca.* 60 % was observed when 3 wt % of the microcellulose was added and this effect did not change after the increase of the content of the microcellulose up to 9 wt %.

The introduction of microcellulose to the PUR matrix leads to an increased content of closed cells in the modified PUR foams, which is very important in the case of heat insulating materials. Rigid PUR foams used as heat insulators are characterized by a high content of closed cells. The obtained foams were characterized by highly preferred closed cell content values in the case of the PUR systems with the addition of microcellulose. This value increased to 95 % for RP6 and RP9 materials, which is probably the effect of the higher initial viscosity of the modified polyol premix compared to the reference system without any microcellulose additive. The low number of closed cells in the foam RP0 is also related to its low value of apparent density.

Another important issue in this work was the analysis of the impact of microcellulose on the mechanical prop-

Fig. 4. The influence of the microcellulose additive on the dielectric polarization during the foaming process of the PUR systems

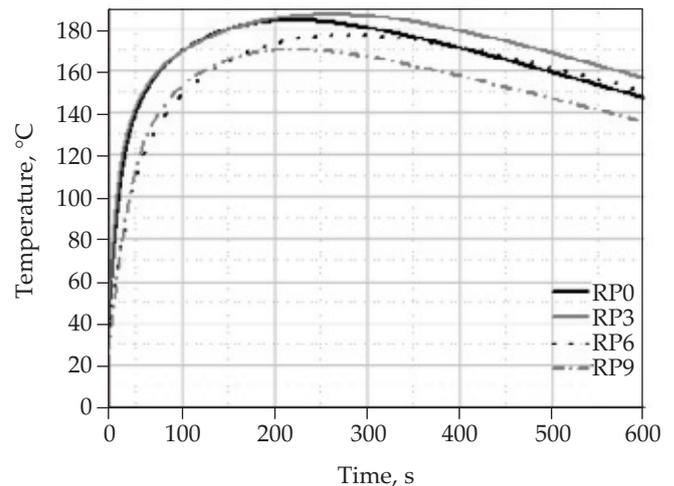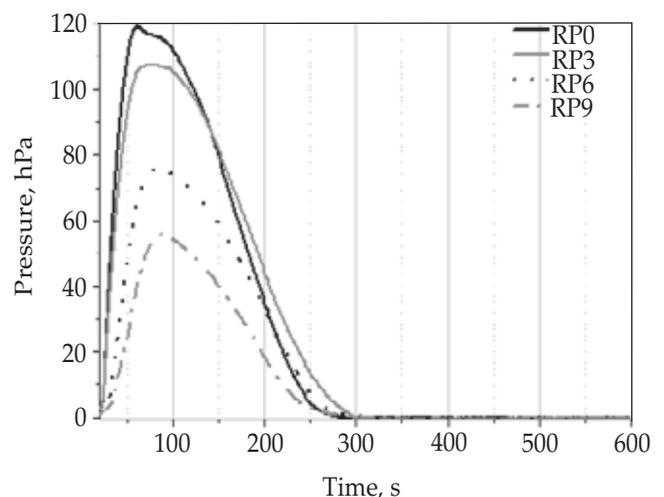Fig. 5. The effect of the microcellulose on the pressure during the foaming process of the PUR systems

T a b l e 3. The effect of the microcellulose additive on selected properties of the rigid PUR foams based on the biopolyol

Symbol of sample	Apparent density kg/m³	Water absorption vol %	Brittleness %	Content of closed cells %
RP0	34.7 ± 0.6	0.53 ± 0.06	48.5 ± 2.8	35.0 ± 4.7
RP3	38.1 ± 1.8	0.76 ± 0.08	20.0 ± 0.8	84.0 ± 4.3
RP6	39.6 ± 1.9	0.87 ± 0.06	18.3 ± 2.1	95.0 ± 1.7
RP9	41.1 ± 1.6	0.74 ± 0.04	21.9 ± 1.5	95.9 ± 1.5
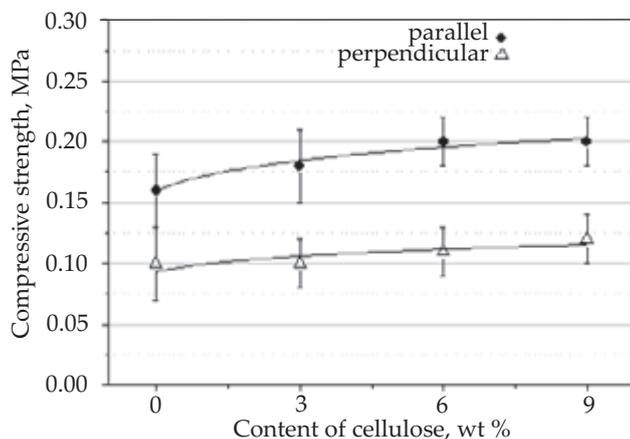
Fig. 6. The compressive strength of the rigid PUR foams modified with microcellulose

erties of rigid PUR foams. Compression tests were performed in the parallel and perpendicular directions to the direction of foam rise due to the anisotropic nature of the cells in the obtained foams. The results of the compressive strength of the rigid PUR foams with an isocyanate index of 150 that were modified with the microcellulose are shown in Fig. 6.

The introduction of the microcellulose to the PUR system had a positive effect on the mechanical properties of the modified foams. Irrespective of the test direction (perpendicular or parallel), an increase in the compressive strength of the foams with an increase of the microcellulose content was observed. This effect can be par-

tially associated with an increase of the apparent density of the modified foams. Such an effect has been explained in the literature [24] by the decisive role of the apparent density in relation to mechanical properties. However, in the case of the foams modified with the microcellulose characterized by a similar apparent density, an improvement of mechanical properties was also noticed. This may be linked to the fact that the microcellulose incorporated in the struts of the cell walls increased the stiffness of the PUR foams (Fig. 7), which was confirmed by an analysis of Young's modulus for selected materials (Fig. 8).

A similar effect as in the case of the compressive strength was observed in the analysis of the Young's modulus. For the foams modified with microcellulose, a similar trend of increases in both the compressive strength and Young's modulus was observed.

There are many factors affecting the filler distribution in PUR foams. Such factors include the viscosity of polyol premixes into which fillers were incorporated. From the viewpoint of mechanical strength, the arrangement of microcellulose is very important because it affects the rigidity of the foam structure. Microcellulose may also be distributed in cell walls, as shown in Fig. 7b.

Luo *et al*. [22] modified rigid PUR foams in which 50 % of the petrochemical polyol mass was substituted with a biopolyol obtained from soybean oil and microcellulose was introduced in an amount of 1, 5 and 10 wt % of the polyol mass. Moreover, the authors observed an increase in the foam apparent density with an increased cellulose

a)
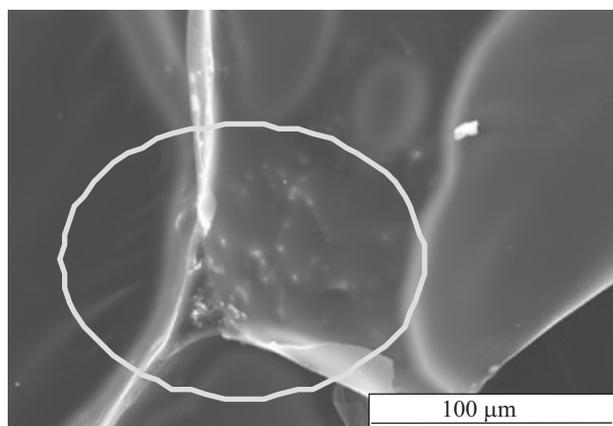
b)
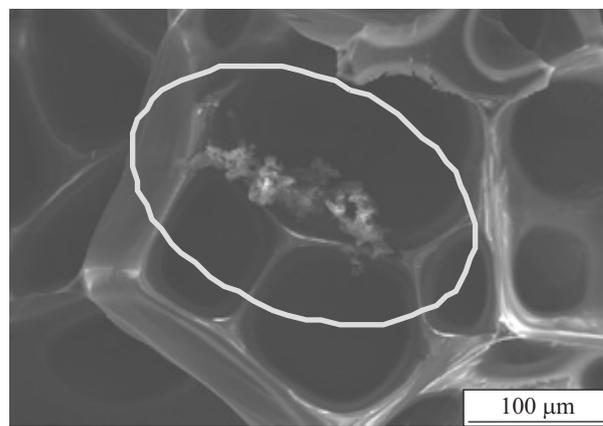
Fig. 7. SEM micrographs of the PUR foams with visible places where the microcellulose is embedded: a) in the struts between cells, b) in the cell walls
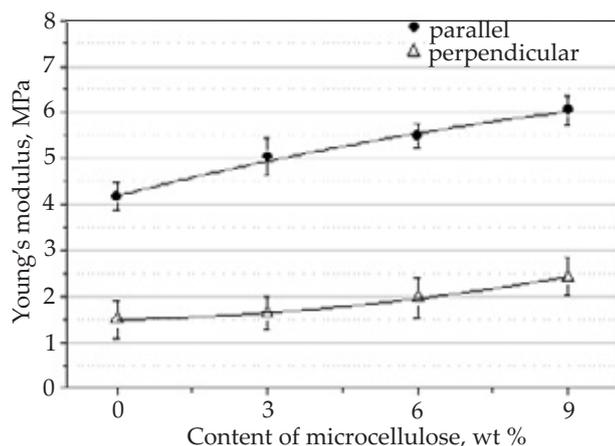
Fig. 8. The Young's modulus of the rigid PUR foams modified with the microcellulose

content in the PUR matrix. The improvement of the compressive strength of the foams was achieved only by the addition of 1 wt % of the microcellulose. In other cases, the mechanical strength of the foams modified was reduced by *ca.* 36 %.

The effect of the microcellulose additive on the cell structure of the selected rigid PUR foams is shown in Fig. 9.

The addition of the microcellulose to the RP0 formulation caused a reduction in the cell size of the modified foams. A similar effect was observed by Luo *et al.* [22] in their work.

Having introduced a filler, which is organic and flammable by its nature, into the PUR matrix, it is important to determine its effect on the flammability and thermal properties of foams. Table 4 shows the results of a thermal analysis of the foams modified with microcellulose and the reference material that did not contain the cellulosic filler.

The modification of the RP0 system with the microcellulose did not considerably affect the thermal properties of the modified foams. The differences in temperatures under which the 5, 25 and 50 % of weight loss of foams took place at certain stages are insignificant.

From the application point of view, the flammability of the composites is one of the most important issues relating to the materials used in construction applications. For this purpose, an analysis of the microcellulose effect on the flammability of the foamed composites was performed. Figure 10 shows the effect of the microcellulose content on the value of the oxygen index for the PUR foams.

It was noted that, unexpectedly, the value of the oxygen index of the biofoams modified with the microcellulose increases linearly with added filler. This can be related to a synergistic effect of the biopolyol and microcellulose. In order to confirm this conclusion, an analysis of the oxygen index of the materials with a different type of biopolyol containing no nitrogen atoms in the structure was performed. The values of the oxygen index for the materials compared were as follows: unmodi-
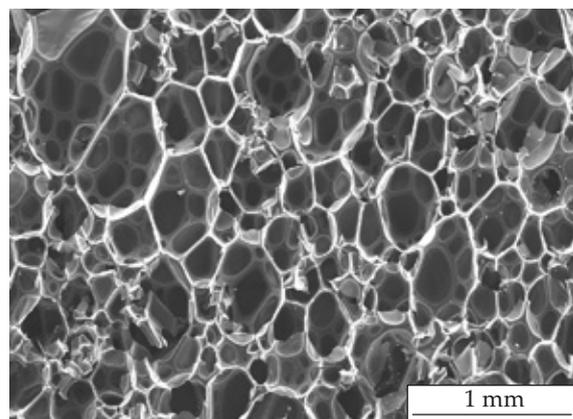
RP0
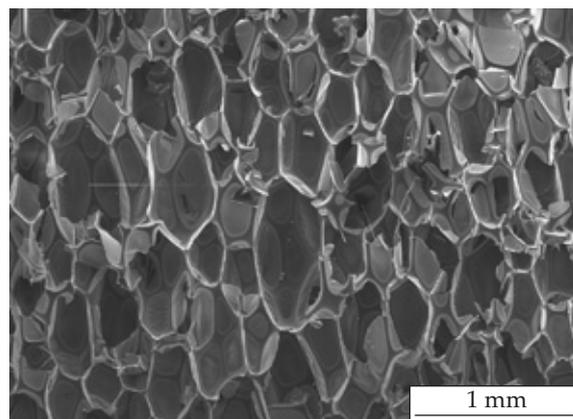
RP3
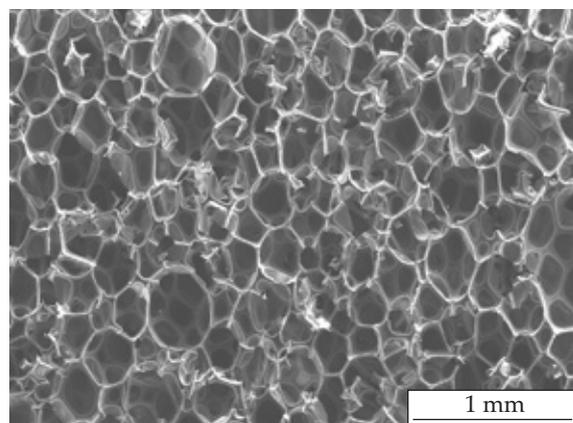
RP9

Fig. 9. SEM micrographs of the PUR foams in parallel cross-sections to the direction of foams' rise

fied foam – 19.6 % and modified foams – 19.4, 19.3 and 19.3 %, respectively with the microcellulose additive in the amount 3, 6 and 9 wt %. It was found that in the case of the foams based on the biopolyol containing no nitrogen atoms, the microcellulose additive slightly decreases the oxygen index of the modified foams [25].

The higher oxygen index could also be related to the finer cell structure with more closed cells. The increase of the number of closed cells with the microcellulose ad-

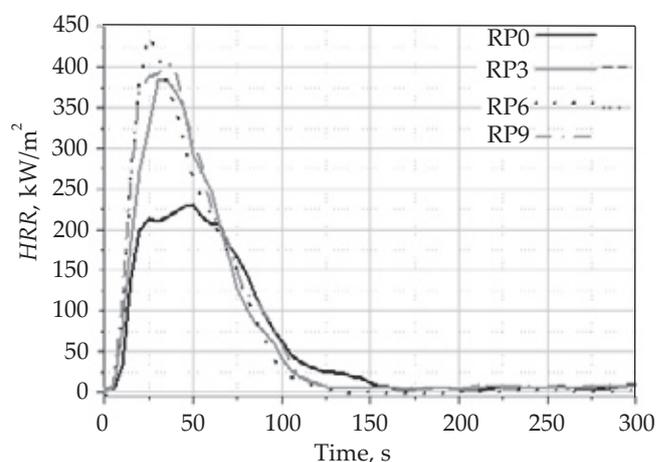T a b l e 4. **The results of the thermogravimetric analysis of the rigid PUR foams**

Symbol of sample	$T_{5\%}$, °C	$T_{25\%}$, °C	$T_{50\%}$, °C	Residue, %
RP0	263	340	415	15.3
RP3	266	340	415	15.3
RP6	264	340	412	15.3
RP9	261	337	409	14.6
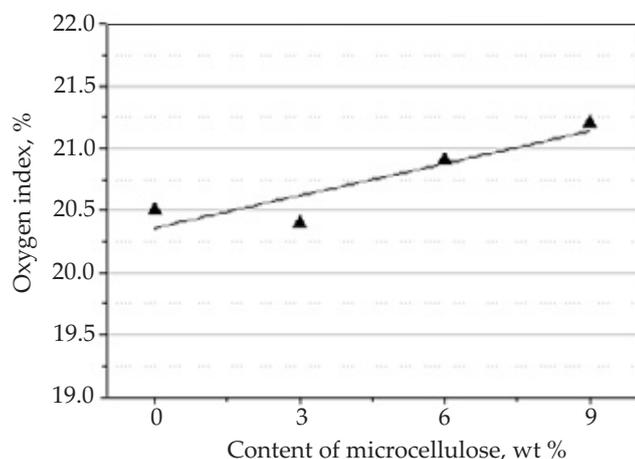
Fig. 10. The influence of the microcellulose on oxygen index values of the PUR foams

Fig. 11. The rate of heat release during the combustion of the prepared rigid PUR foams

ditive limits the specific area of burning material, which reduces the released heat of burning material. Although noticeable, an increase on ~1 % of oxygen index should not be considered a significant decrease of fire retardancy.

Figure 11 shows the change in the *HRR* over time, while Table 5 presents characteristic values obtained during the combustion test (using cone calorimetry) of the rigid PUR foams.

In the cone calorimeter test, it was noted that, with an addition of microcellulose particles, the flammability of the PUR foams increased significantly. Although the *THR* was increased only from 18.0 to 23.9 MJ/m², the most noticeable change of flammability parameters was in the case of the p-*HRR*. It was increased by almost 88 % to the highest value of p-*HRR* 439 kW/m² for the RP6 foams. The microcellulose additive not only increased the p-*HRR*, but also the time at which it occurs was significantly decreased. For the neat RP0 foam, the p-*HRR* occurred at 50 s, but the PUR foams modified the time to p-*HRR* was 25–35 s. Since the microcellulose particles are inherently a burning material, there was no protective barrier effect like in the cases of nanoclay [26] or graphite fillers [27].

CONCLUSIONS

The introduction of ultrafine cellulose to rigid PUR foams was investigated. The upper limit of the microcellulose concentration is 9 wt %, above which there is a significant increase of the viscosity the polyol premixes. PUR foams with a finer cell structure were obtained after the introduction of the microcellulose. The fine cell structure had a positive influence on the closed cell content and brittleness of the PUR foams and, at the same time, the apparent density was slightly increased.

In the case of two different PUR foams, the fire resistance tests showed contradictory results. The oxygen index method showed an improvement of the flame resistance with the introduction of microcellulose in contrast to the results of the cone calorimeter tests. The difference can be explained through an analysis of the cell structure of the foams, as well as the heat flux intensity during the tests. In the case of the oxygen index method, a finer cell structure protects the foam materials from burning but in the case of the cone calorimeter test, a strong heat flux in a short period destroys cells and the microcellulose acts as a fuel.

T a b l e 5. **Characteristic parameters of the flammability of rigid PUR foams**

Symbol of sample	*THR*, MJ/m²	*TSR*, m²/m²	*HRR*, kW/m²	p-*HRR*, kW/m²	Time to p-*HRR*, s
RP0	18.0	522	59.1	233	50
RP3	21.5	529	72.9	384	35
RP6	21.4	572	72.2	439	25
RP9	23.9	563	82.2	405	35

The aforementioned results demonstrate once again how specific flammability test methods are. There are so many limitations to draw conclusions about material flammability or the influence of any additive on the flame resistance of PUR foams if only one separate method is used.

REFERENCES

[1] Cuk N., Fabjan E., Grzelj P., Kunaver M.: *Journal of Applied Polymer Science* **2015**, *132*, 41 522. http://dx.doi.org/10.1002/app.41522

[2] Sarier N., Onder E.: *Thermochimica Acta* **2007**, *454*, 90. http://dx.doi.org/10.1016/j.tca.2006.12.024

[3] Sonnenschein M.F., Wendt B.L.: *Polymer* **2013**, *54*, 2511. http://dx.doi.org/10.1016/j.polymer.2013.03.020

[4] Dworakowska S., Bogdał D., Prociak A.: *Polymers* **2012**, *4*, 1462. http://dx.doi.org/10.3390/polym4031462

[5] Rojek P., Prociak A.: *Journal of Applied Polymer Science* **2012**, *125*, 2936. http://dx.doi.org/10.1002/app.36500

[6] Cinelli P., Anguillesi I., Lazzeri A.: *European Polymer Journal* **2013**, *49*, 1174. http://dx.doi.org/10.1016/j.eurpolymj.2013.04.005

[7] Fan H., Tekeei A., Suppes G.J., Hsieh F.: *Journal of Applied Polymer Science* **2013**, *127*, 1623. http://dx.doi.org/10.1002/app.37508

[8] Yang L.T., Zhao C.S., Dai C.L. *et al*.: *Journal of Polymers and the Environment* **2012**, *20*, 230. http://dx.doi.org/10.1007/s10924-011-0381-6

[9] Palanisamy A., Karuna M.S.L., Satyavani T., Rohini Kumar D.B.: *Journal of the American Oil Chemists' Society* **2011**, *88*, 541. http://dx.doi.org/10.1007/s11746-010-1694-7

[10] Pietrzak K., Kirpluks M., Cabulis U., Ryszkowska J.: *Polymer Degradation and Stability* **2014**, *108*, 201. http://dx.doi.org/10.1016/j.polymdegradstab.2014.03.038

[11] Zieleniewska M., Auguścik M., Prociak A. *et al*.: *Polymer Degradation and Stability* **2014**, *108*, 241. http://dx.doi.org/10.1016/j.polymdegradstab.2014.03.010

[12] Stirna U., Cabulis U.: *Journal of Cellular Plastics* **2008**, *44*, 139. http://dx.doi.org/10.1177/0021955X07084705

[13] Suresh N.S., Kong X., Bouzidi L., Sporns P.: *Journal of the American Oil Chemists' Society* **2007**, *84*, 65. http://dx.doi.org/10.1007/s11746-006-1008-2

[14] Hu Y.H., Gao Y., Wang D.N. *et al*.: *Journal of Applied Polymer Science* **2002**, *84*, 591. http://dx.doi.org/10.1002/app.10311

[15] Kurańska M., Prociak A.: *Composite Science and Technology* **2012**, *72*, 299. http://dx.doi.org/10.1016/j.compscitech.2011.11.016

[16] Mosiewicki M.A., Dell'Arciprete G.A., Aranguren M.I., Marcovich N.E.: *Journal of Composite Materials* **2009**, *43*, 3057. http://dx.doi.org/10.1177/0021998309345342

[17] Luo X., Mohanty A., Misra M.: *Industrial Crops and Products* **2013**, *47*, 13. http://dx.doi.org/10.1016/j.indcrop.2013.01.040

[18] Silva M.C., Takahashi J.A., Chaussy D. *et al*.: *Journal of Applied Polymer Science* **2010**, *117*, 3665. http://dx.doi.org/10.1002/app.32281

[19] Kirpluks M., Cabulis U., Kurańska M., Prociak A.: *Key Engineering Materials* **2013**, *59*, 69. http://dx.doi.org/10.4028/www.scientific.net/KEM.559.69

[20] Prociak A., Kurańska M., Malewska E. *et al*.: *Polimery* **2015**, *60*, 592. http://dx.doi.org/10.14314/polimery.2015.592

[21] Sousa A.F., Matos M., Pinto R.J.B. *et al*.: *Cellulose* **2014**, *21*, 1723. http://dx.doi.org/10.1007/s10570-014-0229-z

[22] Luo X., Mohanty A., Manju M.: *Journal Oil Chemists' Society* **2012**, *89*, 2057. http://dx.doi.org/10.1007/s11746-012-2100-4

[23] Andrade R.D., Skurtys O., Osorio F. *et al*.: *Food Science and Technology International* **2015**, *21*, 332. http://dx.doi.org/10.1177/1082013214535944

[24] Thirumal M., Khastgir D., Singha N.K. *et al*.: *Journal of Applied Polymer Science* **2008**, *108*, 1810. http://dx.doi.org/10.1002/app.27712

[25] Kurańska M.: „Porowate materiały poliuretanowe z udziałem surowców odnawialnych", Cracow University of Technology 2014, PhD thesis.

[26] Zatorski W., Brzozowski Z.K., Kolbrecki A.: *Polymer Degradation and Stability* **2008**, *93*, 2071. http://dx.doi.org/10.1016/j.polymdegradstab.2008.05.032

[27] Kurańska M., Cabulis U., Auguścik M. *et al*.: *Polymer Degradation and Stability* **2016**, *127*, 11. http://dx.doi.org/10.1016/j.polymdegradstab.2016.02.005