

New Compounds for Production of Polyurethane Foams

Joanna Paciorek-Sadowska, Bogusław Czupryński

Casimir the Great University, Chodkiewicza str. 30, 85-064 Bydgoszcz, Poland

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ABSTRACT: A method of boroorganic compound preparation with boric acid, 1,3-propanediol, 2,3-butanediol, and 1,4-butanediol is described in this article. The obtained compounds were characterized with respect to their usability as polyol components for the production of polyurethane (PUR) foams. New boroorganic compounds were applied as polyol components for the foaming of rigid PUR–polyisocyanurate (PIR) foams. The method of preparation, foaming parameters, and physicochemical properties of the PUR–PIR foams and their results are presented.

Application of the prepared borates as polyol components in the production of foams had a favorable effect on the properties of the foams. The obtained rigid foams were characterized by lower brittleness, higher compressive strength, content of closed cells, and considerably reduced flammability in comparison with standard foams. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 5918–5926, 2006

Key words: mechanical properties; modification; polyurethanes; thermal properties

INTRODUCTION

Rigid polyurethane (PUR) foams are widely applied as heat-insulating and construction materials. Therefore, they must have both a low heat conductivity and a suitable mechanical strength at a relatively low density.

During the last decade, fundamental changes have taken place in PUR systems applied to prepare rigid foams, which have mainly been caused by the necessity to eliminate physical porophors that have a detrimental effect on the ozonosphere.^{1,2}

Nowadays, water-blown foams, that is, foams obtained by the foaming process with the use of carbon dioxide generated in a reaction of water with an isocyanate component, have generated interest. Unfortunately, PUR foams expanded by carbon dioxide are characterized by a relatively high heat conductivity and a higher brittleness in comparison with foams expanded by fluorohydrocarbons or pentane isomers.^{3–5} That is why the investigations carried out in various research centers all over the world have been focused on attempts to find chemical compounds whose introduction into the receipt (premix) would improve the processing properties of raw materials and whose use would not change the suitable functional properties of the final product.

The mass production of PUR materials results in an escalation of requirements concerning both the products and the production technology. The feature limiting the application of nonmodified PUR foams

is their flammability.⁶ Results of studies on flammability of PURs has proven that new chemical compounds introduced into the foam structure cause changes in the foam properties. When these results are taken into account, research works are focused on attempts to compose recipes applicable for the production of foams with reduced flammability and unchanged or better mechanical properties.^{7,8}

The aim of this study was to obtain new multihydroxyl compounds containing boron to improve the physicochemical properties of rigid PUR–polyisocyanurate (PIR) foams and to reduce foam flammability when added to receipt. Moreover, attempts were undertaken to partially substitute the oligoetherols (Organic Industry Plants Rokita, Brzeg Dolny, Poland) with the obtained multihydroxyl compounds in the receipt for the production of foams. The new compounds were prepared from boric acid and various diols on a laboratory scale in the Faculty of Chemistry, Technology of Polymers and Ecotechnology, Casimir the Great University in Bydgoszcz, Poland.

EXPERIMENTAL

Characteristics of the raw materials

Pure boric acid (H_3BO_3) in the form of a white powder with a molecular weight of 61.84 g/mol and diols purchased from Polish Chemical Reagents (Gliwice, Poland) were used to prepare new boroorganic compounds. The selected characteristics of the diols according to the producer's specifications are listed in Table I.

Correspondence to: J. Paciorek-Sadowska (sadowska@ukw.edu.pl).

TABLE I
Some Properties of the Diols Used to Prepare the Boroorganic Compounds

Compound used to prepare borate	Formula	Molecular weight (g/mol)	Density (g/cm ³)	Boiling point (°C)	Melting point (°C)
1,3-propanediol	HO(CH ₂) ₃ OH	76.10	1.053	214	-26
2,3-butanediol	CH ₃ (CHOH) ₂ CH ₃	90.12	1.002	181	19
1,4-butanediol	HO(CH ₂) ₄ OH	90.12	1.014	230	16

A polyether with the trade name Rokopol RF-55 (a product of the oxypropylation of sorbitol [hydroxyl number (L_{OH}) = 495.0 mg of KOH/g], NZPO Rokita, Brzeg Dolny, Poland) and Ongromat CR 30-20 (a technical polyisocyanate whose main component was diphenylmethane 4,4'-diisocyanate, Hungary) were used to prepare the rigid PUR-PIR foams. The density of Ongromat CR 30-20 at 25°C was 1.23 g/cm³, its viscosity was 200 mPa s, and the content of NCO groups was 31.0%. The polyether and polyisocyanate mentioned previously were characterized according to ASTM D 2849-69 and ASTM D 1638-70.

Anhydrous potassium acetate (Gliwice) applied in the form of a 33% solution in diethylene glycol (Catalyst-12) and triethylenediamine (Hülls, Germany) applied in the form of a 33% solution in dipropylene glycol (DABCO 33LV) were applied as catalysts in the process. A polysiloxane-polyoxyalkylene surface-active agent (Silicone L-6900, Witco, Sweden) was used as a stabilizer of the foam structure.

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

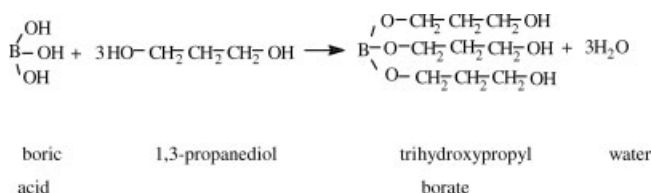
Tri(2-chloro-1-methyl-ethyl) phosphate (Antiblaze TMCP, Albright and Wilson, UK) was introduced into the foams.

The compounds obtained in reactions between boric acid and the diols (borates) were applied as modifiers for the production of foams, and they were as follows: tri(2-hydroxypropyl) borate, tri(2-hydroxy-3-methylpropyl) borate, and trihydroxybutyl borate.

Preparation of boroorganic compounds

Synthesis of boroorganic oligomerol based on boric acid and 1,3-propanediol

The synthesis of boroorganic oligomerol based on boric acid and 1,3-propanediol was conducted according to eq. (1):



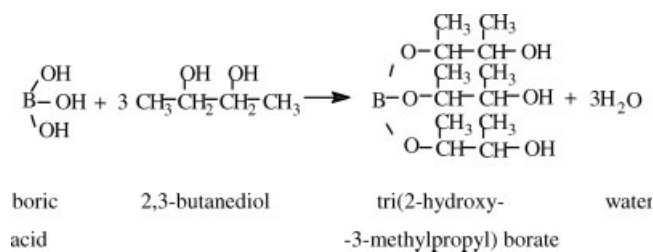
The following reagents were used in the process: 15.5 g of boric acid (0.25 mol), 57 g of 1,3-propanediol (0.75 mol), 1.2 cm³ of sulfuric acid, and 75 cm³ of xylene.

Boric acid and ethanediol were introduced at room temperature into a three-necked flask (250 cm³) equipped with a Dean-Stark head used for azeotropic distillation, a thermometer, and a stirrer. To reduce the time of reaction, a catalyst in the form of concentrated sulfuric acid was applied in the amount of 3 wt % in relation to the sum of boric acid and diol. Then, xylene in the amount of 75 cm³ was added. The flask content was continuously stirred at the xylene boiling temperature, and simultaneously, the water formed during reaction was azeotropically distilled off. The time of reaction was 145 min, and 13.5 cm³ of water was distilled off. The temperature of the reaction was 145°C.

The obtained product, that is, trihydroxypropyl borate, was a clear liquid that was a straw-yellow color.

Synthesis of boroorganic oligomerol based on boric acid and 2,3-butanediol

The synthesis of boroorganic oligomerol based on boric acid and 2,3-butanediol was done according to eq. (2)



The amounts of the reagents used for the synthesis were as follows: 15.5 g of boric acid (0.25 mol), 67.5 g of 2,3-butanediol (0.75 mol), 67.5 g of 2,3-butanediol (0.75 mol), 1.4 cm³ of sulfuric acid, and 75 cm³ of xylene.

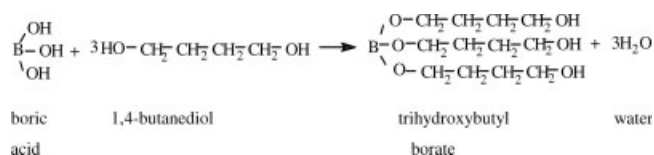
The preparation of tri(2-hydroxy-3-methylpropyl) borate was carried out according to the procedure described for the previous reaction.

The time of reaction was 160 min, and 15 cm³ of water was distilled off. The temperature of the reaction was 115°C.

The obtained product, that is, tri(2-hydroxy-3-methylpropyl) borate, was a dark yellow liquid.

Synthesis of boroorganic oligomerol based on boric acid and 1,4-butanediol

The synthesis of boroorganic oligomerol based on boric acid and 1,4-butanediol was carried out according to eq. (3):



The amounts of the reagents used for the synthesis were as follows: 15.5 g of boric acid (0.25 mol), 67.5 g of 1,4-butanediol (0.75 mol), 1.4 cm³ of sulfuric acid, 1.4 cm³ of sulfuric acid, and 75 cm³ of xylene.

The preparation of trihydroxybutyl borate was carried out according to the procedure described for the previous reaction.

The time of reaction was 85 min, and 15.5 cm³ of water was distilled off. The temperature of the reaction was 119°C.

The obtained product, that is, trihydroxybutyl borate, was a cloudy yellow liquid.

Characteristic of the boroorganic compounds

Studies on the boroorganic compounds included the determination of properties having an effect on their application as polyol components for the production of the PUR-PIR foams, namely, L_{OH} (ASTM D 2849-69), viscosity (ISO 2555 : 1989), and density (ISO 845 : 1988).

L_{OH} has an effect on the amount of isocyanate indispensable to form urethane bonds; however, viscosity has a significant effect on the parameters of processing. L_{OH} was determined as the amount of KOH (mg) equivalent to the amount of acetic anhydride reacting with the free hydroxyl groups contained in 1 g of the substance investigated. L_{OH} was determined by acylation with acetic anhydride in the xylene medium. After hydrolysis, the excess of anhydride, together with the acid formed in reaction, was titrated with KOH in the presence of phenolphthalein.

Viscosity was determined with a digital viscometer (Bröckfield DV-III) at a temperature of 20°C (293 K). Measurements were carried out with a DIN 87 spindle mated with a ULA-DIN-87 sleeve. To maintain a constant temperature in the measurements, a Bröckfield ULA-DIN-87 sleeve was enclosed with a ULA-40Y water jacket combined with a U3 No. 26435 type thermostat.

Density was determined at a temperature of 25°C (298 K) with an adiabatic pycnometer. Density was

related to the constant pycnometer volume by eq. (4):

$$d^T = \frac{m_2 - m_1}{V_{\text{pycn}}} \quad (4)$$

where d^T is the density at specified temperature, m_1 is the mass of the empty pycnometer (g), m_2 is the mass of the pycnometer with oligomerol (g), and V_{pycn} is the volume of the pycnometer (cm³).

Fundamental investigations of the foaming process, namely, the solubility of the obtained oligomerols, pH, IR spectroscopy analysis, thermogravimetric analysis, and NMR spectroscopy, were carried out.

The solubility of the borates obtained was investigated both in oligomerols commonly used for the production of rigid PUR foams and in selected organic solvents. For this aim, the borates obtained were mixed with oligomerols and organic solvents within the range of concentrations from 10 to 90% w/w, and the homogeneity of the obtained mixtures was visually evaluated. After about 7 days, we also checked whether the mixture was separated. The solvents used for analysis were as follows: methanol, toluene, methyl acetate, hexane, and the oligomerols Rokopol RF-55 (polyoxypropylenehexanol), Rokopol T (a polyoxypropylenated mixture of triethanolamine and *o*-toluidenamine), Rokopol TG-500 (polyoxyalkenetriol), and Rokopol PT-44 (polyoxypropylen-tetrol).

The pH values of the obtained oligomerols were measured with a pH/ORP/ISO/°C laboratory micro-processor meter with a RS 232 C connector (HANNA Instruments).

IR spectra were recorded with the KBr technique with a Vector spectrophotometer (Bruker) within the range 400–4000 cm⁻¹.

Thermogravimetric analysis was carried out with derivatograph produced by MOM Budapest (Paulik-Paulik-Erdey) in an air atmosphere at a heating rate of 5°C/min within the temperature range 20–500°C.

¹H-NMR spectra were recorded with a spectrophotometer (NMR Gemini 2000, Varian; basic frequency = 200 MHz).

The properties determined for the borates are presented in Table II.

Preparation of rigid PUR-PIR foams

The synthesized boroorganic compounds were applied to the preparation of the rigid PUR-PIR foams. The compositions of the rigid PUR-PIR foams are given in Table III.

The recipes for the preparation of the rigid PUR-PIR foams were composed on the basis of literature data.⁹ The basis for the calculations was L_{OH} of oligomerol.

Directions of studies on the properties of the rigid PUR-PIR foams

A continuous increase in the application of the rigid PUR-PIR foams has forced producers to develop a unified and obligatory methodology of testing. The directions of studies on the properties of rigid PUR-PIR foams are determined by their physical properties (density, water absorbability, flammability, and heat conduction), mechanical properties (compressive strength and brittleness), and chemical properties (aging and content of closed cells).

The apparent density of the foams was determined with cubical samples (50 mm on a side, ISO 845-1988), and it was expressed as a ratio of foam mass to its geometric volume.

The determination of water absorption was carried out according to DIN 53433. The method consisted of the measurement of the buoyant force of the sample (150 mm × 150 mm × 25 mm) immersed in distilled water for 24 h.

The flammability of the obtained PUR-PIR foams was tested by method 2 according to ASTM D 3014-73, a simplified chimney test (Butler's vertical test). The apparatus used to determine the flammability according to the vertical test consisted of a vertical column (300 mm × 57 mm × 54 mm); three of the walls were made from a metal plate, and the fourth one was a movable pane. Six foam samples (150 mm × 19 mm × 19 mm) were tested. Before burning, the samples were weighed to 0.0001 mm accuracy, and then, they were placed inside a chimney. A pane was installed, and a flame from the burner, supplied with a gas, propane or butane, was brought into contact with the sample for 10 s. Then, the burner was removed, and the time of the sample free burning and retention (residue after burning) were measured by a stopwatch in a vertical test. Retention was calculated from eq. (5):

$$R_e = \frac{m}{m_0} \times 100\% \quad (5)$$

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

Compressive strength was determined by the use of a general-purpose strength machine (Instron 5544).

Brittleness of foams was determined with a standard apparatus according to ASTM C 421-61. It was calculated as a loss of mass (%) of 12 foam cubes (25 mm × 25 mm × 25 mm) in relation to their initial mass. The apparatus applied to determine the brittleness of the PUR foams was a cubical box (190 mm × 197 mm × 197 mm) made from oaken wood that rotated about an axis at a speed of 60 rpm. The box was filled with 24 oak cubes (20 mm × 20 mm × 20 mm).

The loss in foam mass (K ; %), that is, the measure of its brittleness, was expressed by eq. (6):

$$K = \frac{m_1 - m_2}{m_1} \times 100\% \quad (6)$$

where m_1 is the mass of the shaped foam before testing and m_2 is the mass of the shaped foam after testing.

Softening point (as a thermal resistance under compressive stress) was determined with the cubical samples (20 mm × 20 mm × 20 mm) longwise to the direction of foam expansion in accordance with DIN 53424. The foam samples were subjected to the action of a compressive load of 24.52 kPa/h at temperature of 50°C. The temperature at which the sample was compressed by 2 mm was accepted as the softening point.

The thermal resistance of the foams was determined under dynamic conditions in an air atmosphere at a heating rate of 5°C/min within the temperature range 20–800°C. Tests were carried out with derivatograph produced by MOM Budapest (Paulik-Paulik-Erdey).

The heat conductivity of the foams was defined by the determination of the thermal conductance. The dimensions of the foam samples were 200 mm × 200 mm × 25 mm, and a FOX 200 apparatus (Lasercomp) was used for testing. This allowed us to determine the thermal conductance value within the range 20–100 mW m⁻¹ K⁻¹.

Changes in the linear dimensions of the foams were determined after 48 h of thermostating at a temperature of 120°C (393 K) with the cubical samples (50 mm × 50 mm × 50 mm). Samples were measured longwise to the direction of the foam expansion. The change in linear dimensions (Δl) was calculated from eq. (7):

$$\Delta l = \frac{l - l_0}{l_0} \times 100\% \quad (7)$$

where l_0 is the length of sample before thermostating (mm) and l is the length of sample after thermostating [mm].

The loss in mass of the foams was determined after 48 h of thermostating at a temperature of 120°C (393 K) with the cubical samples (50 mm × 50 mm). The loss in the mass of the foams (Δm) was calculated from eq. (8):

$$\Delta m = \frac{m_0 - m}{m_0} \times 100\% \quad (8)$$

where m_0 is the mass of sample before thermostating (g) and m is the mass of sample after thermostating (g).

The changes in the volume of the foams were determined after 48 h of thermostating at a temperature of 120°C (393 K) with the cubical samples (50 mm × 50 mm × 50 mm). Samples were measured

longwise to the direction of foam expansion. The change in volume (ΔV) was calculated from eq. (9):

$$\Delta V = \frac{V - V_0}{V_0} \times 100\% \quad (9)$$

where V_0 is the volume of the sample before thermostating and V is the volume of sample after thermostating.

The content of the closed cells was determined in accordance with PN-ISO 4590:1994 by method II (dimensions of samples = 100 mm \times 30 mm \times 30 mm). The method consisted of the determination of the relative pressure drop (calibrated earlier for the volume standards) from the differences in indications on the scale of the manometer, whose one arm was open to the atmosphere.

RESULTS AND DISCUSSION

The compounds obtained in the reactions of boric acid with the diols (1,3-propanediol, 1,4-butanediol, and 2,3-butanediol) were liquids, and they were characterized by the physicochemical properties listed in Table II. Studies on the solubility of the new compounds showed that they were soluble both in commonly applied solvents and in polyols used to produce PUR foams. The first loss in mass, the extrapolated beginning of the first loss in mass, and the highest rate of loss in mass were determined by derivatographic analysis. The first loss in mass for the prepared borates was within the range of tem-

TABLE IV
Analysis of the IR Spectra

Rotation	Experimental ν (cm^{-1})
B—O	1340–1336
O—H	
R—CH ₂ —OH	3425–3384
C—OH	1053–1042
C—H	
—CH ₂ —O—	1492–1427
—CH ₂ —	2936–2932

peratures from 58°C (for trihydroxypropyl borate) to 75°C (for trihydroxybutyl borate). The extrapolated beginning of the first loss in mass was observed within temperature range from 180°C (for trihydroxybutyl borate) to 198°C (for trihydroxypropyl borate). However, the highest rate of loss in mass was determined within the range of temperatures from 220°C [for tri(2-hydroxy-3-methylpropyl) borate] to 242°C [for tri(2-hydroxypropyl) borate].

Spectral analysis of the prepared boroorganic compounds was carried out by IR spectroscopy. The results are presented in Table IV.

To determine the structure of the obtained boroorganic compounds, their ¹H-NMR spectra with chloroform as a solvent were recorded. A sample NMR spectrum for trihydroxypropyl borate is presented in Figure 1. The number of hydrogen atoms respective to the individual groups and the values of the chemical shift were as follows: 3 and 4.445 ppm for —OH groups, 12 and from 3.329 to 3.983 ppm for

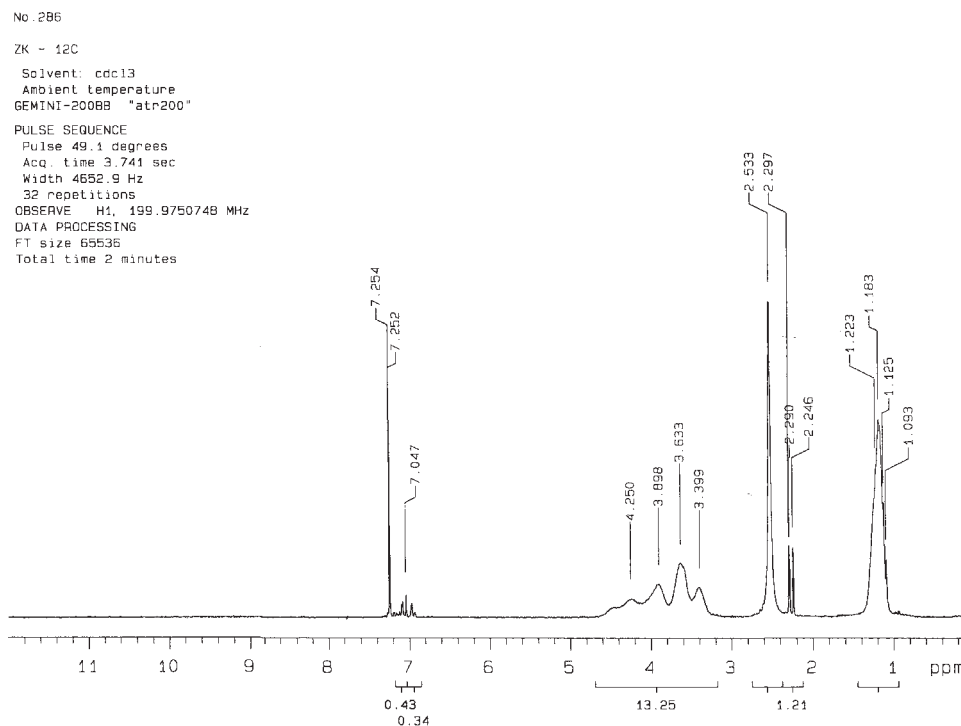


Figure 1 ¹H-NMR spectrum of trihydroxypropyl borate.

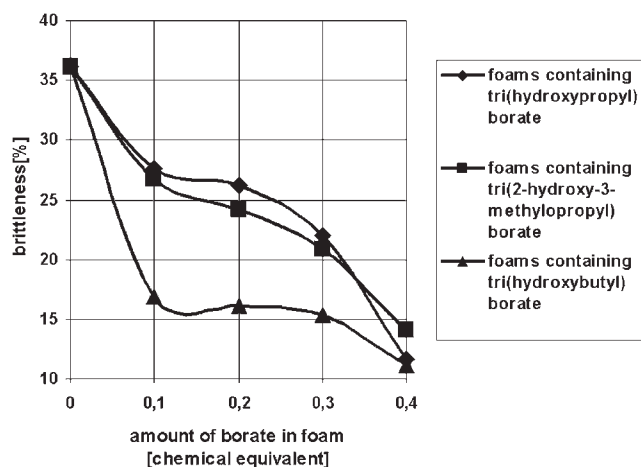


Figure 2 Dependence between the brittleness and content of bororganic compounds in the foams.

—O—CH₂— groups, and 6 and from 1.025 to 1.118 ppm for C—CH₂—C groups, respectively.

The physicochemical properties of the obtained bororganic oligomerols were determined, and they were then used to produce a series of PUR-PIR foams in an open form. The foams were prepared on a laboratory scale by a one-stage method from a two-component system at an equivalent ratio of NCO to OH groups equal to 3 : 1.

In the first stage of studies, the standard foam (without borates added) and the foams with the each of borates added in amounts from 0.1 to 0.4 chemical equivalents were prepared. The foaming gas in the systems was carbon dioxide produced in the reaction of PMDI with water.

The progressive addition (in the amount of 0.1 chemical equivalents) of bororganic compound to the foam composition resulted in the elongation in the processing parameters, such as start time, time of expansion, time of gelation, and time of shape stabilization, in comparison with the standard foam.

Thus, the obtained bororganic compounds were less reactive with PMDI compared to commonly applied polyols.

The values of the apparent density of the obtained foams with borates added were near that of the standard foam (36.96 kg/m³).

The bororganic compounds applied to produce the rigid PUR-PIR foams behaved in foam composition similarly to the common crosslinking agents, which caused the foam structure to become more ordered. Therefore, on the basis of the brittleness determinations, we found that the addition of bororganic compounds to the foam composition caused a reduction in the foam brittleness. For the standard foam, it was equal to 36.2%. The addition of compounds containing boron caused a reduction in the brittleness from 27.56% for foam C1 (containing 0.1

chemical equivalents of trihydroxypropyl borate) to 11.2% for foam H4 (containing 0.4 chemical equivalents of trihydroxybutyl borate). An increase in the content of the given bororganic compound in the foam composition resulted in a considerable reduction in the brittleness of the foams. The dependence is presented in Figure 2.

The mechanical compressive strength of the prepared foams was very high. It was equal to 237.5 kPa for the standard foam. For other foams with progressively reduced amounts of industrial oligomerol (Rokopolu RF-55) at the cost of the same quantity of bororganic compound, the mechanical compressive strength was within the range from 219.7 kPa for foam H1 (containing 0.1 chemical equivalents of trihydroxybutyl borate) to 397.2 kPa for foam F4 [with 0.4 chemical equivalents of tri(2-hydroxy-3-methylpropyl) borate]. The results allow us to state that the mechanical compressive strength of the prepared foams increased as the amount of bororganic compounds was increased in foam composition; however, it decreased as the chain of the compound increased. This relationship is presented in Figure 3.

The application of bororganic compounds to the production of rigid PUR-PIR foams resulted in a significant increase in the amount of closed cells in comparison with the standard foam. The content of closed cells was within the range from 83.4% for the standard foam to 94.5% for foam F1 [containing 0.1 chemical equivalents of tri(2-hydroxy-3-methylpropyl) borate]. The application of bororganic compounds allowed us to prepare foams containing over 90% closed cells.

The softening point results show its decrease in foams containing bororganic compounds in comparison to the standard foam. The softening point decreased within the range from 230°C (for the standard foam) to 180°C for foam H4 [containing 0.4 chemical equivalents of tri(2-hydroxy-3-methylpropyl) borate]. The dependence is presented in Figure 4.

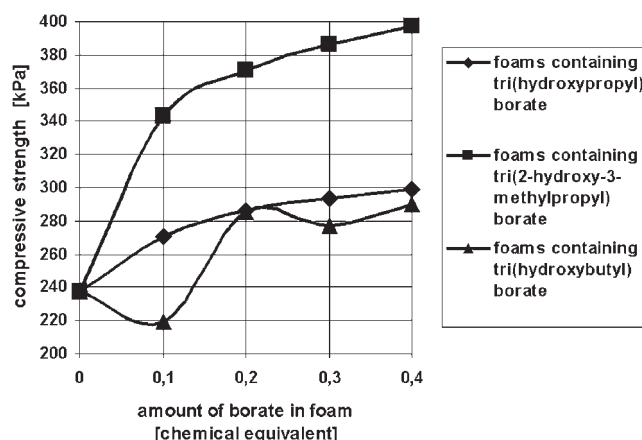


Figure 3 Dependence between the compressive strength and content of bororganic compounds in the foams.

The addition of bororganic compounds to the rigid PUR–PIR foams caused a reduction in water absorbability. This was equal to 1.8 vol % for the standard foam, and for other foams, water absorbability was reduced to about 0.87 vol %.

Changes in the linear dimensions, volume, and loss in mass after 48 h of thermostating at a temperature of 120°C were practically analogous. The type and amount of the applied compounds containing boron had no effect on changes in the linear dimensions, volume, and loss in mass of the foams in the sphere of the experiments.

To confirm the presence of groups typical for foams, the foams were grinded in an Iantzki's mill, and then, IR analysis was carried out with a potassium bromide technique.

IR spectroscopy of the PUR–PIR foams confirmed the presence of the bands characteristic for urethane groups ($1742\text{--}1700\text{ cm}^{-1}$) and isocyanurate rings ($1710\text{--}1690$ and 1410 cm^{-1}).

To obtain the full characteristic of the thermal resistance of the obtained foams, thermogravimetric analysis was carried out in an air atmosphere at a heating rate of 5°C/min within the temperature range 20–800°C. The first loss in mass, the extrapolated beginning of the first loss in mass, and the highest rate of loss in mass in the foams were determined.

The first loss in mass occurred for the obtained foams within the range of temperature from 173°C (for foam F1) to 227°C (for foam H4). The extrapolated beginning of the main loss in mass occurred within the range of temperatures from 190°C (for foam F3) to 269°C (for foam H3). However, the highest rate of loss in mass was observed within the range of temperature from 297°C (for foam F1) to 335°C (for foam H4).

The heat conductivity was within the range 34–35 mV/mK for all of the prepared foams, and there was no strict correlation with the content of the closed pores in the foams.

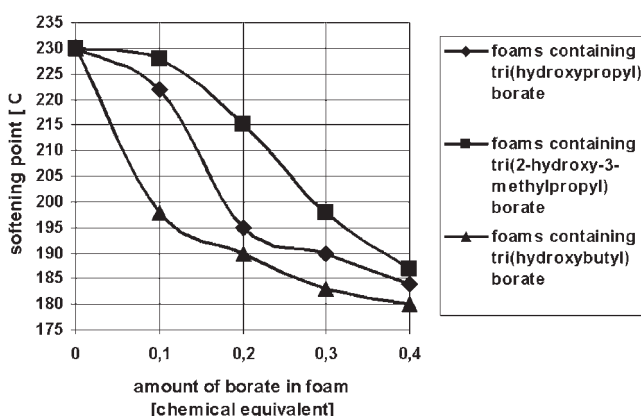


Figure 4 Dependence between the softening point and content of bororganic compounds in the foams.

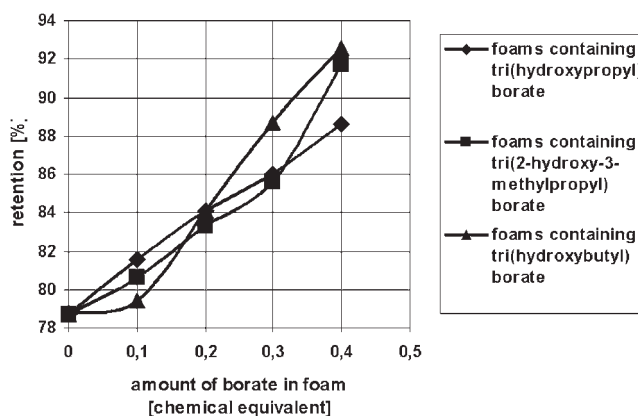


Figure 5 Dependence between the retention and content of bororganic compounds in the foams.

Analysis of the results regarding the flammability of the PUR–PIR foams (vertical test) showed that the residue after burning (retention) increased as the content of bororganic oligomerol was increased in foams containing the same type of oligomerol. The retention values were within the range from 79.4% (for foam H1) to 93.9% (for foam B4). All foams containing bororganic compounds were characterized by retention values higher than that of the standard foam (78.7%). The dependence between retention and the amount of oligomerols containing boron is presented in Figure 5.

CONCLUSIONS

New bororganic compounds were obtained by the reaction of boric acid and diols (1,3-propanediol, 2,3-butanediol, and 1,4-butanediol), their physicochemical properties were determined, and these compounds were used to produce rigid PUR–PIR foams. To prepare the bororganic compounds, reactions were led under laboratory conditions with the use of sulfuric acid as a catalyst.

The rigid PUR–PIR foams with the addition of compounds containing boron were produced by a one-stage method at an equivalent ratio of isocyanate (NCO) to hydroxyl (OH) groups equal to 3 : 1. Addition of the prepared compounds caused the start time, time of growth, and time of gelation to increase.

The addition of bororganic compounds to the foam compositions resulted in a decrease in the water absorbability; however, a distinct increase in amount of the closed cells was observed in comparison with the standard foam.

Moreover, the brittleness of the foams produced with the addition of compounds containing boron was significantly reduced. The brittleness of the foams decreased as the amount of new bororganic compound added to foam composition was increased. The

lowest brittleness value (11.2%) was obtained for foams prepared with the use of trihydroxybutyl borate.

The softening point of the foams decreased as the amount of new compounds added to the foam composition increased.

The analysis of the flammability tests (extinguishing of the flame and the range of the flame) of the foams allowed us to qualify them to the group of self-extinguishing foams. The maximum reduction of foam flammability (the highest retention) was obtained for foams containing trihydroxybutyl borate. An increase in the amount of the new compounds added had a favorable effect on the reduction of the foam flammability.

In particular, the developed foam receipts guaranteed the preparation of PUR-PIR foams characterized by a compressive strength of about 400 kPa, a significantly reduced flammability, a higher amount of closed pores, and a reduced brittleness in comparison with the standard foam (without bororganic compound added). The system with the use of trihydroxybutyl borate is particularly recommended because it allowed us to prepare foams characterized by a low

brittleness value and a high retention (residue after burning).

References

1. Randall, D.; Lee, S. *The Polyurethanes Book*; Wiley: New York, 2002.
2. Zipfel, L.; Boerner, K. In *Conference Proceedings of the Fifth International Conference on Blowing Agents and Foaming Processes*, Munich, Germany, 2003; p 47.
3. Prociak, A.; Pielichowski, J.; Sałapatek, M. In *Conference Proceedings of the 7th International Conference on Blowing Agents and Foaming Processes*, Stuttgart, Germany, 2005; Paper 17.
4. Frisch, K. C. *Polimery* 1996, 41, 193 (in Polish).
5. Hyung Choe, K.; Lee Soo, D.; Seo Jin, W.; Kim Nyon, W. *Polym J* 2004, 36, 368.
6. Moore, S. E.; Bhattacharjee, D.; Dressel, D. *J Cell Plast* 1996, 32, 23.
7. Czupryński, B.; Paciorek-Sadowska, J.; Liszkowska, J. *J Appl Polym Sci* 2006, 100, 2020.
8. Czupryński, B.; Liszkowska, J.; Paciorek-Sadowska, J. *J Appl Polym Sci* 2005, 95, 400.
9. Wirpsza, Z. In *Chemia Polimerów*; Florjańczyk, Z.; Penczek, S., Eds.; Warsaw Technical University: Warsaw, 1997 (in Polish).