

# PHYSICAL AND MECHANICAL PROPERTIES OF RIGID POLYURETHANE FAOMS MODIFIED WITH SELECTED FLAME RETARDANTS OR LAYERED SILICATES

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## ABSTRACT

The flame retardants: expandable graphite, decabromodiphenyloxid, triethylphosphate and nanofillers: natural montmorillonite [MMT] – Nanofil®116, natural MMT modified with a quaternary ammonium salt - Cloisite®10A, synthetic layered silicate – Laponite®RD has been used in rigid polyurethane foams (PUFs). The influence of fillers amounts on processing parameters, physical–mechanical properties (compression strength, density, water absorption, brittleness, mass loss and volume change) and thermal properties (thermal stability and storage modulus in DMA methods) of such foams has been analysed. The morphology has been characterized by X-ray diffraction and scanning electron microscopy (SEM). The X-ray diffraction of the polyurethane nanocomposite foams has been indicated the partial exfoliation of the clay in the polyurethane matrix. The flame retardancy and the thermal stability of all polyurethane modified systems was improved by an addition of flame retardants or nanoclays. Best results, in comparison for pure polyurethane foam, was obtained for polyurethane modified with organically modified montmorillonite (Cloisite 10A).

**Keywords:** polyurethane foams, flame retardant, montmorillonite, nanocomposites, clays.

## 1. INTRODUCTION

Rigid polyurethane foams [PUFs], thanks to their unique properties and wide range of applications, are placed on the top of polyurethane [PU] production list, making 80% of total PU production [1]. PUFs are mainly utilized in engineering due to their good heat-insulating properties, water and climatic resistance, sound absorption and adherence to various surfaces. The heat insulations based on PUFs systems have a wide range of thermal applicability, starting from -70°C up to 140°C [2].

To improve the flame resistance of PUFs, different flame retardants are added into a reaction mixture, mainly based on chlorine and phosphorous compounds [3, 4]. Flame retardants [FR] are supposed to reduce smoke emission and flammability of PU foams, and the processing parameters and the toxicity of gases produced at burning of the foam should not be enhanced by the flame retardants addition.

There are two well known methods of reducing the flammability of polymer materials: chemical and physical. Physical methods are based on limiting the heat and oxygen access into a polymer material. They impair the conditions of reacting substances

flow into the flame front (creating charring) and in the result of an endothermic reaction of FR reduce the plastics temperature. Chemical methods include the changes in polymer macromolecule composition by incorporating atoms of elements lowering the polymer flammability. The elements behave as inhibitors of the combustion process of the polymers [5].

The most recent researches focus mainly on the influence of FR on the polymer foams properties, such as: molecular structure, mechanical, thermal, physical and chemical properties and flammability of the polymers [6-8].

The use of halogen-free flame retardants has been reported in the literature [9-12]. The characteristics of the fire behavior shows that the introduction of increasing content of an expandable graphite [EG] gives a significant improvement in the fire reaction of materials; moreover, it has been showed that the addition of a small amount of red-phosphorus [RP] and triethylphosphate [TEP] brings further benefits, without any negative influence on the physical-mechanical properties. In particular, one of the most important results is the significant improvement of

an oxygen index in presence of 15 wt.% of EG and 3 wt.% of TEP [9]. Modesti et al. [10] studied the influence of two flame retardants - EG and TEP on properties of polyisocyanurate-polyurethane foams. The physical-mechanical and morphological characterization shows that the presence of filler causes only slight worsening of the physical and mechanical properties; in particular the greatest effect of flame retardants has been seen on the thermal conductivity measurements taken for EG filled foams. The filled foams show an overall improvement of their fire behavior: the higher the filler content, the higher the oxygen index and the lower the heat release is; in particular, the best fire performances are obtained using both TEP and EG in a synergistic combination.

Nanocomposites are relatively new class of materials which includes more than one solid phase, where at least one phase has dimension of a nanometer range, typically in a range of 1-100 nm. The nanoparticles generally possess very high mechanical strength and high thermal stability, whereas polymer materials comparing to metals and ceramics are weak both thermally and mechanically. However, due to their higher surface energy nanoparticles tend to agglomerate and in most cases, it is very difficult to disperse them into a polymer matrix. Agglomerated nanoparticles act as structure defects and can have detrimental effect on polymer performances. Thus, it is imperative to disperse the nanoparticles into the polymer matrix, when they are in liquid stage so that interactions at the molecular level can be achieved to produce a material with the superior thermal and mechanical properties [13, 14].

Macosko et al. [15] incorporated montmorillonite based on organoclay into the rigid polyurethane foams. The clay was first ultrasonically dispersed in the isocyanate component. It was found that using toluene as a common solvent enhanced the dispersion significantly. The addition of 1 wt. % clay results in reduced cell size from 0.40 to 0.28 mm and increased cell number. Gas chromatography results show that a diffusion of blowing agent out of the closed cells of the foam decreases by more than 82% with clay loading. The reduction in permeability is caused by the combined effect of smaller cell size and dispersed nanoclay acting as a diffusion barrier. At 1% of clay no mechanical strength improvements can be observed. Higher ratios of the clay loading causes significant viscosity increase and a yield stress that renders mixing the reactive components difficult.

Mondal and Khakhar [16] prepared the rigid polyurethane-clay nanocomposite foams based on different clay types and with different clay concentrations. The densities of the foams are in a range of 140–160 kg/m<sup>3</sup>. The compressive modules were found to increase by about 9 and 23% in the parallel to foam with 4 wt% of Cloisite Na<sup>+</sup> and Cloisite 30B clays, respectively. The storage modulus increases by about 25% for both the clays (Cloisite Na<sup>+</sup> and Cloisite<sup>®</sup>30B) at 4 wt%. However, the absorption of water at elevated pressures increases with the clay content, indicating the weaker cell windows.

In a work of Modesti et al. [17] a potential synergy between a phosphate flame retardant and nanocomposites has been studied. In their work, in particular it was proved that phosphate is an effective flame retardant for PUFs and acts in both, gas and solid phases. Commonly available layered silicates, unmodified as well as the organically modified ones, act through a physical rather than a chemical mechanism as they act in condensed phase behaving like inert filler and promoting the formation of a very compact barrier layer. Thus, they are effective in delaying the onset of thermo-oxidative degradation and improving the thermal stability to some extent, but they show no synergy with the flame retardant when dealing with the fire behavior. Only a suitably developed layered silicate, modified with phosphonium, shows both condensed and gas-phase actions, causing, like phosphate, a radical trapping mechanism. The system phosphate and phosphonium modified clay shows then a synergy which is very effective in improving the fire behavior of the polyurethane foams. Moreover this system also shows delaying effect on thermo-oxidative degradation of the polymer.

Umasankar et al. [18] obtained the rigid polyurethane-vermiculite nanocomposite foams via in situ polymerization. A good dispersion of clay layers in the polymer matrix was obtained in a case of the nanocomposite foams. The thermal conductivity of the nanocomposite was found to be reduced by about 10%, due to finer cells produced in the nanocomposite foam by the bubble nucleation induced by vermiculite. The compressive strength and modulus showed a considerable increase, 40 and 34%, respectively, higher than polyurethane foam without clay. A foam prepared by clay dispersion in an isocyanate showed greater increase in compressive strength and modulus than those prepared by dispersing in a polyol. The thermal stability of the foam was found to be improved, and the onset of degradation was in-

creased to 108°C. The thermal conductivity is lower, and the compressive strength and modulus are significantly higher than previously reported studies based on montmorillonite clay.

An innovative on this paper were comparison of influence flame retardants and nanofiller on physical-mechanical properties of rigid polyurethane foams.

## 2. EXPERIMENTAL

### 2.1. Materials

A polyether polyol, Rokopol RF551 were purchased from Rokita S.A (Poland). According to the manufacturer, the density of Rokopol RF551 (at. 25 °C) is 1,1 gcm<sup>-3</sup>; typical hydroxyl number is 400-440 mg KOH equiv g<sup>-1</sup> of resin; viscosity (25 °C) is 5,842 Pa.s; number average molecular weight is 600 gmol<sup>-1</sup>. Silicone oil SR-393, a surfactant, catalyst: 33 % wt. solution of potassium acetate in ethylene glycol and n-pentane, a blowing agent were purchased from POCh (Poland). Catalyst Polycat 41 were purchased from Air Products and Chemicals Inc (Netherlands). Polyisocyanate, pMDI (Izocyn B) were purchased from Chemical Plant Zachem (Poland). According to the manufacturer, NCO groups content equal to 31 %; the density of pMDI (at. 25 °C) is 1,22 gcm<sup>-3</sup>. Flame retardants were used: expandable graphite (EG), decabromodiphenyloxid (DECA), triethylphosphate (TEP) were purchased from GmbH (Germany). Expandable graphite according to the manufacture, the size of particles were 0,3 mm; pH 6-8; water content 1%. Nanofillers were used: natural montmorillonite modified with a quaternary ammonium salt, Cloisite®10A; synthetic layered silicate, Laponite®RD and natural montmorillonite, Nanofil®116 were purchased from Southern Clay Products, Rockwood Additives (USA).

### 2.2. Preparation of rigid polyurethane foams/ modified nanofillers/ modified flame retardants

The rigid polyurethane foams were obtained in a laboratory scale by one-shot method from a two-component (A+B) system at the equivalent proportion of NCO and OH groups equals 3. The component A (polyol mixture) consisted of proper amounts of oligoether- Rokopol RF 551, catalysts, a chemical blowing agent was prepared by 5 minutes homogenization at 3000 rpm. The component B was polyisocyanate pMDI. The components A and B were mixed at a predetermined mass ratio (10 s at 3000 rpm) and the resulting reaction mixture was poured into an open metal mould of dimensions of approximately 100 x 100 x 50 mm<sup>3</sup>. PUF samples, after demoulding, were held at 60°C for 24 hours

and seasoned at the room temperature for another 24 hours.

The rigid polyurethane foams with nanofillers were preparation in this way. In the first step, nanofillers were seasoned at the 100°C for another 6 hours. Then were preparation polyol mixture and nanofillers were dispersed in this polyol matrix in weight percent of 5 and 10 by vigorous stirring and sonication with mechanical stirrer for 30 min and ultrasonic homogenizer for 20 min. In the next step, nanoparticulated polyol matrix was mixed with component B at a predetermined mass ratio (10 s at 3000 rpm) and the resulting reaction mixture was poured into an open metal mould of dimensions of approximately 100 x 100 x 50 mm<sup>3</sup>. PUF samples, after demoulding, were held at 60°C for 24 hours and seasoned at the room temperature for another 24 hours.

The rigid polyurethane foams modified flame retardants were preparation in this way. In the first step, flame retardants were dispersion in polyol mixture in weight percent 5 and 10 by with mechanical stirrer for 30 min. In the next step, flame retardants polyol matrix was mixed with component B at a predetermined mass ratio (10 s at 3000 rpm) and the resulting reaction mixture was poured into an open metal mould of dimensions of approximately 100 x 100 x 50 mm<sup>3</sup>. PUF samples, after demoulding, were held at 60°C for 24 hours and seasoned at the room temperature for another 24 hours.

As fillers one of six different substances was introduced into PUFs structure and designated with an appropriate letter: C – Cloisite®10A, R – Laponie®RD, B – Nanofil®116, D - decabromodiphenyloxid, T – triethylphosphate, G - expandable graphite. As a control a sample with neither flame retardant nor nanofiller was analyzed. The samples identification consists of a letter referring to proper filler and a number meaning %wt of fillers, for example: P<sub>w</sub> – the control foam, P<sub>C 5%</sub> - the foam with Cloisite®10A 5 wt.%.

### 2.3. Method of testing

After seasoning, the foams were cut and their basic properties were determined according to the standards.

Following parameters were observed: the cream time (T<sub>c</sub>), time when the mixture starts to foam; the rise time (T<sub>R</sub>), time when the foam has the maximum height and gel time (T<sub>G</sub>), time when a surface

of the foam stops being tacky to the touch.

The density of PUFs samples was calculated with accordance to PN-EN ISO 845: 2000, as the ratio of the sample weight to the sample volume  $\text{gcm}^{-3}$ . The samples with a cubic shape were measured with a slide caliper with an accuracy of 0.1 mm and weighed using electronic analytical balance with an accuracy of 0.0001g.

The water absorption of PUF was characterized in accordance with PN-EN ISO 62: 2008. Dried PUF disks with the dimensions of 20 mm in the diameter and 10 mm of height were immersed in the vessel with distilled water at room temperature for 24 hours. After 24h the samples were removed from the medium, blotted on a filter paper to remove excess water and weighed with an accuracy of 0.001g.

The brittleness of PUF was determined in accordance with ASTM C – 421 – 61 and was calculated as a percentage mass loss of 12 cubic samples ( $25 \times 25 \times 25 \text{ mm}^3$ ) during 10-minutes movement of the barrel. The estimation was performed in a wooden case with dimensions of  $190 \times 197 \times 197 \text{ mm}^3$ , rotating at a speed of 60 rpm.

The mass loss and volume change of PUFs (according to PN-EN ISO 62:2008) was observed using the cubic samples during 48 hours at  $120^\circ\text{C}$  in an oven with forced air circulation. The mass loss was investigated by weighing samples before and after the annealing, using electronic analytical balance with an accuracy of 0.0001g and the volume change – by measurements taken with a slide caliper with an accuracy of 0.1 mm.

The compression strength of PUFs samples was estimated with accordance to PN-EN ISO 604:2006. The samples with cubic shape and dimensions of  $50 \times 50 \times 50 \text{ mm}^3$  were measured with a slide caliper with an accuracy of 0.1 mm. The compression test was performed on the tensile tester Zwick/Roell at a constant speed of 10 mm/min to 20% deformation.

Dynamic-mechanical thermal analysis (DMA) were performed using *DMA Q800 TA* Instruments apparatus with Single Cantilever holders according to the ASTM D4065 standard. Measurements were taken for samples of  $37 \times 12 \times 5 \text{ mm}^3$  at the temperature range starting from  $-70$  up to  $250^\circ\text{C}$ , at heating rate  $3^\circ\text{C}/\text{min}$  and frequency of 0.1 Hz.

The thermogravimetric analysis (TGA) were per-

formed by observing the thermal stability of PUFs on the *NETZSCH TG 209* apparatus using the samples of 5 mg at a temperature range of  $100\text{-}600^\circ\text{C}$  and under argon atmosphere, at a heating rate  $15^\circ\text{C}/\text{min}$ .

The X-ray diffraction (XRD) measurements were investigated using Bragg-Brentano *X'PERT PHILIPS* diffractometer with the radiation source (40kV, 30 mA),  $\text{CuK}\alpha_1=0,1546 \text{ nm}$ . The PUFs samples were scanned in an angle range of  $1\text{-}10^\circ$  with a scanning rate of  $^\circ25/\text{sec}$ .

The cellular morphologies of polyurethane foams were investigated by a Philips-FEI XL 30 ESEM (*Environmental Scanning Electron Microscope*). Samples were cut at room temperature and the observation were performed in wet mode.

### 3. RESULTS AND DISCUSSION

#### 3.1. Physical and mechanical properties

The date of characterization of the foams (reported in Table 1 and 2) shows that the interdiction of the flame retardants, causes a slight worsening of the physical-mechanical properties, as frequently occurs when a filler is introduced into a polymer matrix. While interdiction of the nanofillers in to polyurethane matrix causes improvement of the physical-mechanical properties of rigid polyurethane foams. Compression strength of modified foams was lower than of the control foams. Only for PUFs with Cloisite®10A noticed values of the compression strength were greater, respectively equal to 1.56 MPa and 1.18 MPa. Processing parameters: the cream, rise and gel time for PUFs modified with the nanofillers or flame retardant observed during synthesis were elongated in a comparison with the model foam (unmodified,  $P_w$ ). The density of investigated PUFs strongly depends on the modification. The highest values of density were obtained for samples modified with Cloisite®10A and were equal to  $148.6 \text{ kgm}^{-3}$  for PC<sub>5%</sub> and  $180.5 \text{ kgm}^{-3}$  for PC<sub>10%</sub>. Water absorption of unmodified PUF expressed as the percentage swelling was equal to 72% and was decreasing with nanofiller addition. PUFs modified with Cloisite®10A can be described by the lowest ability of water absorption, correspondingly PC<sub>5%</sub>-13.8 and PC<sub>10%</sub>-12.2%. The brittleness of PUF decreases in case of all the modification with nanofillers, but the 10% addition of triethylene phosphate, where the increase was observed ( $P_w=14.9\%$ ; PT 10%=26.2%). The samples modified with expandable graphite can be characterized by the lowest values of brittleness, equal respectively 8.4 and 7.3%.

**Table 1:** The cream, rise and gel time during foaming process.

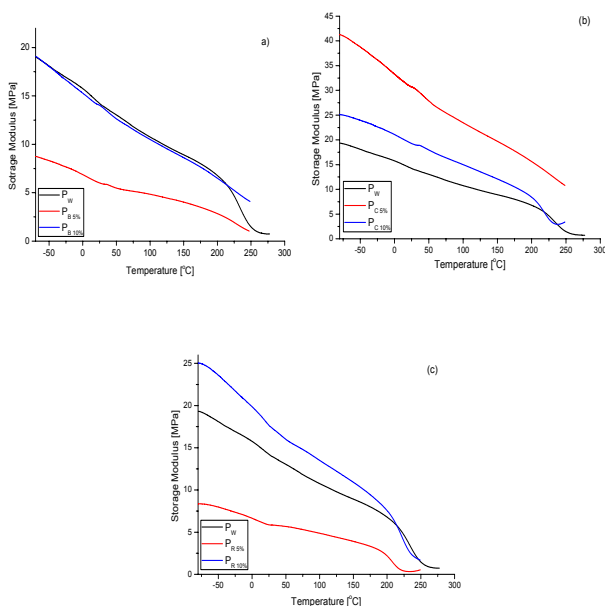
Foam symbol	Processing parameters		
	Cream time s	Rise time [s]	Gel time [s]
P <sub>W</sub>	10	41	56
P <sub>C</sub> 5%	29	46	78
P <sub>C</sub> 10%	31	52	71
P <sub>R</sub> 5%	30	59	90
P <sub>R</sub> 10%	33	60	93
P <sub>B</sub> 5%	24	79	91
P <sub>B</sub> 10%	27	60	71
P <sub>D</sub> 5%	25	50	61
P <sub>D</sub> 10%	25	48	59
P <sub>T</sub> 5%	22	40	76
P <sub>T</sub> 10%	22	50	55
P <sub>G</sub> 5%	22	52	66
P <sub>G</sub> 10%	25	53	59

**Table 2:** Physical and mechanical properties of foams.

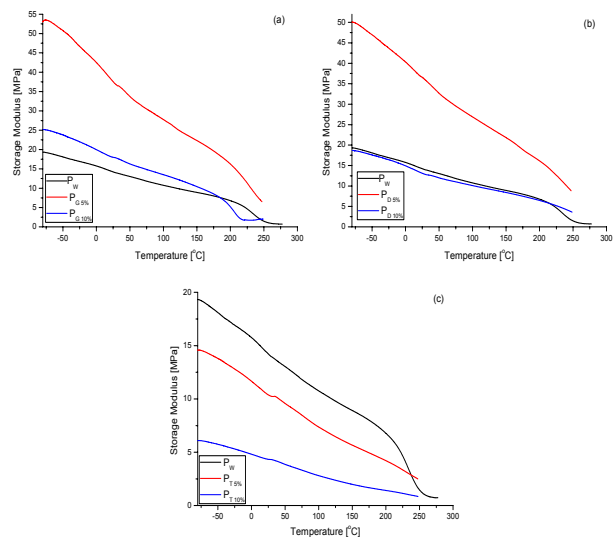
Foam symbol	Density [kgm <sup>-3</sup> ]	Compression strength [MPa]	Water absorption [%]	Brittleness [%]	Mass loss [%]	Volume changes [%]
P <sub>W</sub>	52.0	0.88	77.2	14.9	1.3	2.5
P <sub>C</sub> 5%	148.6	1.56	13.8	10.1	1.9	5.5
P <sub>C</sub> 10%	180.5	1.18	12.2	10.2	1.5	4.3
P <sub>R</sub> 5%	94.9	0.71	23.9	12.4	2.4	4.8
P <sub>R</sub> 10%	102.7	0.61	36.8	10.8	3.2	1.7
P <sub>B</sub> 5%	75.2	0.31	36.5	14.3	1.8	3.4
P <sub>B</sub> 10%	106.9	0.71	28.0	12.3	2.1	5.3
P <sub>D</sub> 5%	117.9	0.72	13.9	9.7	2.3	0.6
P <sub>D</sub> 10%	96.3	0.75	12.9	9.0	2.5	1.1
P <sub>T</sub> 5%	90.3	0.66	24.5	13.9	2.1	1.8
P <sub>T</sub> 10%	132.4	0.75	43.1	26.2	1.5	5.8
P <sub>G</sub> 5%	84.1	0.77	24.3	8.4	2.0	4.5
P <sub>G</sub> 10%	93.1	0.74	36.1	7.3	1.8	4.6

**3.2. Thermal properties**

The changes of storage modulus of elasticity in dependence of temperature are presented in the Fig. 1: a) foams modified by Nanofil<sup>®</sup>116; b) foams modified by Cloisite<sup>®</sup>10A, c) foams modified by Laponite<sup>®</sup>RD; and Fig. 2: a) foams modified by EG; b) foams modified by DECA; c) foams modified by TEP.



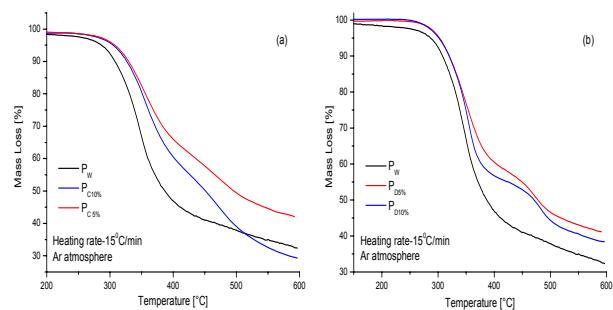
**Fig. 1:** Storage modulus of: foams modified by Nanofil<sup>®</sup>116; b) foams modified by Cloisite<sup>®</sup>10A, c) foams modified by Laponite<sup>®</sup>RD.



**Fig. 2:** Storage modulus of: a) foams modified by EG; b) foams modified by DECA; c) foams modified by TEP.

Analyzes of the storage modulus in DMA methods for rigid polyurethane foams modified by nanofillers and flame retardants shows that the foams PD5% and PG5% show the highest storage modulus from all foams. Storage modulus of foam with 5 wt.% of expandable graphite was equal to 50.62 MPa at temperature -50 °C, 33.4 MPa at 50 °C and 22.4 MPa at 150 °C. For the control the modulus was 18.1 MPa at temperature -50 °C, 13.1 MPa at 50 °C and 9.0 MPa at 150 °C.

The Thermogravimetric analysis results are expressed as the correlation of the temperature and percentage mass loss, for foams modified with two selected fillers (Cloisite<sup>®</sup>10A and decabromodiphenyloxid), and are shown in Fig. 3a and 3b. The decomposition behavior of foams can be distinguished by a two step degradation process. Three samples containing each filler were tested and the data are presented in Table 3.



**Fig. 3:** Termogravimetric analysis (TGA) of control PUFs (P<sub>W</sub>): a) and foams modification by Cloisite<sup>®</sup>10A in 5 and 10 %wt. (P<sub>C</sub> 5% and P<sub>C</sub> 10%); b) foams modification by decabromodiphenyloxid in 5 and 10 %wt. (P<sub>D</sub> 5% and P<sub>D</sub> 10%)

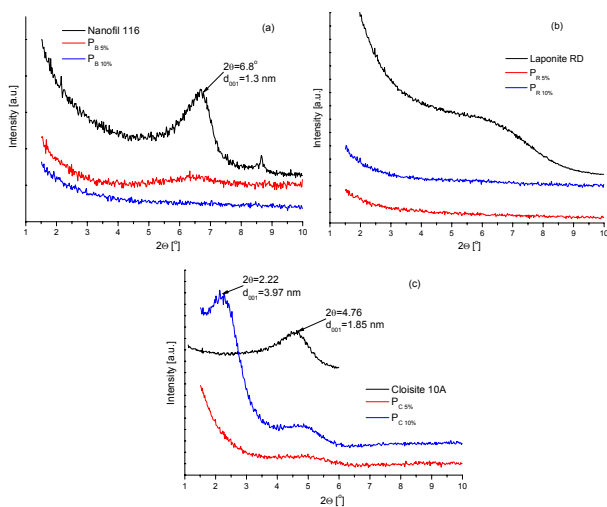
**Table 3:** TGA results for control foam and foams modification by nanofillers and flame retardants.

Foam symbol	Mass Loss [%]		
	5	10	50
	Temperature [°C]		
P <sub>w</sub>	285	307	388
P <sub>C</sub> 5%	307	330	492
P <sub>C</sub> 10%	303	325	451
P <sub>R</sub> 5%	300	318	410
P <sub>R</sub> 10%	285	306	448
P <sub>B</sub> 5%	280	298	392
P <sub>B</sub> 10%	293	312	418
P <sub>D</sub> 5%	302	319	479
P <sub>D</sub> 10%	300	319	468
P <sub>T</sub> 5%	250	290	418
P <sub>T</sub> 10%	234	273	451
P <sub>G</sub> 5%	287	307	409
P <sub>G</sub> 10%	283	305	424

The decomposition temperatures:  $T_5$ ,  $T_{10}$  and  $T_{50}$  are defined as the temperatures when 5%, 10% and 50% weight loss occurs. The best thermal stability was observed for foams modified with 5wt.% of Cloisite® 10A and %wt.% of decabromodiphenyloxid where  $T_{50}$  corresponding to 50% mass loss for P<sub>C</sub> 5% was equal to 492 °C and for P<sub>D</sub> 5% - 479 °C. In all cases the usage of the fillers improves the thermal stability parameters of the rigid polyurethane foams.

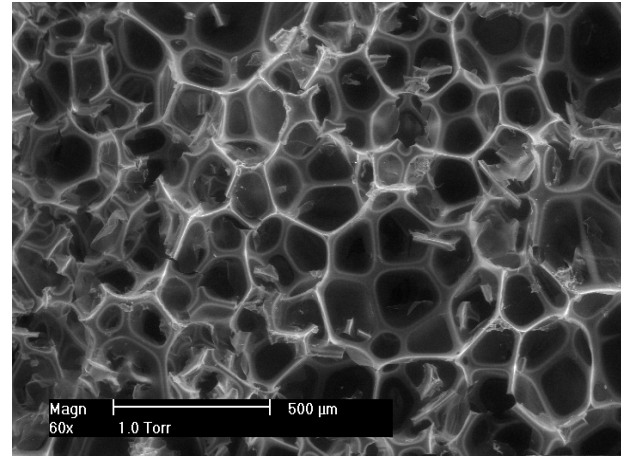
### 3.3. Structure of foams modification by nanofillers.

The nanofillers dispersion in the rigid polyurethane foams was studied by means X-ray diffraction. Wide angle X-ray diffraction was carried out for  $2\theta$  and between 1-10°, where CuK $\alpha$  radiation was used for X-ray source of wavelength 0.1546 nm. Fig. 3 shows the X-ray diffraction patterns of control rigid polyurethane foams (PW) and foams modified with the nanofillers.

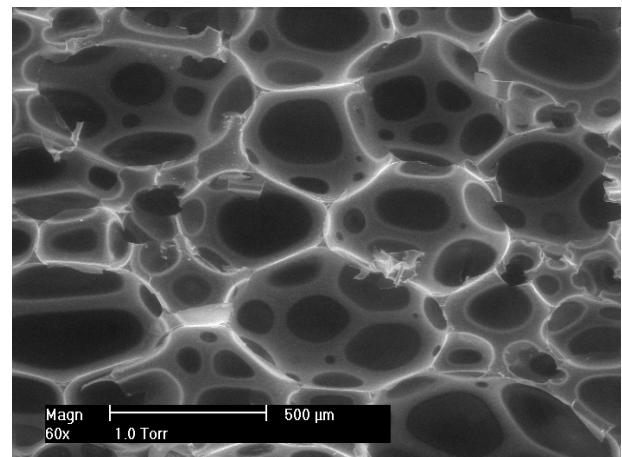


**Fig. 3:** XRD patterns of Nanofil® 116, P<sub>B</sub> 5% and P<sub>B</sub> 10% (a), Laponite® RD, P<sub>R</sub> 5% and P<sub>R</sub> 10% (b), Cloisite® 10A, P<sub>C</sub> 5% and P<sub>C</sub> 10% (c).

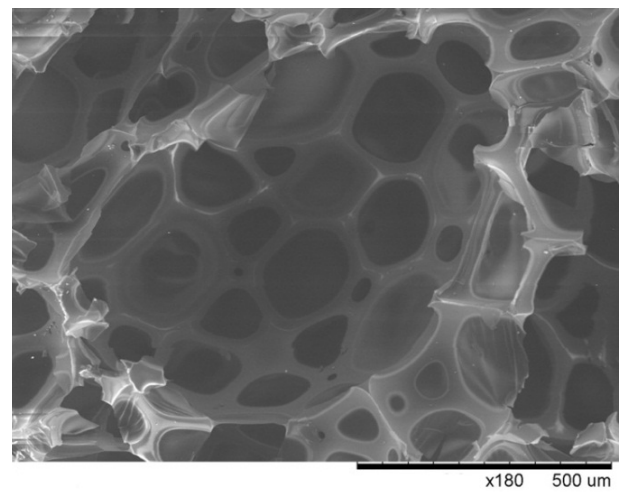
The XRD patterns for the foams modified with Laponite® RD and Nanofil® 116 are very similar to those obtained for unmodified PUF XRD pattern and show no significant peak in the  $2\theta$  range of 1-10° (Fig. The result implies that the Laponite® RD and Nanofil® 116 in the foams could be mostly exfo-



**Fig. 4a:** P<sub>w</sub> (nonmodified polyurethane foam).



**Fig. 4b:** P<sub>C</sub> (polyurethane foam modified with 9% Cloisite 10A).



**Fig. 4c:** P<sub>G</sub> (polyurethane foam modified with 6% expandable graphite).

liated in the polyurethane matrix. The Cloisite®10A has a characteristic diffraction peak ( $d_{001}$  plate)  $2\theta = 4.76^\circ$ , corresponding to a gallery spacing of 1.85 nm. Polyurethane foam nanocomposite containing 5% Cloisite® 10A has diffraction maximum at  $d_{001} = 3.97$  nm, what is connected with increase intergallery spacing in about 2.12 nm. These indicates intercalated structure for polyurethane foams containing 5% organically modified montmorillonite. In all modified polyurethane foams were observed good dispersion of clays.

### 3.4. Morphology of polyurethane foam systems

Morphology of polyurethane foam systems was verified using Scanning Electron Microscopy. All polyurethane foams exhibit closed-cell structures (Fig. 4a-c). Nonmodified polyurethane foam has more brittle cells in comparison to the PU foam modified with 9% Cloisite® 10A. SEM micrographs for P<sub>G</sub> (Fig. 4c) and PC (Fig. 4b) shows, that the dimension of wall cells are thicker than for P<sub>w</sub> are observed.

## 4. CONCLUSIONS

In this work flame retarded and nanofilled rigid polyurethane foams have been synthesized in a laboratory scale by one-shot method from the two-component system. As a flame retardant: expandable graphite, decabromodiphenyloxid and triethylphosphate were used, while as nanofillers: natural montmorillonite, natural montmorillonite modified with a quaternary ammonium salt and synthetic layered silicate were applied. The fillers were dispersed in a polyol.

The foaming parameters (the cream, rise and gel time) for PUFs modified with nanofillers or flame retardants observed during synthesis were elongated in comparison with the unmodified foam. The density of investigated PUFs strongly depends on the modification methods. The foams modified with nanofillers exhibit higher density than the foams with flame retardants. The compressive strength of modified foams was lower than of the control rigid polyurethane foam. In case of the foams filled with Cloisite®10A the compressive strength is higher than PUFs without fillers. The thermal stability in all cases was higher than P<sub>w</sub>. The XRD patterns of foams modified by Laponite® RD and Nanolif®116 shows the highest filler exfoliation in the polyurethane matrix. The structure of foams with Cloisite®10A is intercalated (diffraction peaks  $2\theta = 4.9^\circ$  for P<sub>C 5%</sub> and  $2.1^\circ$  for P<sub>C 10%</sub>).

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