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Modification of PUR-PIR foams by boroorganic compound obtained on the basis of bis(hydroxymethyl)urea

Summary — A method for the preparation of a boroorganic compound with the application of *N,N'*-bis(methyleneoxy-2-hydroxyethyl)urea and boric acid has been presented. The prepared borate was evaluated mainly in respect of its applicability as a polyol component and antipirene for the production of polyurethane-polyisocyanurate foams. The preparation method, the determination of foaming parameters and methods for the determination of physicomechanical properties and flammability of the PUR-PIR foams were described and the results were presented. On the basis of studies, it was found that application of the new compound in the preparation of foams was advantageous. The rigid foam obtained was characterized by reduced brittleness, higher ultimate compressive strength and a significantly reduced flammability in comparison with standard foam.

Key words: rigid polyurethane-polyisocyanurate foams, physical properties, mechanical properties, polyol, flammability.

MODYFIKACJA PIANEK PUR-PIR ZWIĄZKIEM BOROORGANICZNYM NA PODSTAWIE BIS(HYDROKSYMETYLO)MOCZNIKA

Streszczenie — W reakcji syntezy *N,N'*-bis(metylenooksy-2-hydroksyetylo)mocznika z kwasem borowym otrzymano nowy związek boroorganiczny, który następnie poddano ocenie z punktu widzenia jego przydatności jako składnika poliolowego a jednocześnie antypirenu w produkcji sztywnych pianek poliuretano-poliizocyjanurowych (PUR-PIR). Omówiono sposób wytwarzania, oznaczania parametrów spieniania oraz metody badań właściwości fizycznych, mechanicznych i palnych uzyskanych pianek PUR-PIR. Stwierdzono, że zastosowanie nowego zsyntezowanego związku boroorganicznego w charakterze poliolowego składnika wytwarzanych pianek wpływa korzystnie na ich charakterystykę, zmniejszając kruchość, zwiększając wytrzymałość na ściskanie oraz palność w porównaniu z wartościami odpowiednich właściwości pianki wzorcowej.

Słowa kluczowe: sztywne pianki poliuretano-poliizocyjanurowe, właściwości fizyczne, właściwości mechaniczne, poliol, palność.

The rise in the market demand for polyurethane plastics has led to the requirement of higher standards for their production and properties of the obtained products [1]. Fire resistance is considered as one of the most important properties especially in materials applied in large facilities, public buildings as well as industrials plants with potential fire hazard [2]. Antipirenes used presently in the production of polyurethanes are expensive, worsen the properties of the obtained products and are environmentally hazardous [3—5]. Moreover, the application of halogens in the reduction of flammability in plastics has been restricted by the EU [6]. Efforts and therefore being made to find effective halogen-free additives whose introduction into the polyurethane composition would allow for the achievement of the required inflammability level of the final product [7—10].

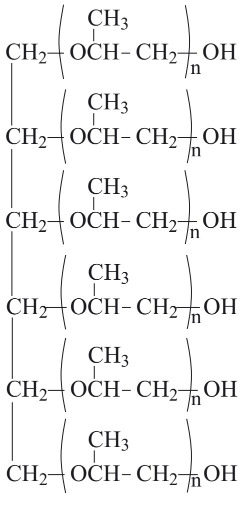
The aim of the studies presented in this paper was to determine the possibilities of applying new boroorganic polyol containing active hydrogen atoms as well as boron and nitrogen atoms for the preparation of rigid polyurethane-polyisocyanurate foams.

EXPERIMENTAL

Materials

In order to prepare boroorganic compounds, the following reagents were applied:

— Home made *N,N'*-bis(methyleneoxy-2-hydroxyethyl)urea in the form of yellow-green liquid (density of 1.193 g/cm^3), ethylene glycol $C_2H_4(OH)_2$ and pure boric acid H_3BO_3 (POCh Gliwice), xylene (mixture of *o*- and *p*-isomers content of water over 0.1 %, density about



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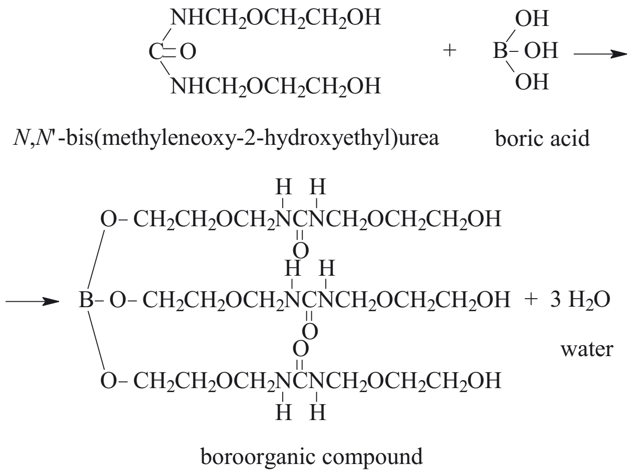

Scheme A. Synthesis of a new boroorganic compound

0.86—0.86 g/cm^3 (Chempur) were used in the preparation of boroorganic compounds.

— The polyether — Rokopol RF-55 [product of oxypropylation of sorbitol, Formula (I), L_{OH} = 495.0 mg KOH/g, produced by NZPO Rokita, Brzeg Dolny] and Ongromat CR 30-20 (technical polyisocyanate whose main component is diphenylmethane 4,4'-diisocyanate, density at 25 °C was 1.23 g/cm^3, viscosity of 200 mPa · s and content of NCO groups — 31.0 %, made in Hungary) were used to prepare the rigid PUR-PIR foams. The polyether and polyisocyanate were characterized according to the following standards: ASTM D 2849-69 and ASTM D 1638-70.

— A 33 % solution of anhydrous potassium acetate in diethylene glycol [Catalyst-12 (POCh Gliwice)] and DABCO 33LV [triethyleneamine (Hülls)] as well as a 33 % solution of dipropylene glycol were applied as catalysts in foam composition.

— The surface-active agent — polysiloxanepolyoxyalkyleneoxydimethylene [Sillicone L-6900 (Witco Corp.)] was used as stabilizer for the foam structure.

— The porophor was carbon dioxide formed in the reaction of water with isocyanate groups.

— Tri(2-chloro-1-methyl-ethyl)phosphate [Antiblaze TMPC (Albright and Wilson)] was also introduced into the foam compositions.

— The product of the reaction of *N,N'*-bis(methyleneoxy-2-hydroxyethyl)urea with boric acid (borate) was applied as a modifying agent for the production of foams.

Preparation of boroorganic polyol

N,N'-bis(methyleneoxy-2-hydroxyethyl)urea was initially prepared as described in the literature [11, 12]. In the next stage, a boroorganic oligomerol derived from *N,N'*-bis(methyleneoxy-2-hydroxyethyl)urea and boric acid was synthesized according to scheme A.

61.81 g of boric acid (H_3BO_3), and 624 g of *N,N'*-bis(methyleneoxy-2-hydroxyethyl)urea were introduced at room temperature into a 500 cm^3 three-necked flask equipped in Deana—Stark head for azeotropic distillation, thermometer and mechanical stirrer. 75 cm^3 of xylene was then added. The mixture in the flask was heated to boiling point under intensive stirring. The water formed during the reaction was distilled off azeotropically. The stirring was stopped at the end of the reaction and the transparent upper layer (xylene) separated from the clear yellow bottom layer containing new boroorganic compound. The separated bottom layer (polyol) was left to cool and then kept for 1 hour in a vacuum drier at temp. of 130 °C under 0.133 kPa to 0.399 kPa pressure range. The reaction temperature, time and volume of distilled water were 141 °C, 200 minutes and 51 cm^3, respectively.

Preparation of the rigid PUR-PIR foams

The rigid PUR-PIR foams were obtained on a laboratory scale in a one-stage method from two components (A and B) at an NCO to OH group ratio of 3 (Table 1). Component A was obtained by mixing adequate amounts of polyol, catalyst, the surface active agent and porophor of 1800 rpm. Polyisocyanate was chosen as component B. Both components were mixed at appropriate volume ratio and poured into an open rectangular tray. The expanded foams were thermostated for 4 h at 120 °C and then seasoned for 48 h at 20 ± 4 °C. Two rigid

Table 1. Preparation materials of the rigid polyurethane-polyisocyanurate foams

Materials/unit	Control foam	Modified foam
Rokopol RF-55/g	56.65	0
Boroorganic polyol/g	0	66.63
Silikon L6900/g	5.2	5.2
DABCO 33LV/g	3.1	3.1
Catalyst 12/g	7.2	7.2
AntiblazeTMCP/g	51.6	0
Distilled water/g	3.8	3.8
Ongromat 20-30/g	284.0	284.0

polyurethane-polyisocyanurate foams were prepared for comparison purposed. The first foam (marked control sample) was used as standard and the second (marked modified sample) contained new boroorganic compound as a polyol. The foams were cut into pieces after seasoning and the basic properties determined according to current standards.

Methods of testing

The boroorganic compounds

— Hydroxyl number, L_{OH}, was determined as the equivalent amount of KOH (in mg) corresponding to the amount of acetic anhydride consumed in the reaction with the free hydroxyl groups contained in 1 g of the investigated substance. L_{OH} was determined by acylation with acetic anhydride in xylene medium. After hydrolysis, the excess anhydride, together with the acid formed in reaction, was titrated with KOH in the presence of phenolphthalein.

— Viscosity was determined using a digital viscometer Brökfield DV-III at 20 °C (293 K). Measurements were carried out using a DIN-87 spindle mating with ULA-DIN-87 sleeve. In order to maintain constant measurements temperature, the ULA-DIN-87 Brökfield sleeve was covered with a thermostated water jacket ULA-40Y.

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

— IR spectra were recorded by KBr technique using a Vector spectrophotometer (Brucker) within the 400 to 4000 cm^{-1} range.

— The thermogravimetric analysis was carried out in air in the 20 to 500 °C using derivatograph produced by MOM Budapest (Paulik-Paulik-Erdey) at heating rate 5 °C/min.

— The ^1H NMR spectra (chloroform as a solvent) and ^{13}C NMR spectra (deutered dimethylsulfoxide as a solvent DMSO-d_6) were recorded by NMR spectrophotometer Gemini 2000 Varian, with a basic frequency of 200 MHz.

Rigid PUR-PIR foams

— An apparent density of foams was determined by using 50 mm cubical samples (ISO 845:1988 standard) and it was expressed as a ratio of foam mass to its geometric volume.

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

— The flammability of the obtained PUR-PIR foams was determined by two methods:

The first was performed according to PN-78/C-05012 standard, *i.e.* the horizontal test. In this method the velocity of superficial propagation of the flame along a horizontal sample (150 × 50 × 13 mm) kindled at one end was measured.

The velocity of the superficial propagation of the flame is defined as the velocity of the flame front shifting along the surface of the tested flammable material.

The tested foam sample was placed on a horizontally fixed net and then a burner with a flame was put at one end for 60 s. A transverse line was marked at 125 mm from the sample end to which the burner was placed. The distance covered flame front and the time necessary for it to reach the marked transverse line were measured. If the ignited foam goes out before flame reaches the control mark, the foam is defined as the self-extinguishing. The ability of foam to self-extinguish can also be evaluated by measuring the length of the burned segment. In the case when foam is not extinguished, does not extinguish itself, the mean burning time of the tested segment or velocity of flame propagation (in mm/s) can be determined on the basis of the distance traversed by the front of flame at a defined time.

The second method was performed according to ASTM D 3014-73 standard, also referred to as simplified chimney test (Butler's vertical test). The apparatus used for this test consisted of a vertical column (300 × 57 × 54 mm) with three walls made from metal plates with the fourth being a movable pane. Six foam samples (150 × 19 × 19 mm) were tested. The samples were weighted with accuracy to 0.0001 mm and then placed in a chimney before burning. The pane was installed and the flame from a propane-butane fuelled burner brought in contact with the sample for 10 s. The burner was then removed and the time of the sample free burning and both the burning duration and retention (residue after burning) time were measured by a stopwatch in the vertical test. The retention was calculated from equation (1):

$$R_e = \frac{m}{m_0} \cdot 100\ \% \qquad (1)$$

where: R_e — *retention*, m_0 — *mass of sample before burning (g)*, m — *mass of sample after burning (g)*.

— Compressive strength was determined using a general-purpose strength machine (Instron 5544).

— Brittleness of foams was determined with the use of a standard apparatus according to ASTM C 421-61 standard. It was calculated as a loss of mass (in percents) of 12 foam cubes (side length of 25 mm) in relation to their initial mass. The apparatus applied to determine the brittleness of PUR foams was a rectangular box (197 × 197 × 197 mm) made from an oaken wood and rotating about its axis at 60 rpm. The box was filled with 24 oak cubes (20 × 20 × 20 mm).

— The loss in foam mass (%) *i.e.* measure of its brittleness (K) is expressed by the equation (2):

$$K = \frac{m_1 - m_2}{m_1} \cdot 100\ \% \qquad (2)$$

where: m_1 — *mass of shaped foam before test*, m_2 — *mass of shaped foam after test*.

— Softening point (as a thermal resistance under compressive stress) was determined by using the cubical samples (side length of 20 mm), longwise the direction of foam expansion, in accordance with DIN 53424 standard. The foam samples were subjected to the action of compressive load of 24.52 kPa per hour at 50 °C. The temperature at which the sample was compressed by 2 mm was regarded as the softening point.

— The thermal resistance of foams was determined under dynamic conditions in air in a 20—800 °C temperature range. The sample temperature was ramped at 5 °C/min by a derivatograph produced by MOM Budapest (Paulik-Paulik-Erdey).

— Heat conductivity of foams was evaluated through the determination of the thermal conductance λ. Foam samples of dimensions 200 × 200 × 25 mm and a FOX 200 (Lasercomp) apparatus were used for testing to determine the λ values within the 20 to 100 mW/(m · K) range.

— Changes of the linear dimensions of the foams were determined after 48 h of thermostating at 120 °C (393 K) by using the cubical samples (side length of 50 mm). The linear expansion of the foam samples was measured.

— The loss in mass of foams was determined after 48 h of thermostating at 120 °C (393 K) by using the cubical samples (side length of 50 mm).

— Changes of volume of the foams were determined after 48 h of thermostating at 120 °C (393 K) by using the cubical samples (side length of 50 mm). The linear expansion of the foam samples was measured.

— The content of the closed cells was determined in accordance with method II of the PN-ISO 4590:1994 standard (sample dimensions — 100 × 30 × 30 mm). The relative pressure drop (earlier calibrated for the volume standards) was determined from the differences in indications on the manometer scale with one arm opened to the atmosphere.

RESULTS AND DISCUSSION

The results of experiments allows for the evaluation of the applicability the new borate as a new polyol for the production of rigid polyurethane-polyisocyanurate foams.

The product of the reaction of boric acid and *N,N'*-bis(methyleneoxy-2-hydroxyethyl)urea was an odourless brightly yellow liquid with a density d_{20} of 1.124 g/cm^3, viscosity of 185.2 mPa · s, hydroxyl number of 421 mg KOH/g and water contents of 0.1 %. In thermal resistance measurements, the first loss in mass for the compound prepared occurred at 160 °C and in extrapolation the main loss in mass was began at 230 °C. However, maximum rate of loss in mass was recorded at 310 °C.

The bands of frequencies characteristic for the groups contained in the new polyol were observed in IR spectra. The results are presented in Fig. 1.

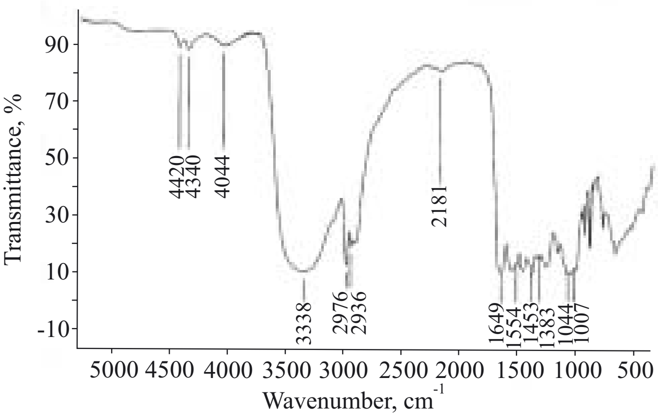

Fig. 1. IR spectrum of boroorganic compound

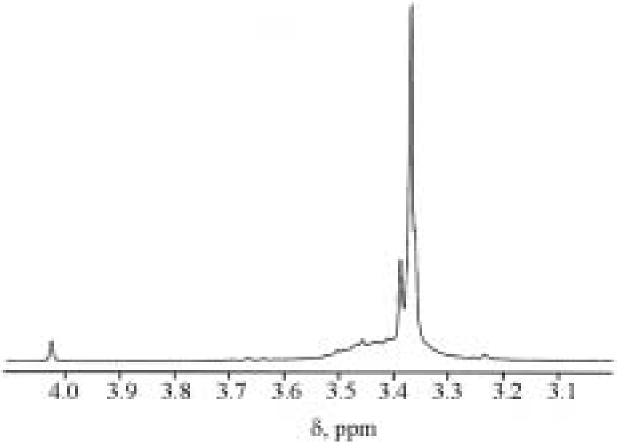

Fig. 2. ^{1}H NMR spectrum of boric acid and N,N'-bis(methyleneoxy-2-hydroxyethyl)urea reaction product

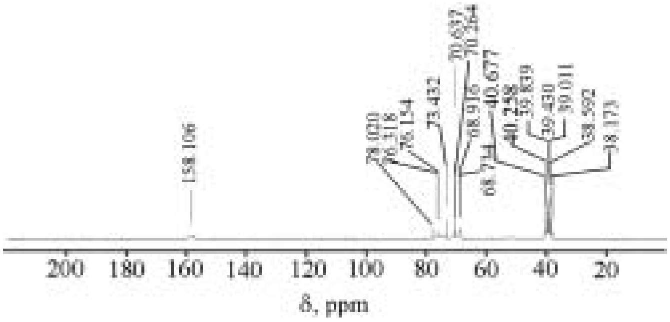

Fig. 3. ^{13}C NMR spectrum of boric acid and N,N'-bis(methyleneoxy-2-hydroxyethyl)urea reaction product

The following bands were observed for the obtained boroorganic compound: ν [cm^{-1}] = 1383—1342 (B-O), 2976—3338 (OH), 1649 (NH-CO-NH), 1007—1073 (C-OH), 1453—1554 (-CH$_2$-O-), 2927—2936 (-CH$_2$-).

Analysis of ^{1}H NMR (Fig. 2) and ^{13}C NMR spectra (Fig. 3) allowed for the determination of the structure of the obtained boroorganic compounds:

3 hydrogen atoms corresponding to an -OH group and a chemical shift from 3.59 ppm to 3.61 ppm, 12 hydrogen atoms corresponding to an -O-CH$_2$- group and a chemical shift from 3.32 to 3.98 ppm, 24 hydrogen atoms corresponding to a CH$_2$-O group and a chemical shift

from 3.36 ppm to 3.38 ppm, 12 hydrogen atoms corresponding to a -CH_2 group and a chemical shift from 3.45 ppm to 3.52 ppm and 6 hydrogen atoms corresponding to an N-H group and a chemical shift equal to 3.41 ppm.

The following observations were made from the ^{13}C NMR spectrum: 3 carbon atoms corresponding to an N-CNO group and a chemical shift at 158.106 ppm, 6 carbon atoms corresponding to an N-**C**H_2-O group and a chemical shift at 68.916 ppm, 6 carbon atoms corresponding to a CH_2-**C**H_2-O group and a chemical shift at 70.637 ppm, 6 carbon atoms corresponding to a BO-**C**H_2-CH_2 group and a chemical shift at 73.432 ppm and 3 carbon atoms corresponding to a CH_2-**C**H_2-OH and a chemical shift is 78.020 ppm.

The rigid polyurethane-polyisocyanurate foams were prepared after the determination of properties essential for defining the premix recipe for production of polyurethanes.

The times of commencement, expansion and gelation were monitored and measured during the formation of polyurethane-polyisocyanurate foams. The different times of loss in stickiness of the expanded foam was observed to depend on the kind of medium (air, wall of the mould) in contact with its surface layer. It was found that the most rapid loss in stickiness was in the case of foam surface in contact with air. Up till now, more objective methods for the determination of phenomena occuring during the expansion of polyurethane foam have not been presented.

The rigid PUR-PIR foam prepared from the new borate is characterized by longer processing times (start time — 241 s, time of expansion — 319 s and time of gelation — 560 s) in comparison with standard foam (start time — 16 s, time of expansion — 18 s and time of gelation — 75 s).

A doubled increase in foam density observed for foam containing the new polyol as compared to the unmodified counterpart (from 36.6 kg/m^3 for control foam to 81.2 kg/m^3 for modified foam). The higher density of the new foam in turn resulted in a distinct increase in compressive strength in direction of the foam expansion. The compressive strength for standard foam was 221.7 kPa and for foam containing boroorganic polyol 429.7 kPa.

Brittleness of PUR-PIR foam with the new polyol was considerably lower (15.1 %) than the value for the standard foam (41.9 %).

The softening point was insignificantly lower *i.e.* 230 °C (control foam) and 208 °C (modified foam).

A reduction in the flammability of foam containing boroorganic compound was also observed. The residue after combustion (retention) of modified foam was 95.6 %, whereas the retention of foam without borate was 67.3 %. Analysis of smoking properties showed that control foam was characterized by almost doubled of smoke emission intensity — 200.5 m^2/m^2 than modified foam — 123.1 m^2/m^2. Higher average CO emission was also observed for the control foam (0.147 g/g) than for the modified foam (0.104 g/g). A similar dependence can be formulated for CO_2 emission. The total amount of heat released was identical (about 2.7 MJ/m^2) for both the foams.

A replacement of industrial polyol with the tested boroorganic counterpart did not lead to any changes in linear dimensions, volume nor loss in foam mass after thermostating for 48 h at 120 °C.

Similar thermal resistance of the prepared rigid PUR-PIR foams was observed in thermogravimetric studies. The first loss in foam mass was noted at about 164 °C. In extrapolation, the main loss in mass commenced at about 200 °C, whereas the highest rate of loss in mass was observed at temperature about 310 °C.

IR spectroscopy confirmed presence of bands characteristic for isocyanurate (1710—1690 cm^{-1}) and urethane (1740—1700 cm^{-1}) bonds (Fig. 4) in the foams.

It was found that the application of the new polyol for foam preparation resulted in a two-fold increase in water absorbability from 1.8 % for the control foam to 4.03 % for the modified foam. This is most probably caused by the smaller amount of closed cells in the modified foam (70.1 %) as compared to the control foam (83.4 %).

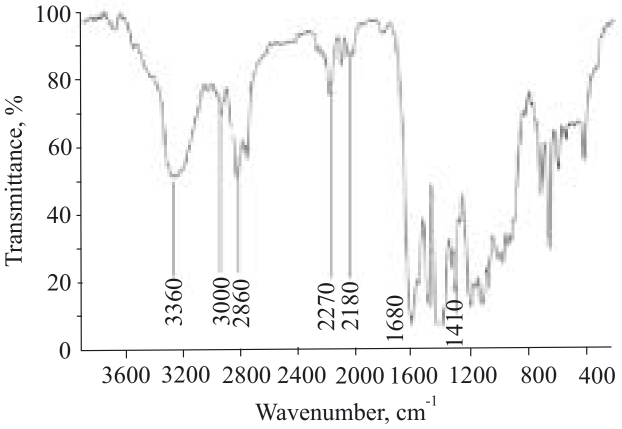

Fig. 4. IR spectrum of PUR-PIR foam containing the new polyol

Thermal conductivity was measured to be 30.0 mV/mK for the control foam and 31.8 mV/mK for the modified foam and no good correlation could be found between it and the content of closed pores.

CONCLUSIONS

A rigid polyurethane-polyisocyanurate foam with the obtained derivative of *N,N'*-bis(methyleneoxy-2-hydroxyethyl)urea and boric acid was prepared by one-stage method at isocyanate (NCO) to hydroxide (OH) group an equilibrium ratio of 3:1. It was found that application of the compound prepared resulted in longer start, expansion and gelation times.

It was found that the introduction of the boroorganic compound into the foam caused an increase in water absorbability and a decrease of the amount of closed cells in the foam as compared to a standard foam.

The results showed considerable reduction in brittleness in the foam prepared with the new polyol and a slight reduction in thermal resistance.

A favourable influence of the new polyol in reducing the flammability of the PUR-PIR foam was observed.

The new compound obtained in these studies — a derivative of *N*,*N'*-bis(methyleneoxy-2-hydroxyethyl)urea and boric acid can be applied as polyol for the preparation of polyurethane foam while also acting as a flammability reducing agent. The presence of active groups able to react with polyisocyanate, boron and chlorine atoms makes it possible to prepare rigid PUR-PIR foam with good combustion resistance and satisfactory physicochemical properties.

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