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Polyol Containing Boron Atoms as a Compound which Reduces Flammability of Rigid Polyurethane-Polyisocyanurate Foams

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Additional information is available at the end of the chapter

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Abstract

The article presents results from multidisciplinary research conducted with the purpose of obtaining new material which reduces flammability and is used for the production of rigid polyurethane-polyisocyanurate foams (PUR-PIR). During the preparation of the foam recipe, special attention was paid to the ability to lower the flammability and the improvement of durability and thermo-insulation properties of rigid foams by using the new, non-halogen polyol. The new boron compound helped obtaining fire-safe PUR-PIR foams, which are characterized by the reduced amount of total exhausted heat, longer time to full combustion, lower amount of produced carbon dioxide and oxide, increased oxygen index and lower maximum burning temperature in shorter time than the reference foam.

Keywords: polyol, flammability of foams, rigid polyurethane-polyisocyanurate foams, properties of the rigid foams

1. Introduction

Polyurethanes are polymer materials that have been significantly developed, especially in the last 10 years worldwide. Many facilities produce new raw materials and new polyurethane materials, keeping in mind the principles of sustainable development. Polyurethane advancement started over 75 years ago with the first patent claim from Otto Bayer. However, the first reaction resulting in polyurethane bond was conducted by Wurtz, using diethyl sulphate and potassium isocyanate [1, 2]. Currently, polyurethanes are one of the largest growing polymer groups. The interest in them is related to their specific characteristics which can

be widely modified. By changing the raw materials, their correlating volume ratio and by selecting appropriate processing conditions, it is possible to obtain solid, porous, composite, leather-like and biodegradable materials, and elastomers, glues, fibres, adhesives and many more. Rigid polyurethane foams have a special place among them. They have low apparent density and excellent mechanical properties. That is why they are used in many fields, for example, construction, automotive, furniture, shoe and packaging industries [3–6]. The superb thermo-insulating properties of the rigid foams are the main reason for their wide usage. They are the best thermo-insulating material used in construction and refrigeration. The main drawback of the foams, and one that may limit the expansion of polyurethanes for new applications, is their flammability. It is an important issue, especially when using polyurethanes on large surfaces and in public buildings [7–20]. Lowering their flammability requires multidisciplinary solutions during the stage of designing the chemical structure and antipirenes. Usually, phosphorous, nitrogen, boron and halogens compounds are introduced to polyurethane materials. Nowadays, however, there is a worldwide tendency to withdraw the antipirenes produced based on chlorine and bromine because of the high toxicity during their thermal decomposition. The addition of large amounts of antipirenes in order to obtain the desired non-flammable effect causes technological issues and significantly decreases the physicomechanical properties and dimensional stability of the produced materials [21–24].

Based on the conducted research, the author stated that in order to omit the inconvenience related to the use of halogen antipirenes, the foamed polyurethanes with high-flame resistance can be produced by using the new polyurethane composition which contains the new boron-nitrogen polyol which decreased flammability.

2. Experimental part

2.1. Characteristics of raw materials

The polyether with trade name Rokopol RF-55 (product of oxypropylation of sorbitol LOH = 495 mg KOH/g, produced by NZPO 'Rokita', Brzeg Dolny, Poland) and Ongromat 20–30 (technical polyisocyanate whose main component is diphenylmethane 4,4'-diisocyanate, made in Hungary) were used to prepare the rigid PUR-PIR foams. The density of Ongromat 20–30 at a temperature of 25°C was 1.23 g/cm³, its viscosity was approx. 200 mPa s. The polyisocyanate contained 31.0% of isocyanate groups. It was characterized according to the ASTM D 1638-70 standard.

An anhydrous potassium acetate in the form of 33% solution in diethylene glycol (Catalyst-12, POCh Gliwice, Poland) and amine catalyst in the form of 33% solution of triethyleneamine in dipropylene glycol (DABCO, Hondrt Hülls, Germany) were applied in the foam composition.

The polysiloxanepolyoxyallyleneoxydimethylene copolymer characterized by the boiling point of 150°C at 1013 hPa and ignition temperature of 90°C (Niax Silicone L 6900, Witco Corp., USA) was used as a surfactant.

The porophor was carbon dioxide formed in situ in reaction of isocyanate with distilled water.

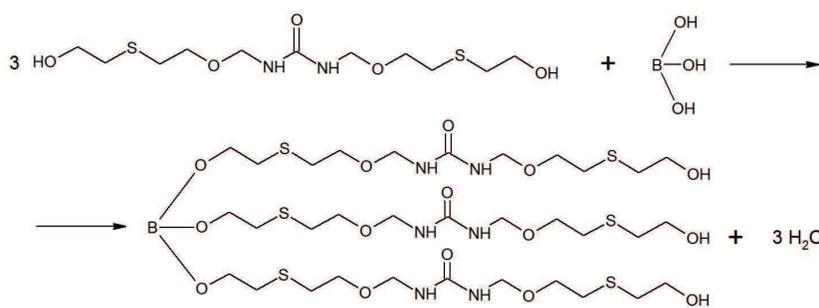
Moreover, tri(2-chloro-1-methyl-ethyl) phosphate (Antiblaze, Albright and Wilson, UK) was introduced into foams.

Boran tri[N,N'-di(metylenooksy-2-hydroksyetylo)mocznika] obtained from the Faculty of Chemistry, Technology of Polymers and Ecotechnology of Bydgoszcz Academy was applied as a modifier for the preparation of foams.

2.2. Synthesis of boronitrogen polyol from boric acid and di(hydroxymethyl)urea

The reaction for obtaining boronitrogen polyol was conducted in an oxygen atmosphere, at the temperature of 131°C, using glass equipment: three-neck flask placed in electric heating mantle. The flask was equipped with Deana-Stark head, thermometer and mechanical stirrer. The flask contained 61.81 g (1 mole) of boric acid (H_3BO_3 as a white powder with a molecular mass of 61.81 g/mol, produced by POCh in Gliwice), 212 g (2 moles) of xylene (a mixture of o- and p-isomers, produced by Chempur in Piekary Śląskie, with water content above 0.1% and density of around 0.860–0.866 g/cm³), 876 g (3 moles) of N,N'-di(metylenooksy-5-hydroksy-pentylo)urea (yellow-brown liquid, with 1193 g/cm³ density, produced in the Chemistry and Technology of Polyurethane Department in Bydgoszcz). The flask content was kept at a boiling temperature for 510 min with constant and intense stirring. When the reaction ended and the stirring stopped, the reactive mixture was separated into an upper clear layer (xylene) and a light-blue bottom layer (new polyol). After cooling, the separated bottom layer was kept for 1 h in the temperature of 130°C in vacuum dryer under the pressure of 0.320 kPa to remove any solvent and water residue.

As a result of the conducted reaction, borane tri[N,N'-di(metylenooksyetylentio-2-hydroksyetylo)urea] was produced (**Scheme 1**).



Scheme 1. Reaction for obtaining borane tri[N,N'-di(metylenooksyetylentio-2-hydroksyetylo)urea].

Examining the physicomechanical properties of the new compound was the next step. The results of the examination helped determining the usability of the obtained borane as a polyol for the production of rigid polyurethane-polyisocyanurate foams. A polyol is a basic component of the polyurethane composition and it determines the properties of produced materials in a significant way. **Table 1** describes the physical properties of the new polyol.

The viscosity of the obtained borane is 283 mPa s; however, the density is 1300 kg/m³. The viscosity value of the new polyol does not exceed the viscosity value of industrial polyols (15,000 mPa s). Higher viscosity values of the raw materials used in polyurethane production

| Polyol's name | Properties | | | | | | |
|---|---------------------------|-------------------------------------|-------------------------|--------------------|------------|--------------------------|-----------------------|
| | Hydroxyl number (mgKOH/g) | Density (20°C) (kg/m ³) | Viscosity (20°C) (Pa s) | Mole mass (g/mole) | Colour | Nitrogen volume (%mass.) | Boron volume (%mass.) |
| Borane tri[N,N'-di(methylenoxyethylentio-2-hydroxyethyl)urea] | 430 | 1300 | 283 | 546 | Colourless | 9.7 | 1.3 |

Table 1. Borane properties.

are not advisable due to the technological limitations of standard equipment used for PUR processing, available on the market.

The structure of the new polyol indicated the presence of boron and nitrogen that have a significant influence on flammability. Based on the conducted calorimeter analysis with carminic acid, it has been noted that the boron value is 1.3% of the mass, and nitrogen value is 9.7% of the mass.

Hydroxyl number is an elementary parameter of a polyol which is important during the calculation of polyurethane composition. That is why it has been determined for the obtained boroorganic compound. The hydroxyl number is 380 mgKOH/g and is similar to its calculated theoretical value. It also proved that the compound is an interesting material for the production of rigid PUR-PIR foams.

The presence of water is also an important characteristic of polyols used for obtaining polyurethane foams. The amount of water needs to be precisely determined in those compounds because it can have a substantial influence on the foaming process during the reaction with the polyisocyanate. The amount of water in the obtained borane is lower than 0.1%. This value does not interfere with the process of foam production and does not have to be included in the recipe. The structure of the obtained borane compound was determined based on proton nuclear magnetic resonance spectrum ¹HNMR, using chloroform as the dissolvent. The results of ¹H NMR analysis of the polyol are represented in **Table 2** and **Figure 1**.

The presence of characteristic groups for obtained compounds was confirmed with the analysis of the spectrum of new boron compounds, using spectroscopy in infrared. The IR spectrum shows bands with frequencies typical for groups present in the new polyol. The results are presented in **Figure 2**.

| Hydrogen atom position | Chemical shift (ppm) | Number of hydrogen atoms |
|------------------------|----------------------|--------------------------|
| 1 | 3689–3609 | 3 |
| 2, 6, 11, 15 | 4693–4308 | 24 |
| 3, 4, 5, 12, 13, 14 | 1426–1294 | 36 |
| 8, 9 | 6995–6532 | 6 |

Table 2. Assigning signals in ¹H NMR spectrum to particular protons for borane tri[N,N'-di(methylenoxyethylentio-2-hydroxyethyl)urea].

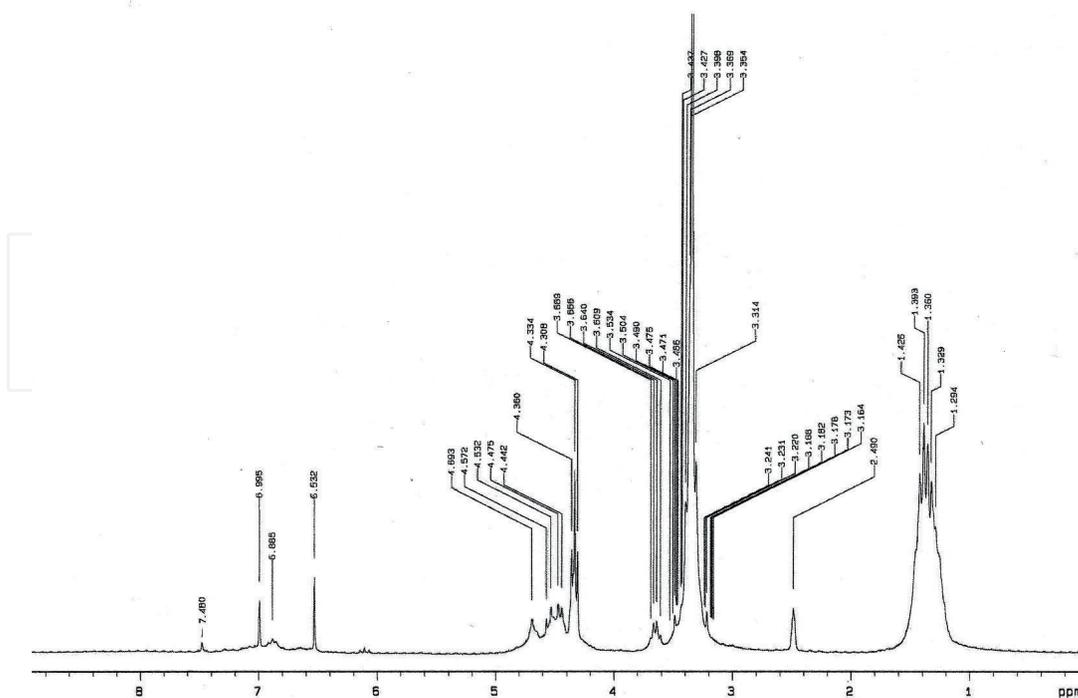


Figure 1. ^1H NMR spectrum of borane tri[N,N'-di(methylenoxyethylentio-2-hydroxyethyl)urea].

The IR spectrum shows, among others, characteristic bonds representing frequencies of NH-CO-NH bonds, at $1648\text{--}1654\text{ cm}^{-1}$, and in the $1290\text{--}1336\text{ cm}^{-1}$ for B-O bonds. Also, a band typical for hydroxyl group -OH appeared in the new polyol at the $2949\text{--}3556\text{ cm}^{-1}$ range which are also confirmed by the results of the determined hydroxyl groups.

2.3. Synthesis of rigid PUR-PIR foams in 18-dm³ mould

Foamed polyurethanes are usually produced based on a so-called polyurethane system which comprises two or more components that react during mixing and give the desired product. This article focuses on the examination of polyurethane-polyisocyanurate foams produced using two-component A+B system. The A component was obtained by mixing polyols (Rokopol RF-55 and N,N'-di(hydroxymethyl)urea derivative), catalysts, surface-active agent, and porophor. Component B on the other hand was polyisocyanate. Foams produced with this system are very simple and the process is not too energy intensive. However, the development of processing technology of foamed polyurethanes encountered a serious issue regarding the requirements for environmental protection. Developing a foaming agent that would be environmentally safe and, at the same time, would help producing materials with valuable properties is a great challenge for polyurethane manufacturers. In the presented research, carbon dioxide was used as the foaming agent which was exhausted during the reaction or water with isocyanate groups. Despite a common opinion that carbon dioxide slightly deteriorates the application properties of a polyurethane foam (heat conductivity, durability and brittleness), initial research on using the new polyol in the polyurethane composition shows a promising final product with beneficial properties. The basis for calculating the polyurethane recipe was the hydroxyl number

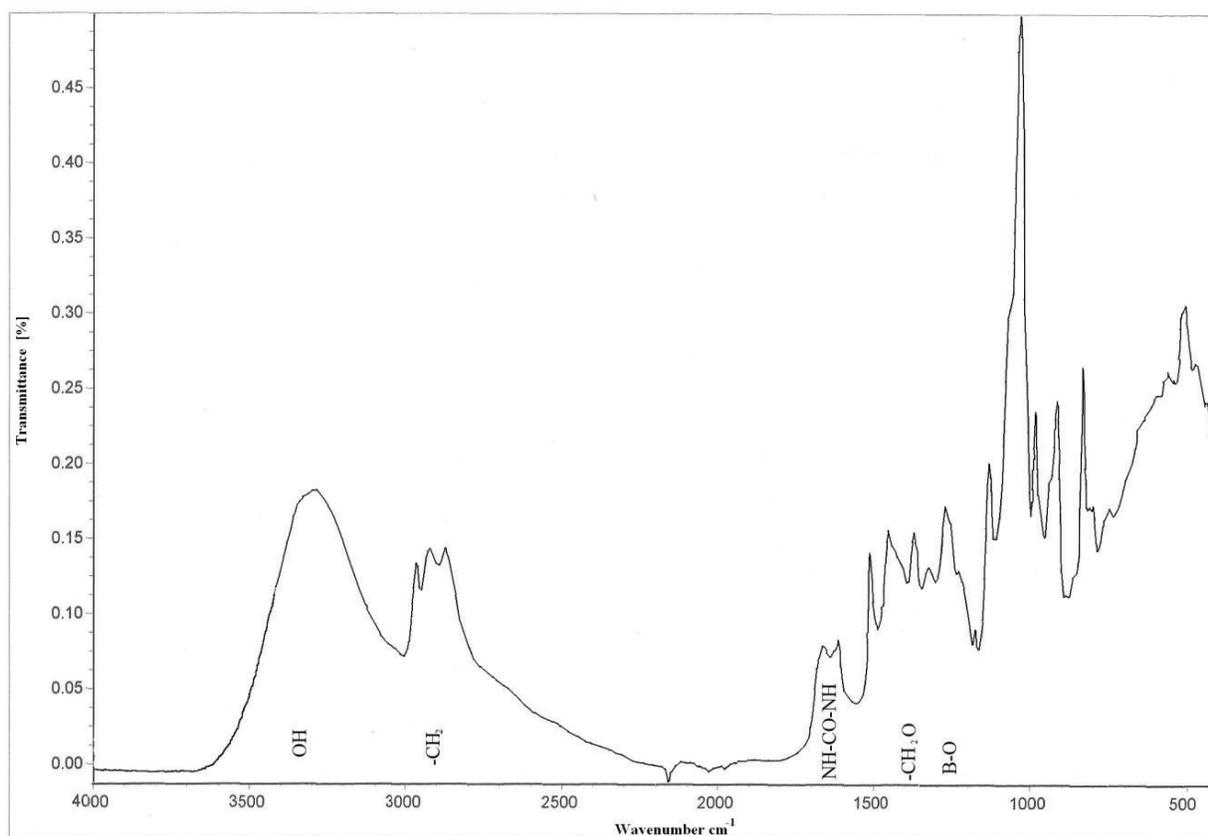


Figure 2. IR spectrum for bororganic compound recorded by KBr technique.

of the used polyols. Then, the values of auxiliary compounds which usually do not contain hydroxyl groups were determined, for example, catalysts, non-reactive flame retardants and surface-active agents. They were described in weighted portions in relation to 100 weighted portions of the polyol. The amount of isocyanate was selected with regard to the ratio of isocyanate groups to hydroxyl groups, which was set to 3:1 for rigid polyurethane-polyisocyanurate foams. The calculated amount of isocyanate was increased by the isocyanate mass needed to conduct a reaction with water, as a result of which CO_2 was exhausted—the gas which foams the reactive mixture. The recipes for obtained foams are described in **Table 3**.

When starting with the rigid PUR-PIR foam production based on the determined recipes (**Table 3**), polyisocyanate was measured in the first 1-dm³ polypropylene vessel, and polyol component polyol with added auxiliary substances was measured in the second vessel. The polyol was thoroughly mixed with other components using electric stirrer with 1800-rpm rotation speed.

The polyisocyanate was combined with the polyol component, stirred for 10 s and both were poured into a mould where the foam's rising process was observed. An open mould was used for the examination which enabled a so-called free-rising process.

During the first stage, the reference K0 foam was obtained, which did not contain any amount of the polyol, and then foams marked from K1 to K5 were produced by adding from 0.1 to 0.5 R of the polyol, respectively.

| | Unit | K0 | K1 | K2 | K3 | K4 | K5 |
|---|------|-------|-------|-------|-------|-------|-------|
| Rokopol RF-55 | R | 1 | 0.9 | 0.8 | 0.7 | 0.6 | 0.5 |
| | g | 55.65 | 50.98 | 44.78 | 31.35 | 18.81 | 9.40 |
| Borane tri[N,N'-di(methylenoxyethylentio-2-hydroxyethyl)urea] | R | 0 | 0.1 | 0.2 | 0.3 | 0.4 | 0.5 |
| | g | 0 | 6.26 | 12.52 | 18.78 | 25.04 | 31.31 |
| Silicone L6900 | g | 4.7 | 4.7 | 4.7 | 4.7 | 4.7 | 4.7 |
| DMCHA | g | 2.8 | 2.8 | 2.8 | 2.8 | 2.8 | 2.8 |
| Catalyst 12 | g | 6.5 | 6.5 | 6.5 | 6.5 | 6.5 | 6.5 |
| AntiblazeTMCP | g | 46.9 | 46.9 | 46.9 | 46.9 | 46.9 | 46.9 |
| Water | R | 0.7 | 0.7 | 0.7 | 0.7 | 0.7 | 0.7 |
| | g | 3.15 | 3.15 | 3.15 | 3.15 | 3.15 | 3.15 |
| Ongromat 30-20 | R | 3.0 | 3.0 | 3.0 | 3.0 | 3.0 | 3.0 |
| | g | 250.6 | 250.6 | 250.6 | 250.6 | 250.6 | 250.6 |

Table 3. The recipes for rigid PUR-PIR foams.

During the polyurethane-polyisocyanurate foam synthesis, the foaming process of the reactive mixture was monitored, and with the help of a stopwatch, the start time, expansion time and gelation time were measured.

Start time is the time measured with a stopwatch from the moment of mixing the components, up to when the foam reached a 'cream state'. It is indicated by the increasing volume of the foam.

Rising time is the time measured with a stopwatch from the moment of mixing the components, up to reaching the maximum volume of the foam.

Gelation time is the time measured with a stopwatch from the moment of mixing the components, up to the moment when the free surface of the foam stops sticking to a clean glass rod.

2.4. Methodology of rigid PUR-PIR foam production

The examination of apparent density was conducted after 24 h of seasoning of the samples in room temperature, according to ISO 845-1988 standard. The apparent density was determined for all the examined samples. The samples were measured with an accuracy up to 0.01 mm and weighted with an accuracy up to 0.01 g.

The brittleness of examined foams was determined according to the ASTM C-421-61 standard. Based on that standard, the brittleness was measured as a percentage mass loss of 12 foam cubes (square cubes with 25 mm sides), during an examination in normalized apparatus, in relation to the initial mass. The apparatus for measuring PUR foam brittleness was a cubical box made out of oak wood, with dimensions of 190 × 197 × 197 mm, rotating along its axis with the speed of 60 rounds per min. The box was filled with 24 oak cubes with the dimensions of 20 × 20 × 20 mm.

The determination of water absorption was conducted in accordance with DIN 53433 standard. This method measures the hydrostatic buoyancy of the sample with the dimensions of $150 \times 150 \times 25$ mm, submerged in distilled water for 24 h.

Thermo-insulating properties of the produced foams were determined by measuring the heat conductivity coefficient λ . Samples with dimensions of $200 \times 200 \times 25$ mm were used for the test. FOX 200 apparatus by Lasercomp was used during this examination. It enables the determination of λ -value in the range of 20–100 mW/(m K). The measurement chamber needs to be fully filled to conduct proper examination.

The heat conductivity coefficient measurement method measures the amount of heat transported through the sample material in a unit of time during the determined heat flow, that is, when the temperature difference is measured on the opposite sides of the examined sample. The measurements are performed in series, in 0.5-s intervals.

Compressive strength was determined by the use of general-purpose strength machine (Instron 5544). The peel and flanks of foam were cut off and the cubic samples were cut out (side of 50 ± 1 mm). Then, the samples were subjected to compressive strain by 10% according to the direction of foam expansion.

The content of closed cells was determined in compliance with PN-ISO 4590 standard, using defect-free samples with the dimensions of $100 \times 25 \times 25$ mm. The method utilizes the Boyle–Mariotte law. It determines a relative pressure decrease based on calibrated volume patterns, measuring the difference on the scale of a manometer with one arm opened to the atmosphere.

The retention (remains after burning) of the PUR-PIR foams was examined according to ASTM D3014-73 standard, by performing the vertical test. The apparatus used for the burning examination using the vertical test had a vertical chimney with $300 \times 57 \times 54$ -mm dimensions. Three of the walls were made out of tin and one was a removable glass wall. The test was conducted on six samples with dimensions of $150 \times 19 \times 19$ mm. Before burning, the samples were weighted with an accuracy up to 0.0001 mm and placed inside the chimney. The glass was placed in place and flame was introduced to the samples from propane-butane burner for 10 s. Then, the burner was moved away and the times of free burning and retention were measured with a stopwatch in the vertical test. Retention was calculated using Eq. (1):

$$R_e = \frac{m}{m_0} \times 100\% \quad (1)$$

where R_e is the retention; m_0 is the sample mass before burning (g), m is the sample mass after burning (g).

Using the cone calorimeter, the examination of flame and smoke parameters was conducted for the produced PUR-PIR foams based on the methodology described in the ISO 5660-1:2001 norm.

Normalized samples with dimensions of 100×100 mm were subjected to heat radiation. During the examination, the following parameters were recorded: the time needed to initiate the burning process, thermokinetic parameters, that is, heat exhaustion rate and the total amount of exhausted heat, and selected toxic and smokegenic properties. The thermokinetic

values were measured using the theory of oxygen usage calorimetry, which states that out of 1 g of used oxygen, there are around 13.1 kJ of heat produced with accuracy up to $\pm 5\%$. The examination was conducted for material samples placed horizontally and the burning reaction was initiated by combustion. The material samples were exposed to heat radiation of 30 kW/m^2 . The examination ended after the burning process faded completely. The temperature distribution during burning was measured using a Vigo V-20E2-25 thermal imaging camera equipped with HgCdTe thermoelectrically cooled detector. The measurement conditions were compliant with conditions for determining the oxygen index (OI).

The oxygen index (OI) was determined in compliance with the methodology described in the ASTM D 2863-1970 standard. It measures the boundary concentration of oxygen in oxygen and nitrogen mixture, sufficient for sustaining burning of a sample with the dimensions of $150 \times 13 \times 13$. The oxygen index was calculated in percentile value according to Eq. (2)

$$\text{OI} = \frac{\text{O}_2}{\text{O}_2 + \text{N}_2} \times 100\% \quad (2)$$

where O_2 is the volumetric flow rate of oxygen for the boundary volume (m^3/h), N_2 is the volumetric flow rate of nitrogen for the boundary oxygen volume (m^3/h).

The examination of cell structure was performed using HITACHI S-4700 scanning electron microscope (SEM) with NORAN Vantage microanalysis system. The reference sample (containing petrochemical polyol) and the modified sample with the largest amount of boron polyol were tested.

IR spectroscopy was used to identify characteristic groups present in PUR-PIR. The polyurethane foams were milled in Janetzky's mill before they were tested with the IR method. The analysis of the milled samples was performed with KBr technique on Bruker spectrophotometer in the range from 200 to 4000 cm^{-1} .

3. Examination results and their analysis

3.1. The influence of raw materials on the density and processing times of the obtained foams

The process of creating PUR-PIR foams is very complicated from the chemical point of view. Additionally, there may be technological issues which make the examination of the foaming process of the PUR composition necessary to obtain products with beneficial properties. The foaming process is an important stage in the production of polyurethanes. Here, the cell structure is formed which significantly influences the application properties of the material. During rigid PUR-PIR foams production, processing times (start time, rising time and gelation time) have been determined. Based on the conducted research, different times can be observed of the foam surface losing its adhesiveness. It is dependent on the type of medium (air, mould wall) that the rising foam's surface is touching. The air causes the foam to lose its

| Foam symbol | Start time (s) | Rising time (s) | Gelation time (s) | Density (kg/m ³) |
|-------------|----------------|-----------------|-------------------|------------------------------|
| K0 | 8 | 15 | 31 | 33.4 |
| K1 | 6 | 14 | 27 | 40.3 |
| K2 | 5 | 10 | 25 | 40.6 |
| K3 | 4 | 10 | 21 | 40.8 |
| K4 | 4 | 9 | 20 | 41.3 |
| K5 | 3 | 8 | 16 | 41.5 |

Table 4. Processing parameters and apparent density of rigid PUR-PIR foams.

adhesiveness the quickest. Apparent density was also measured for the rigid foams and the results of all tests are represented in **Table 4**.

The processing times of modified foams were reduced by about 50% in comparison to the reference foam. The start time for P0 reference foam was 8 s; however, for the foam containing 0.5 R of the boron polyol, it was 3 s. Similar changes were observed for rising and gelation times. This shows a higher reactivity of the boron-nitrogen polyol in comparison to the industrial one.

Apparent density is one of the most important factors that determine the mechanical properties of rigid PUR foams. From the economical point of view, it is beneficial to produce materials with the lowest possible apparent density. Nevertheless, the apparent density of a PUR foam is in close correlation with its thermo-insulation properties, mechanical properties and dimensional stability. That is why the most commonly used rigid polyurethanes have the density values in the range of 30–60 kg/m³. By using the new boron polyol, a slight increase in the density of produced PUR-PIR foams was observed in comparison to the reference foam. Foam density is in the range from 33.4 kg/m³ for K0 foam up to 41.5 kg/m³ for K5 foam, containing 0.5 R of the new polyol. The decrease in the apparent density of K1–K5 PUR-PIR foams is related to the amount of the boron introduced to the PUR system. By replacing the petrochemical polyol (with 9200 mPa s viscosity) with the boron polyol (with viscosity 283 mPa s), the total viscosity of the premix containing the new polyol was decreased. The amount of water used as a chemical foaming agent stayed at the same level for all recipes and generates the same amount of CO₂.

3.2. Influence of raw material type on thermo-insulating properties of obtained PUR-PIR foams

Rigid foams are mainly used as thermo-insulating materials. That is why a low heat conductivity of those materials is one of their most sought-after characteristic. The thermo-insulating properties of the obtained foam materials were determined by measuring the heat conductivity coefficient λ and the amount of closed cells (**Table 5**).

Rigid polyurethane-polyisocyanurate foams are cellular materials, where the amount of closed cells is significantly more prominent, and the share of open pores is in the range of

| | K0 | K1 | K2 | K3 | K4 | K5 |
|--|------|------|------|------|------|------|
| Heat conductivity coefficient λ (mW/m K) | 30.7 | 26.4 | 26.4 | 26.5 | 26.5 | 26.5 |
| Amount of closed cells (%) | 83.2 | 92.5 | 92.6 | 92.5 | 92.5 | 93.0 |

Table 5. Value of heat conductivity coefficient and amount of closed cells in obtained foams.

5–10%. At the same time, the amount of closed pores is dependent on their size. The gas closed in the foam cells and also the structure of a polyurethane matrix (but to a lesser degree), both take part in the heat flow process. The boron polyol used in the rigid PUR-PIR foam production causes an increase in the amount of closed cells in comparison to the K0 reference foam. The amount of closed cells in K0 foam is 83.2%. For foams containing tri[N,N'-di(methylenoxyethylentio-2-hydroxyethyl)urea], the amount of closed cells ranges from 92.9%, K1 foam, to 93%, K5 foam. It has been determined that the amount of new polyol does not influence the amount of closed cells; however, the application of those polyols during foam production has been significant. All rigid PUR-PIR foams obtained with the use of the new boron polyol have over 90% of closed cells. The increase in this number is not indifferent towards the value of the heat conductivity coefficient of those foams. In rigid foams designated for thermal insulation, the definite majority of cells should be closed so that the foaming gas could remain enclosed within the material. The value of the heat conductivity of the gas closed in cells comprises over 80% of the total value of heat conductivity coefficient of rigid polyurethanes. It is mostly dependent on the type of porophor, foam density and the amount of closed cells. It is worth keeping in mind that the thermo-insulating properties change during foam exploitation. It is with correlation to the changes in the composition of the gas mixture in the cells. By choosing the chemical method of foaming PUR-PIR foams, porous materials were produced that contained carbon dioxide in the cells. The polyurethane's cell walls are permeable for carbon dioxide which diffuses into the outside during material use due to its small particles. Then, oxygen takes place of the carbon dioxide. Foams that do not have a solid protective coating lose their initial insulating properties very quickly. **Figure 3** represents the changes in the values of heat conductivity coefficient for K0 and K5 foams in relation to the amount of days they were used.

It can be observed that the changes in the values of heat conductivity coefficient during the ageing process take longer time in the structures with the boron polyol. In the initial stage, the heat conductivity coefficient for the K0 reference foam was 30.7 mW/mK. During foam exploitation in room temperature, the λ -coefficient value increased to 37.2 mW/mK after 120 days. However, in the K5 foam, the initial λ -coefficient value was 26 mW/mK. During the ageing process in room temperature, the coefficient value increased to 28.9 mW/mK. The decreased heat flow in the foam modified with the new polyol is related to its more organized structure and larger amount of closed cells.

The heat conductivity coefficient depends mainly on the cell structure in the final product. That is why a thorough analysis of the cell structure is so important. At an early stage of the foaming process, there is a chain of reactions that start with the creation of micro-bubbles.

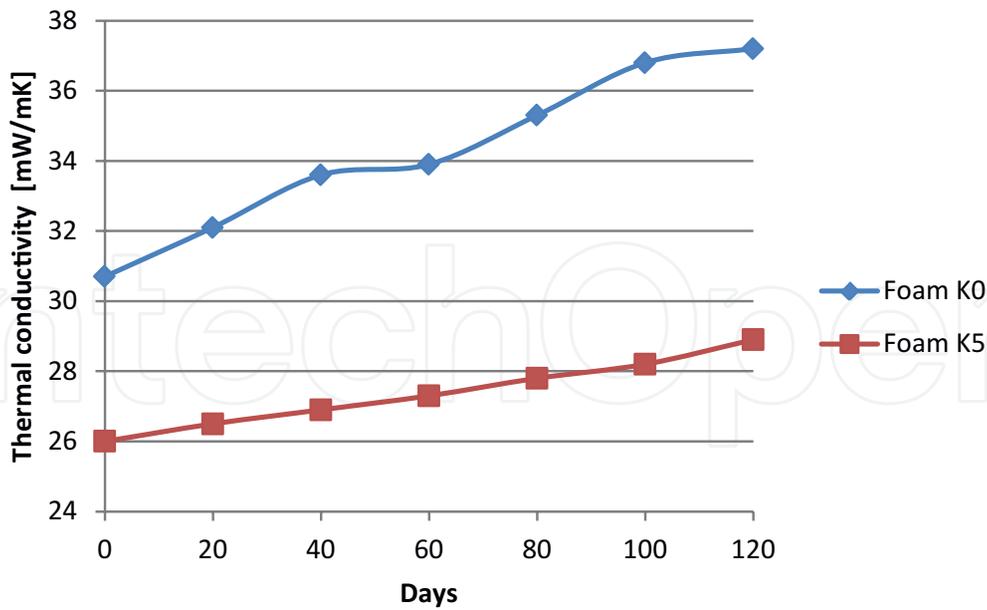


Figure 3. Changes in the values of heat conductivity coefficient for foam during ageing process in room temperature.

The cell growth comes next and is related to the porophor evaporation. Growing cells start to touch. Cell walls start to form in a form of thin membranes and ridges in the place where three cell walls meet. The construction stability is dependent on the chemical composition of the walls and ridges, and the size and shape of cells. The pictures of the obtained rigid foams using SEM method are depicted in Figure 4.

By analysing the SEM pictures of the cell structure, it can be observed that they depict internal closed-cell structure of the produced foams. The applied boron polyol supports the surface-active agent by creating more regular and smaller cells. By examining the shape of the closed cells in the photographs, it can be easily seen that the addition of boron polyol to the foam recipe contributes to a more uniform cell structure in comparison to the reference foam.

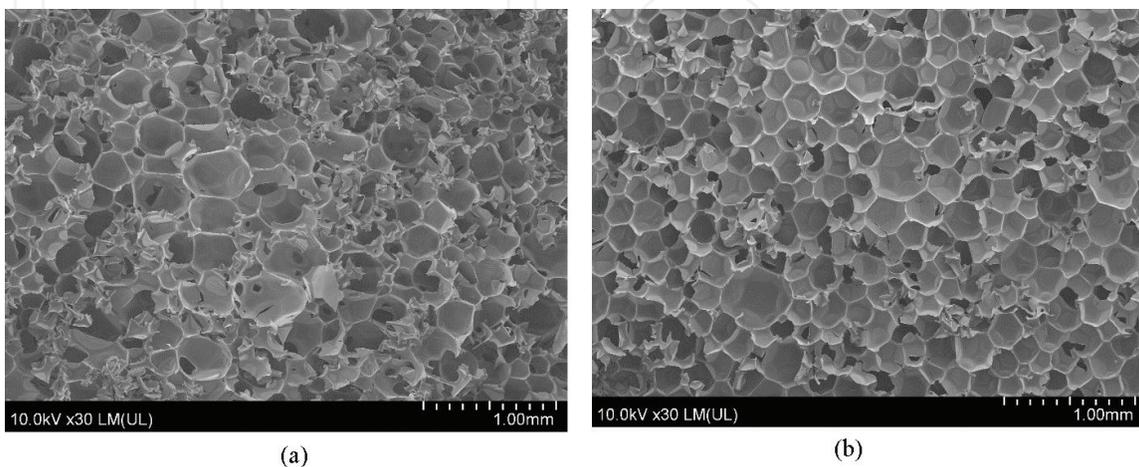


Figure 4. Cell structure of PUR-PIR foams: (a) K0 foam and (b) K5 foam.

3.3. Mechanical properties and dimensional stability of produced PUR-PIR foams

The structure of the polyurethane matrix has a significant influence on the mechanical properties and the durability of the cells in foam materials. By changing the recipe of the foams, some characteristics of the final product can be modified. However, the greatest significance in the shaping of PUR foam's mechanical properties is due to the apparent density and cell structure. The new boron polyol used in the foam composition improved the mechanical properties of the obtained rigid polyurethane-polyisocyanurate foams. **Table 6** presents the examination results of compressive strength, brittleness, water absorption and ageing.

The research conducted on mechanical properties of PUR-PIR foams helps determine that the new boron polyol significantly improves those properties. The compressive strength measured in a perpendicular direction increased after using the boron-nitrogen polyol in the foam production. The value increases along with the amount of the equivalent of the boron compound used in the foams. For the reference foam (without boron), the compressive strength is 238 kPa. For other foams, in which the petrochemical polyol Rokopolu RF-55 was subtracted to add the boron polyol, this value was in the range from 273 kPa (K1 foam with 0.1 R of borane tri[N,N'-di(methylenoxyethylentio-2-hydroxyethyl)urea]) to 339 kPa (K5 foam containing 0.5 R of borane tri[N,N'-di(methylenoxyethylentio-2-hydroxyethyl)urea]). The increase in compressive strength has to be correlated with the apparent density of the PUR-PIR foams (**Figure 5**).

The mechanical strength measured according to the foam's growth direction is usually higher than the one measured perpendicularly to the growth, because the cells are elongated in the direction in which the foam grows. The improvement in strength measured perpendicularly can be attributed to the changes in foam's morphology, that is, increased amount of polar urea groups capable of creating hydrogen bond. Additionally, the closed-cell structure gives the materials better compressive strength, in comparison to materials with large open cells.

The boron polyol used in the production of rigid polyurethane-polyisocyanurate foams reacts with the polyurethane composition in a way similar to a typical crosslinking compound, helping create a more unified foam structure. Because of that, the examination of brittleness

| Foam | Compressive strength (kPa) | Brittleness (%) | Water absorption (%) | Mass loss (%) | Changes in linear dimensions (%) | Changes in volume (%) |
|------|----------------------------|-----------------|----------------------|---------------|----------------------------------|-----------------------|
| K0 | 238 | 36.2 | 1.98 | 0.6 | 1.9 | 1.8 |
| K1 | 273 | 11.9 | 0.85 | 0.4 | 1.8 | 1.4 |
| K2 | 288 | 10.2 | 0.86 | 0.4 | 1.3 | 1.7 |
| K3 | 295 | 9.6 | 0.86 | 0.9 | 1.5 | 1.5 |
| K4 | 326 | 8.4 | 0.86 | 0.8 | 1.1 | 1.3 |
| K5 | 339 | 8.0 | 0.85 | 0.6 | 1.6 | 1.7 |

Table 6. Mechanical and ageing properties of the rigid PUR-PIR foams.

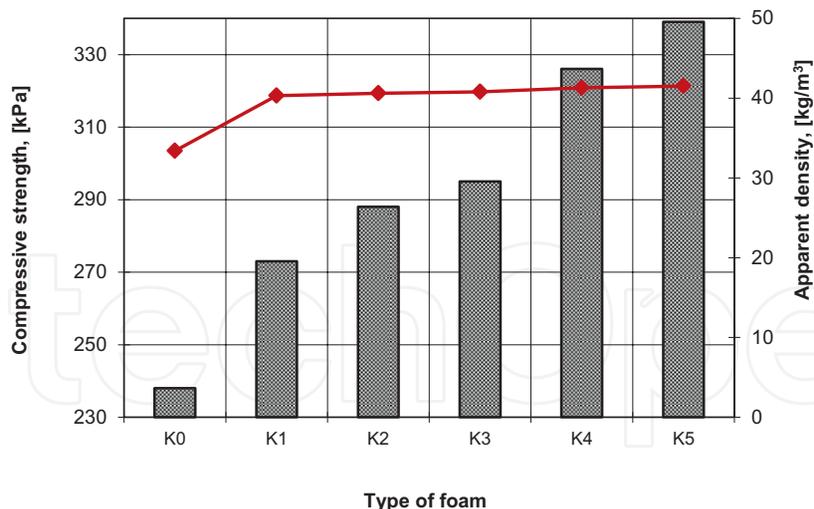


Figure 5. The correlation between compressive strength and apparent density, and the amount of boron polyol in the foams.

helped determine that the addition of the boron polyol into the foam recipe causes significant decrease in the foam's brittleness. The higher the amount of boron polyol in the foams, the lower the brittleness, from 36.2% for K0 reference foam to 8% for K5 foam modified with the new polyol. Similar to the compressive strength, the brittleness examination of the obtained foams shows a correlation between this value and the apparent density of the samples. Higher apparent density of PUR-PIR foams enables a significant decrease in their brittleness.

There is also a correlation between the compressive strength and the linear dimension stability. Along with the changes in the temperature, the internal pressure of the gas inside the cell changes. It creates a difference in pressure between foam cells and external atmospheric pressure. This difference of pressures needs to be lower than the foam's compressive strength to retain its dimensional stability. Foam deformation should not occur when the compressive strength is greater than 100 kPa, which is a value higher than the possible difference between atmospheric pressure and the pressure inside foam cells, which is close to zero. When comparing the results of the ageing test for the produced rigid PUR-PIR foams, it was determined that there is a strong correlation between the stability of linear dimensions, mass loss and changes in volume, and the use of the new polyol in foam recipe. During the simulated ageing of the samples, it was observed that mass loss did not exceed 1% for all foams. Similarly, the changes in linear dimensions did not exceed 2%. This qualifies those products for the use in thermal insulation.

3.4. Combustible properties of rigid PUR-PIR foams with new polyol

Rigid global statistical studies regarding fires in the recent years show that vast majority of fatal accidents during fires (60–80%) was caused by inhaling the products of thermal decomposition and burning, as well as limited visibility due to the generated smoke. The cause of a smoke with higher density and toxicity is incomplete burning of the gas phase. It also increases the ratio between carbon oxide and carbon dioxide, which makes the smoke more toxic. That is why the best way to lower the combustible properties of polyurethane materials is to produce

them with raw materials that will help obtain a polymer with slow burning speed and low burning efficiency of flammable gas phase. Despite the obstruction of material combustion and limitation of flame spreading, the antipirene should not affect the processing and should not worsen the application properties of the product. The tendencies of boron and nitrogen atoms for supplementing and strengthening flame-retardant properties were used to determine the boron polyol. The percentage value of those atoms in the new polyol is around 14%; hence, positive results can be expected for the examination of non-halogen method of lowering the burning of new foams. Boron participates in endothermic reactions, whose end result is the release of water and creation of protective glasslike layer. This layer protects the base from oxygen and heat from the flame. Nitrogen compounds, on the other hand, decompose into gas products that take part in creating foamed carbon layers in the condensed phase. After reaching the gas layer, they burn and become free radical scavengers.

In order to test the foam behaviour in flame, various tests were conducted. Cone calorimeter method helps to define burning properties of the material and to characterize the reactions that take place during the burning process. The comparison of parameters of the pyrolysis process in selected rigid polyurethane-polyisocyanurate foams obtained with the use of new boron polyols has been presented in **Table 7**.

The produced rigid polyurethane-polyisocyanurate foams with the new polyol (K1 and K5), as well as the K0 reference foam (containing only the petrochemical polyol), were subjected to the burning process using cone calorimeter method. For the K0 reference foam, the combustion time was very short and equalled 1.48 s. The same time is characteristic for materials with porous structure that are highly flammable. After introducing the boron polyol to the foam recipe, the combustion time was significantly longer. For the K5 foam, containing the highest amount of the new polyol, the time was 14 s. On the other hand, in the K1 foam, containing the least amount of the polyol, the combustion time was shortened to 7 s. During the burning test using cone calorimeter method, the total heat release (THR) value was also measured, which determines the total heat released by the burning foam. The largest amount of heat, equalling 14.3 MJ/m², was released while testing the K0 reference foam. The use of the new polyol in the composition helped lowering the THR value, not exceeding 4 MJ/m². The total heat release value was the lowest for the K5 reference foam, with the largest amount of the boron polyol. The THR value can indicate that the new polyol shows cooling properties, by lowering this parameter by around 80%.

| Foam symbol | Average time to steady combustion (T_{comb}) (s) | Total heat released (THR) (MJ/m ²) | Average mass loss rate (MLR) (gm ² /s) | Maximum heat release rate (HRR) (kW/m ²) | Time to reach max. HRR (s) | Amount of CO released (g/g) | Amount of CO ₂ released (g/g) | Oxygen index (%) |
|-------------|--|--|---|--|----------------------------|-----------------------------|--|------------------|
| K0 | 1.48 | 14.3 | 10.22 | 278.90 | 10 | 1.352 | 11.2 | 19.6 |
| K1 | 7.00 | 3.7 | 7.03 | 221.21 | 27 | 0.589 | 1.6 | 23.2 |
| K5 | 14.36 | 2.8 | 4.87 | 189.77 | 37 | 0.243 | 1.1 | 26.4 |

Table 7. Results of flame tests in selected rigid PUR-PIR foams.

The path of the heat release rate (HRR) curves shows information regarding the mechanism of lowering the flammability, which depicts the maximum value of the heat release rate. It is a very important parameter and an indicator of the material's tendency to self-extinguish in case of fire. The HRR values in **Table 8** were determined for data from the moment of combustion until the end of the test. **Figure 6** presents the curves showing the course of heat release (HRR) in the new foams.

The HRR curves of rigid PUR-PIR foams modified with the new polyol and the non-modified foam show subsequent stages of the burning process. It can be observed that initially the foams become warm, then the volatile parts and flammable gas products are produced. The burning of gases is the reason for creating large amounts of heat. The curves indicate that for the K0 reference foam, the rate of released heat is very energetic. Also, the flame on this foam is sustained. However, the foams modified with the new polyol burn in less rapid manner and reach lower values of heat release. The elongation of maximum HRR time value from 10 s (K0) to 37 s (K5) also shows flame-retardant properties of boron polyols.

The amount of exhausted CO is much higher for the reference foam than for the foams modified with the new polyol. Carbon oxide in the reference foam was emitted in the amount of 1.352 g/g. After using the boron polyol, the amount of carbon oxide was lowered almost four times, until reaching 0.243 g/g value for the K5 foam, containing 0.5 R of borane tri[N,N'-di(methylenoxyethylentio-2-hydroxyethyl)urea]. Similar correlation can be seen in the carbon dioxide emission during the burning test. The conducted analysis of carbon oxide and dioxide emissions uniformly indicates that the new boron polyol is an effective addition that reduces the amount of gases produced during a fire. Rigid polyurethane-polyisocyanurate foams with the new polyol have substantially longer time value for permanent combustion than the reference foam.

The oxygen index for the reference foam is 19.6%; however, in foams with borane polyol it is in the range from 23.2% (K1 foam) to 26.4% (K5 foam). By using the oxygen index method, it has been determined that the presence of the new polyol in the PUR-PIR foam helps reducing flammability of this material by about 21%. During the examination in cone calorimeter, foams modified with the new polyol produced less charred residue. Also during this test, it was observed that the K5 reference foam did not burn but rather glowed. It is caused by minor mass loss of this foam (4.87 gm²/s) during the burning test. The speed of fire spreading, flash-over, is an important parameter used for the comparison of different materials with regard to fire safety. It is the value opposite to time to reach flashover ($1/t_{\text{flashover}}$) (Eq. (3)) [14]:

| Foam sample | $1/t_{\text{flashover}}$, fire hazard (kW/m ² s) | RTFH _{CO/CO₂} , relative toxic fire hazard |
|-------------|--|--|
| K0 | 188.4 | 2.8745 |
| K1 | 31.6 | 0.1655 |
| K5 | 13.2 | 0.0238 |

Table 8. Properties of selected rigid PUR-PIR foams determining their behaviour during fire.

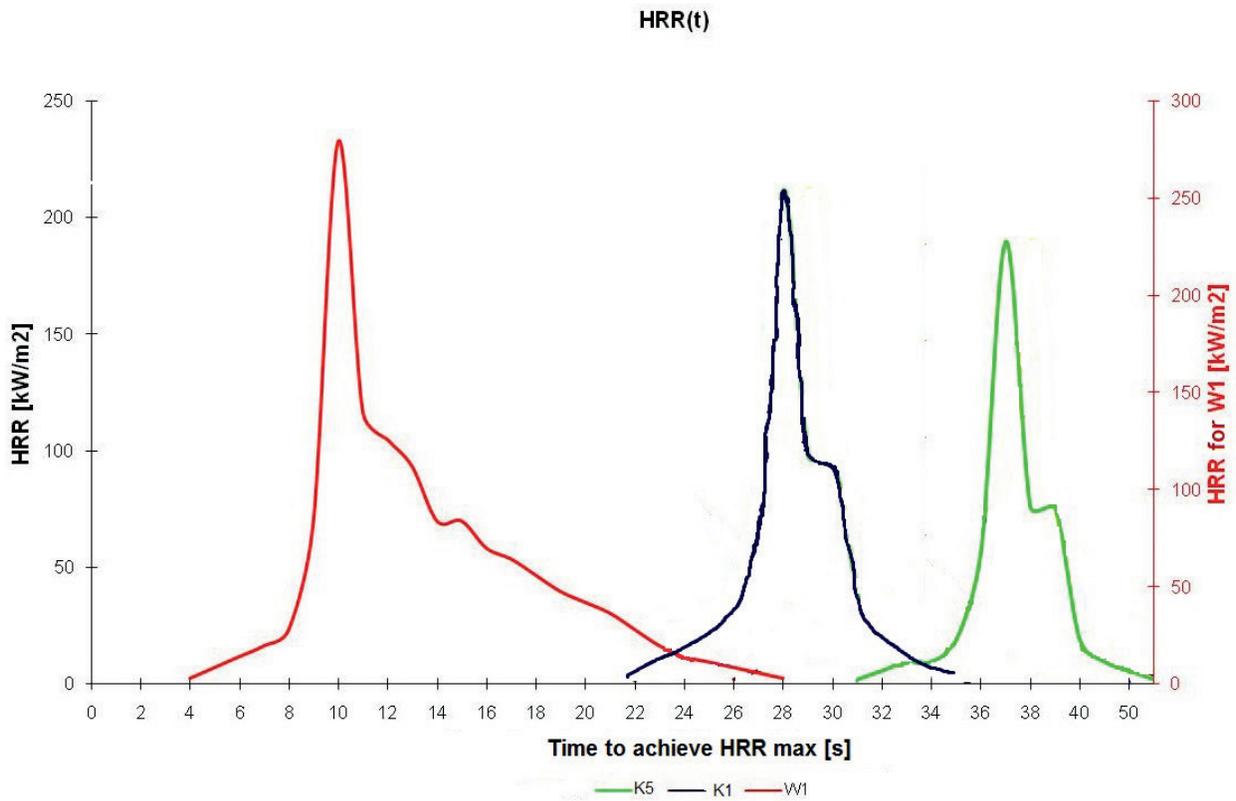


Figure 6. Heat release rate (HRR) for rigid PUR-PIR reference foam and foams containing new polyols (chart from cone calorimeter).

$$\frac{1}{t_{\text{flashover}}} = \frac{\text{HRR}_{\text{max.}}}{T_{\text{comb.}}} \quad (3)$$

where $\text{HRR}_{\text{max.}}$ is the maximum heat release rate; $T_{\text{comb.}}$ is the time to combustion.

Relative toxic fire hazard (RTFH) is another parameter that can help determine the fire danger rating. In this research, the determined RTFH indicators relate to carbon oxide and dioxide, because the use of cone calorimeter can measure only CO and CO₂ emissions. Those indicators are calculated according to Eq. (4):

$$\text{RTFH}_{\text{CO/CO}_2} = \frac{\text{MLR}}{\text{TTI}} \cdot \left(\frac{\text{CO yield}}{\text{LC}_{50}^{30} \text{CO}} + \frac{\text{CO}_2 \text{ yield}}{\text{LC}_{50}^{30} \text{CO}_2} \right) \quad (4)$$

where MLR is the average mass loss rate; CO yield is the average CO emission; CO₂ yield is the average CO₂ emission; LC₅₀³⁰ CO and LC₅₀³⁰ CO₂ are the lethal concentration of CO and CO₂, respectively, causing death of 50% of tested animals during 30-min exposition, in accordance with PN-88/B-02855.

The results of examined fire hazard related to the flashover and toxicity during the burning process of selected rigid PR-PIR foams are represented in **Table 8**.

The calculations show that the danger related to the speed of fire spread ($1/t_{\text{flashover}}$) in the tested rigid PUR-PIR foams can be lowered by using the new boron polyol. The value decreased

from 188.4 kW/m²s for the reference foam to around 13 kW/m²s for the K5 foam, containing the largest amount of boron polyol. When looking at the values of carbon oxide and dioxide emissions, it can be stated that the use of the new boron polyol helps reducing the toxic fire hazard for the obtained rigid PUR-PIR foams. The toxic fire hazard for the K0 reference foam is 2.8745; however, the use of the new polyol in the foam production decreased this value by around 99%.

4. Summary

The examination results presented in this paper are the answer for the search of fire-safe polyurethanes with good application properties. The study proved that the modification of the premix for polyurethane foam production can give the foams the desired properties. The right selection of polyol materials, isocyanate and auxiliary compounds during the recipe creation is very important. Including the boron polyol in the foam recipe allowed obtaining new thermo-insulating material with good physicomechanical properties. The research showed that the new compound, which was a derivative of N,N'-di(methylenoxy-3-hydroxypropyle)urea and boric acid, could be used as a polyol in the production of polyurethane materials, and simultaneously act as flame-retardant agent. Complex study on the flammability conducted using various methods helped assessing the behaviour of produced rigid polyurethane-polyisocyanurate foams in case of fire. The research proved that the use of the new polyol, containing boron and nitrogen atoms, increased flame resistance. The efficiency of this resistance was mainly shown by the total value of released heat, prolongation of the time for steady combustion, lower amount of carbon oxide and dioxide emission, increase in the oxygen index and by the lower maximum burning temperature reached in shorter time in comparison to the reference foam.

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