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Preparation and properties of polyurethane foams obtained with hydroxyethyl derivatives of oxamide modified with boric acid

Summary — The homogeneous mixture of *N,N'*-bis(2-hydroxyethyl)oxamide (BHEOD) and boric acid reacted with an excess of ethylene carbonate (EC). Obtained hydroxyethyl derivatives of oxamide (OD) modified with boric acid are characterized by high thermal stability and exhibit physical properties of typical polyols used in the preparation of foamed polyurethane materials. The rigid polyurethane foams obtained with the use of these derivatives and 4,4'-diphenylmethane diisocyanate exhibited higher thermal stability and compressive strength compared to the foams obtained from hydroxyethyl derivatives of oxamide without boric acid.
Keywords: *N,N'*-bis(2-hydroxyethyl)oxamide, boric acid, ethylene carbonate, product structure, rigid polyurethane foams, thermal stability and compressive strength.

OTRZYMYWANIE I WŁAŚCIWOŚCI PIANEK POLIURETANOWYCH WYTWORZONYCH Z UDZIAŁEM HYDROKSYETYLOWYCH POCHODNYCH OKSAMIDU MODYFIKOWANYCH KWASEM BOROWYM

Streszczenie — *N,N'*-bis(2-hydroksyetylo)oksamid zhomogenizowano z kwasem borowym, a uzyskaną mieszaninę poddano hydroksyalkilowaniu przy użyciu nadmiaru węglanu etylenu. Otrzymane z udziałem *N,N'*-bis(2-hydroksyetylo)oksamidu, kwasu borowego i nadmiaru węglanu etylenu hydroksyalkilowe pochodne charakteryzowały się dużą odpornością termiczną oraz wykazywały właściwości typowych polioli stosowanych do otrzymywania pianek poliuretanowych. Uzyskane z ich udziałem sztywne pianki poliuretanowe odznaczały się dobrą stabilnością wymiarów, dużą termoodpornością, niezbyt dużymi ubytkami masy podczas ekspozycji temperaturowej oraz dużą wytrzymałością na ściskanie. Wprowadzony do struktury pianek poliuretanowych bor wpłynął na zwiększenie ich termoodporności i wytrzymałości na ściskanie.
Słowa kluczowe: *N,N'*-bis(2-hydroksyetylo)oksamid, kwas borowy, węglan etylenu, struktura produktu, sztywne pianki poliuretanowe, odporność termiczna i wytrzymałość na ściskanie.

INTRODUCTION

Hydroxyalkoxy derivatives of oxamide (OD) obtained in the reactions of *N,N'*-bis(2-hydroxyalkyl)oxamides and alkylene carbonates show high thermal stability; the temperature of its maximum decomposition is in the range of 210—350 °C [1]. These products can be used as a polyol component for the preparation of rigid polyurethane foamed materials [1]. Foams obtained with their participation have good physical properties and high thermal stability. Compressive strength of polyurethane foams obtained from hydroxypropyl derivatives of the OD is enhanced compared to the classical polyurethane foams (0.1—0.2 MPa) [2] and it's in the range of 0.15—0.64 MPa [1]. However the compressive strength of polyurethane foams obtained from the hydroxyethyl derivatives of OD is 0.11—0.16 MPa [1].

The analysis of literature data shows that the use of borates in the compositions of foams causes a significant increase in their compressive strength. The use of boric acid derivatives creates a more orderly structure of the polymer, and thus reduces the brittleness of materials [3]. At the same time the presence of borates does not change the dimensions and shape of pores in foams and improves the functional properties of rigid polyurethane foams [4].

Hence the insertion of borates to structure of foams obtained with the participation of hydroxyethyl derivatives of oxamide should increase their mechanical strength. These foams might be used to thermal insulation in building and heat engineering.

In this paper *N,N'*-bis(2-hydroxyethyl)oxamide (BHEOD) was homogenized with boric acid, and the resulting mixture was hydroxyalkylated with an excess of ethylene carbonate (EC). Thus obtained hydroxyethyl derivatives of OD modified with boric acid was used as the polyol component for rigid polyurethane foams preparation. The properties of these foams were investigated.

EXPERIMENTAL

Materials

— Boric acid (H_3BO_3, pure, POCh, Poland);

— ethylene carbonate (EC, pure, Fluka, Switzerland);

— potassium carbonate (K_2CO_3, pure for analysis, POCh, Poland);

— surfactant (Silicon L-6900, Momentive, US);

— catalyst triethylamine (TEA, pure, Avocado, Germany);

— 4,4'-diphenylmethane diisocyanate (MDI, pure, Merck, Germany).

Homogenization of BHEOD with boric acid

In a round bottom flask 4.4 g (0.025 mole) BHEOD (obtained according to [5]) and 3.1 g (0.050 mole) H_3BO_3 were placed. The reaction mixture was stirred mechanically in 120—150 °C temperature range.

Reactions of the mixture of BHEOD and boric acid with excess of EC

In a 100 cm^3 three-necked round bottom flask 7.5 g mixture of 4.4 g (0.025 mole) BHEOD and 3.1 g (0.050 mole) boric acid and the appropriate amount of EC, were placed to reach the molar ratio of reagents of 1:6, 1:10 or 1:14 and 0.21—0.41 g potassium carbonate (8.28—16.56 g/mole BHEOD, 0.06—0.12 mole/mole BHEOD) was added. The reaction mixture was protected from moisture (by tube filled with magnesium sulfate) and stirred mechanically at 160 °C with monitoring of progress of reaction by determination of unreacted EC [6] and the analysis of IR spectra of samples taken during the reaction.

Foam preparation

Attempts of foaming the reactions products of BHEOD and boric acid with EC were carried out in small 250 cm^3 test cups at room temperature. To 10 g of hydroxyethoxy derivatives of OD, 0.1 g of surfactant, 1.6—6.9 wt. % of triethylamine (TEA) and 3—6 wt. % of water were added. After careful mixing of the components, a preweighed amount (w_p) of 4,4'-diphenylmethane diisocyanate was added, calculated according to equation:

$$w_{NCO} = \frac{42 \cdot w_p}{p_{NCO}} \cdot \left(\frac{f \cdot 100}{M} + \frac{p_{H_2O}}{18} \right) \tag{1}$$

where: w_p — *weight of hydroxyalkylated derivatives (polyol) used to foaming process (g),* f — *functionality of polyol (-),* p_{NCO} — *percentage of -NCO groups in isocyanate (wt. %),* p_{H_2O} — *percentage of water by weight of polyol (wt. %),* M — *molecular weight of polyol (g/mole).*

Each composition was vigorously mixed until it started to cream (see Table 4). The samples for testing were cut out from the foams thus obtained after *ca*. 48 hrs.

Methods of testing

— Mixture of BHEOD and boric acid were analyzed by determination of acid number (*AN*) by alkacymetric titration [with 0.1 M KOH(aq)] as described in [7].

— ^{1}H and ^{11}B NMR spectra of products were recorded with 500 MHz spectrometer (Bruker, Germany) in deuterated dimethyl sulfoxide (d_6-DMSO), and hexamethyldisiloxane (HMDS) or boron trifluoride references.

— IR spectra of products were recorded from a capillary film or KBr pellets on a PARAGON 1000 FT spectrometer (Perkin-Elmer).

— Chromatographic analysis of by-products, *i.e.* ethylene glycol (EG) and products of its consecutive reactions with EC [diethylene glycols (DEG), triethylene glycols (TRIEG) and tetraethylene glycols (TETRAEG)] and *N*-(2-hydroxyethyl)oxazolidinone (OXON) were performed with gas chromatograph HP 4890A (Hewlett Packard, Ringoes, NJ, US) with FID detector and HP1 30 m × 0.53 mm column packed with crosslinked methylsiloxane film of 1.5 μm thickness. Initial temperature was 50 °C, heating rate: 20 °C/min, end temperature: 220 °C, time of heating at 220 °C: 6 min, loader temperature: 250 °C, detector temperature: 300 °C. The samples were dissolved in methanol (0.01 M). Internal reference was cyclohexanone. Percentage of diols and polyols was calculated according to calibration curves.

— MALDI ToF (Matrix-Assisted Laser Desorption/Ionization Time of Flight) spectra were obtained on Voyager-Elite Perseptive Biosystems (US) mass spectrometer working at linear mode with delayed ion extraction, equipped with nitrogen laser working at 337 nm. The matrix was 2,5-hydroxybenzoic acid in THF at 10 mg/cm^3 concentration. The samples were diluted with methanol to 1 mg/cm^3, followed by addition of 10 mg/cm^3 NaI in acetone. Therefore in some cases the molecular ion weights were increased by the weight of Na^+, K^+, H^+ and CH_3OH.

— Thermal analyses (DTG and TG) of hydroxyethoxy derivatives of OD modified with boric acid and polyurethane foams were performed in ceramic crucible, in the temperature range 20—600 °C, on app. 2 mg sample, under a nitrogen atmosphere with Termbalance TGA/DSC 1 derivatograph, Mettler Toledo.

— The following properties of hydroxyethoxy derivatives of OD modified with boric acid were determined: pycnometer density [8], Höppler viscosity [9], and surface tension by ring detach method [10]. All measurements were carried out in temperature range 20—80 °C.

— The following properties of foams were determined: apparent density by PN-EN ISO 845, water uptake PN-EN ISO 2896, stability of dimensions PN-EN ISO 2786, glass transition temperature (by DSC), thermal stability as the weight loss after heating at 150, 175 and 200 °C for a month, and the compressive strength PN-93/C-89071, ISO 884:1978.

— The differential scanning calorimetry (DSC) measurements of foams were made using a DSC822e Mettler Toledo instrument, in 20—200 °C temperature range and 10 deg/min heating rate under nitrogen atmosphere. The results were recorded as heat flow in (W/g) versus temperature.

— The microscopic observation of foams was carried out using optical microscope Nikon Eclipse LV100 POL, camera Digital Sight DS-5Mc, objective 2.5 or 5 x L Plan. Microscopy measurements were carried out in the Biophysical Laboratory of the Department of Physic of Rzeszow University of Technology. The Laboratory has been established in the frame of UE Polish Integrated Regional Operation Program.

RESULTS AND DISCUSSION

Homogenization of BHEOD with boric acid

BHEOD was mixed with boric acid and heated initially at 120 °C. Since in these conditions some problems with mixing of the compounds, occurred temperature was increased in increments of 10 °C to achieve a complete homogenization, which took place at 150 °C.

Assuming that boric acid is monofunctional the *AN* of the starting mixture calculated theoretically, was equal to 374 mg KOH/g. Knowing that experimental *AN* of boric acid is 74.5 mg KOH/g and taking this value into account in calculations of *AN* of the reaction mixture, the obtained *AN* value was equal to 42 mg KOH/g. After homogenization of the reactants *i.e.* after 5 minutes of heating, the *AN* of the mixture was 40.6 mg KOH/g, suggesting lack of BHEOD with boric acid reaction.

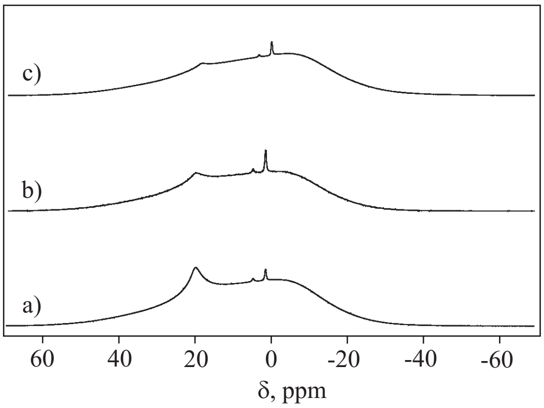


Fig. 1. ^{11}B NMR spectra of the reaction product of BHEOD with boric acid taken after: a) 5, b) 15, c) 25 minutes of reaction

Further heating of the mixture caused decrease of *AN* (after 15 min *AN* = 7.6 mg KOH/g), which indicated the esterification process.

This was confirmed by NMR analysis, after prolonged heating of BHEOD mixture with boric acid. In ^{11}B NMR spectrum a clear decrease of the signal at 19.75 ppm, characteristic for boron in boric acid has been observed (Fig. 1).

In ^{1}H NMR spectrum of BHEOD mixture with boric acid (Fig. 2) after 5 minutes of heating there were no changes in signals shifts of protons of methylene group at nitrogen atom (3.2 ppm) or at oxygen (3.45 ppm) as compared with ^{1}H NMR spectrum of pure BHEOD.

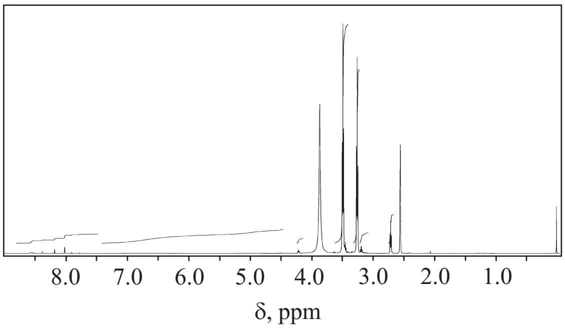
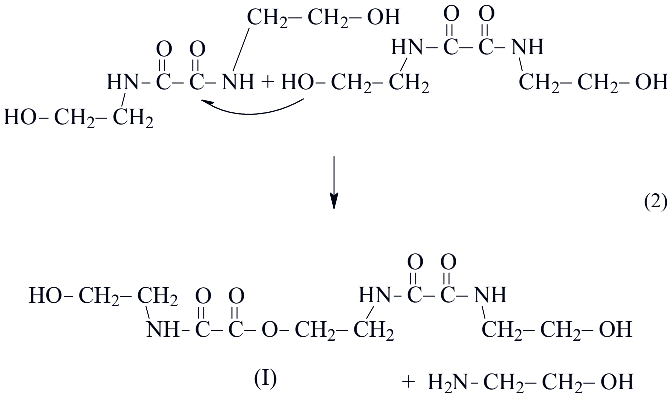


Fig. 2. ^{1}H NMR spectrum of the reaction product of BHEOD with boric acid with the addition of D_2O

The presence of signal at 4.2 ppm, characteristic for protons of methylene group localized at ester group indicated little participation of BHEOD homocondensation reaction.



(2)

A content of the ester, estimated by comparison of signals intensity at 4.2 and 3.45 ppm was about 3 mole %. Such condensation took place during reaction of BHEOD with EC (I).

Reactions of the mixture of BHEOD and boric acid with EC

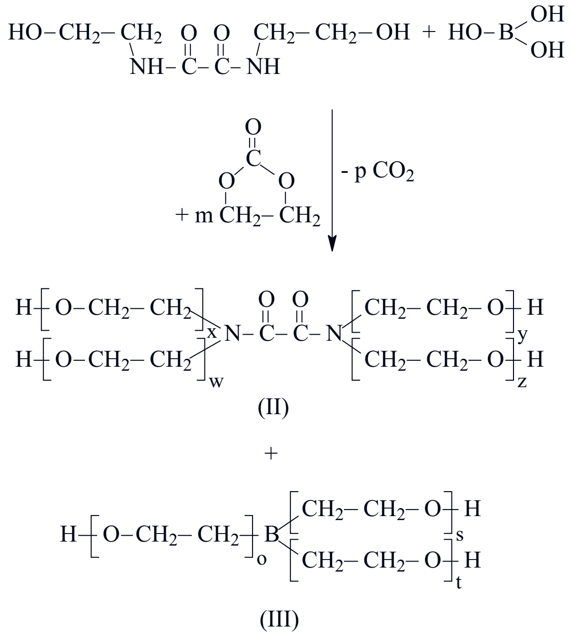
BHEOD homogenized with boric acid (5 minutes heating at 150 °C) were subject of reactions with an excess

Table 1. Reaction conditions of mixture of BHEOD and boric acid with EC

Synth.	Initial molar ratio of reagents	Amount of K_2CO_3 mole /mole BHEOD	Temp., °C	Time of reaction, h	Molar ratio BHEOD:x*) in post-reaction mixture (from mass balance)
1.	1:6	0.06	160	24.0	—
2.	1:6	0.09	160	9.0	1.0:5.7
3.	1:10	0.09	160	20.5	1.0:9.5
4.	1:14	0.12	160	20.0	1.0:13.1

*) x — oxyethylene unit.

of EC at 160 °C in the presence of potassium carbonate as the catalyst (Table 1). It was observed that white solid precipitated when the initial molar ratio of BHEOD:EC was as 1:6 (Table 1, synth. 1). The solid was identified on the basis of IR spectra as free boric acid. An increase in the catalyst amount did not decrease the process of boric acid participation from the reaction mixture (Table 1, synth. 2). The amount of sludge depended on the excess of EC in the reaction and decreased with its increase. The product obtained with a 10 molar excess of EC remained homogeneous for a long time, and then a small amount of boric acid precipitated; at 14-molar EC excess, boric acid did not precipitated from the reaction mixture. MALDI-ToF spectrum of the reaction products of BHEOD and boric acid with a 10 molar excess of EC showed that the products were hydroxyethyl derivatives of OD (II) and hydroxyethyl derivatives of boric acid (III) (Fig. 3).



(3)

where: x, y, z > 1, w ≥ 0, m = 10 or 14

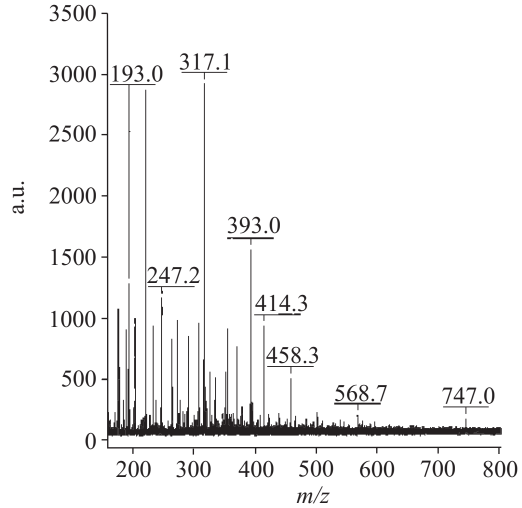


Fig. 3. MALDI ToF spectrum of the reaction product of mixture BHEOD and boric acid with EC 1:10 in the presence of 0.09 mole K_2CO_3/mole BHEOD at 160 °C

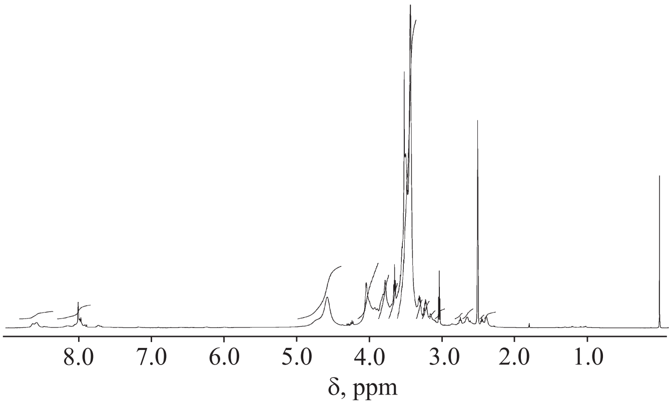


Fig. 4. ^1H NMR spectrum of the reaction product of mixture BHEOD and boric acid with EC 1:14 in the presence of 0.12 mole K_2CO_3/mole BHEOD at 160 °C

Analysis of ^1H NMR spectra of the products indicated the presence of unreacted secondary amide groups in their structure, even when 14-molar excess of EC was applied, as was evidenced by the presence of signal at 8.5 ppm, characteristic for protons of secondary amide group (Fig. 4). Two bands at 1669 and 1519 cm^{-1} in the IR spectrum of the products (Fig. 5) confirmed the presence of secondary amide groups.

Moreover the signals at 4.25 ppm and 4.35 ppm, from the protons of methylene groups presented at ester group were evidenced in the spectra of the products obtained with a 6 and 10-molar excess of EC. During the reactions similar to that as BHEOD with EC incorporation of carbo-

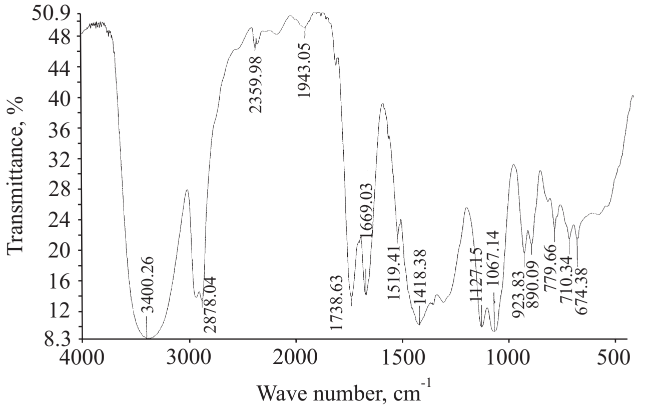


Fig. 5. IR spectrum of the reaction product of mixture BHEOD and boric acid with EC 1:14 in the presence of 0.12 mole K_2CO_3/mole BHEOD at 160 °C

nate groups into the product structure (4.25 ppm) and condensation of hydroxyethyl derivatives of OD with the formation of oxamidoester groups (4.35 ppm) took place. The presence of ester groups was confirmed by the presence of band at 1738 cm^{-1}, characteristic for the valence vibrations of ester C=O group, in IR spectrum (Fig. 5).

The condensation process was confirmed, in turn, by the presence of signal at 8.0 ppm, coming from the proton of secondary amide group of oxamidoester (Fig. 4).

The signal at 4.35 ppm was no more observed in the obtained product obtain with a 14 molar excess of EC spectrum.

A quantitative contribution of condensation process in the obtained products was estimated based on determination of the content of OXON in the products (Table 2) by gas chromatography (GC) [1]. The content of OXON was small, about 0.1 wt. %, therefore a participation of dimerization of hydroxyethyl OD derivatives was also small.

GC analysis of the reaction mixtures showed the presence of other by-products, namely poly(ethylene glycols) formed in the reaction of EC with water and in side reactions of EG forming from EC. A contribution of glycols was also small; EG, DEG and TETRAEG were formed, but their total amount did not exceed 1 wt. % (Table 2).

The obtained products were characterized by good thermal stability (Table 3). Two peaks at 210 and 355 °C were observed on DTG curve of the products. The first one resulted from borate [11] and carbonate [12] groups decomposition, and the second one from decomposition of oxamidoester and oxamide groups.

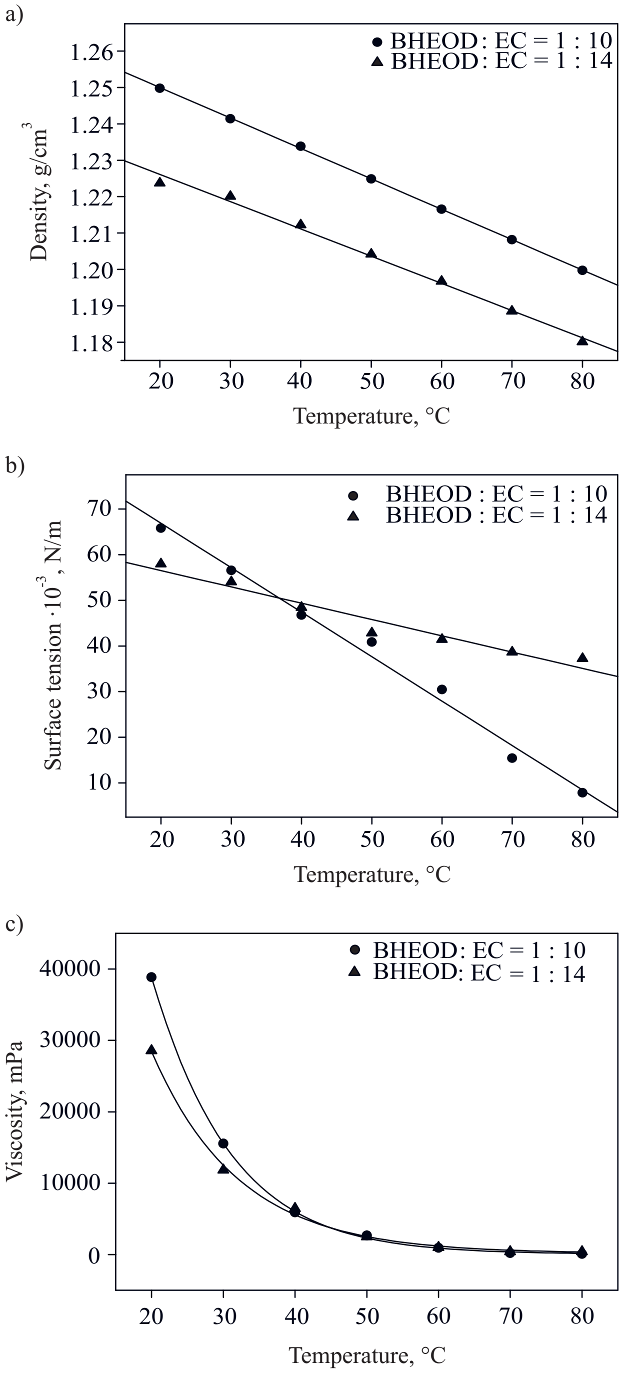


Fig. 6. Physical properties of products of reactions of mixture BHEOD and boric acid with EC as a function of temperature

Table 2. Percentage of by-products

Entry*)	Percentage of OXON in post-reaction mixtures, wt. %	Percentage of poly(ethylene glycols) in post-reaction mixtures, wt. %				
		EG	DEG	TRIEG	TETRAEG	Σ
2.	0.10 ± 0.01	0.10 ± 0.02	0.00	0.0	0.20 ± 0.01	0.3
3.	0.10 ± 0.01	0.10 ± 0.02	0.20 ± 0.02	0.0	0.10 ± 0.01	0.4
4.	0.00	0.10 ± 0.03	0.20 ± 0.03	0.0	0.30 ± 0.03	0.6

*) Entry according to Table 1.

Thermal stability of the reaction products is comparable with this of the products of the BHEOD reaction with an excess of EC [1].

T a b l e 3. Thermal stability of obtained products[*)]

Entry	Initial molar ratio of reagents	$T_{5\,\%}$ °C	$T_{10\,\%}$ °C	$T_{20\,\%}$ °C	$T_{50\,\%}$ °C	T_{max}, °C
1.	1:10	115	155	185	275	210 and 355
2.	1:14	90	130	175	270	205 and 370

[*)] $T_{x\,\%}$ — temperature at which the weight loss is x %. T_{max} — maximum decomposition temperature.

Some physical properties of the products obtained in reactions with 10- and 14-molar excess of EC, such as: density, surface tension, and viscosity (Fig. 6) were investigated as a function of temperature (20—80 °C). It was observed that an increase in temperature causes a linear decrease of density, surface tension and exponential decrease of viscosity. Such changes are typical for polyols, traditionally used for polyurethane foams preparation [2].

Preparation and properties of obtained polyurethane foams

Polyols with oxamide groups modified with boric acid obtained in the reactions of BHEOD and boric acid with an excess of EC were used as polyols component for polyurethane foams preparation (Table 4).

Foaming was carried out in a laboratory scale. The amount of isocyanate was precalculated with the equation (1), and then on the basis of the course of foaming process and the initial inspection of the foam the composition of the foaming mixture was modified. If too little amount of isocyanate was used, the foam was unhardened. If too high amount of isocyanate was used, foam exhibited shrinkage. In turn, on the base of the growth rate of the foam, appropriate quantity of catalyst (TEA) was found.

Similarly it was investigated that the optimal water amount during foaming was 6 wt. % with respect to polyol mass, and such amount was applied in further attempts (Table 4). Amount of water were change on the base of visual estimation of foams. In case when the amount of water was too small the foams characterized low foaming degree. On the other hand, too large amount of water causes that foams had irregular pores.

The amount of the catalyst — TEA depended on the kind of derivative applied and increased with increasing number of oxyethylene units in polyol. It was observed that the creaming time was usually about one minute and the foam expanding time was within the range 0.25—2.5 minutes and decreased with an increase of the catalyst amount (Table 4, comp. 7 and 9). The foams drying time was about 1 minute (Table 4).

The properties of the obtained polyurethane foams were investigated. It was stated that apparent density of the foams was within the range 40—60 kg/m^3 (Table 5). The foams prepared with the participation of polyols obtained at larger excess of EC, that means, with lower boron content, are characterized by lower apparent density.

T a b l e 4. Parameters of foaming process

Initial	Determined	Composition No.	Composition, g/100 g of polyol			Foaming process; time, s		
Molar ratio BHEOD:EC in polyol			isocyanate[a)]	water	catalyst[b)]	creaming[c)]	expanding[d)]	drying[e)]
1:10	1:9.5	1.	192	3	1.60	79	60	15
		2.	192	4	2.67	48	25	11
		3.	192	4	2.14	51	45	10
		4.	208	6	2.14	56	120	32
		5.	248	6	2.14	66	122	46
		6.	208	6	1.87	54	82	40
1: 14	1:13.3	7.	248	6	2.67	167	92	55
		8.	280	6	5.34	116	162	65
		9.	248	6	7.48	43	15	20
		10.	248	6	6.94	54	16	14

[a)] 4,4′-Diphenylmethane diisocyanate.

[b)] Triethylamine.

[c)] Time of creaming: time elapsed from the moment of mixing to the start of volume expansion, measured with an accuracy of 1 second.

[d)] Time of expanding: time from the start of expansion to the moment of reaching the sample final volume, measured with an accuracy of 1 second.

[e)] Time of drying: time from reaching by the sample its final volume to the moment of losing its surface adhesion to powdered substances, measured with an accuracy of 1 second.

Table 5. Properties of foams

Comp. No.*)	Apparent density kg/m^3	Water uptake, wt. %			Linear dimension change after heating at 150 °C, linear %					
		after 5 min	after 3 hrs.	after 24 hrs.	length		width		thickness	
					after 20 hrs.	after 40 hrs.	after 20 hrs.	after 40 hrs.	after 20 hrs.	after 40 hrs.
6.	60.37 ± 2.28	8.06 ± 0.47	19.54 ± 2.37	44.79 ± 3.02	0.38 ± 0.03	0.38 ±0.03	1.53 ± 0.13	2.45 ± 0.16	3.62 ± 0.15	3.99 ± 0.40
9.	40.03 ± 1.89	2.67 ± 0.09	5.74 ± 0.73	9.62 ± 0.82	0.18 ± 0.01	0.36 ± 0.03	0.75 ± 0.02	1.00 ± 0.02	4.46 ± 0.23	4.46 ± 0.23

*) Comp. No. according Table 4.

Water uptake of the foams depended on the boron content and decreases with the boron content decrease up to 10 wt. % (Table 5).

Optical microscope observations showed that the foams contain close pores. However in the case of the foams obtained with the participation of BHEOD and boric acid reaction product with a 10-molar excess of EC, the pores walls are inconsistent but have also porous structure. A consequence of this fact was large water absorption (45 wt. %). The pores dimensions were within the range of 0.35—0.86 mm, and the walls thickness was 0.19—0.22 mm (Fig. 7a). In turn, the foams obtained with the participation of BHEOD and boric acid reaction product at 14-molar excess of EC had rounded shape pores (with dimensions 0.06—0.19 mm) and uniform walls, which thickness was 20—24 μm (Fig. 7b).

The glass transition temperature of the selected foams was within the range 97—108 °C (Table 6). It was stated that the temperature decreased with an increase in EC excess in polyol. However, the glass transition temperature of all foams obtained was significantly higher than room temperature, therefore the foams can be classified as rigid ones [2].

Thermogravimetric analysis confirmed high thermal stability of the obtained polyurethane foams — 5 % weight loss occured only at about 210 °C and maximal decomposition temperature was within the range 265—400 °C (Table 6).

Table 6. Thermal stability of polyurethane foams and temperature of glass transition

Comp. No.*)	$T_{5\,\%}$**) °C	$T_{10\,\%}$ °C	$T_{20\,\%}$ °C	$T_{50\,\%}$ °C	T_{max} °C	T_g °C
6.	220	240	260	325	265, 310 and 400	107.5
9.	210	240	260	305	295	97.3

*) Comp. No. according Table 4.

**) $T_{x\,\%}$ — temperature at which the weight loss is x %.

To investigate the possibility of work of the foams at 150 °C and higher temperatures, the heating tests for 30 days at 150, 175 and 200 °C were performed and weight loss during heating was studied. The lowest value of weight loss was observed for foams, heated at 150 °C (about 10 wt. %), and this value was comparable for the foams obtained from polyols obtain at different EC excess. It should be emphasized that the weight loss of the foams heated 200 °C did not exceed 37 wt. % (Table 7).

The weight losses of the foams was quite high but lower than weight losses of the foams obtained with par-

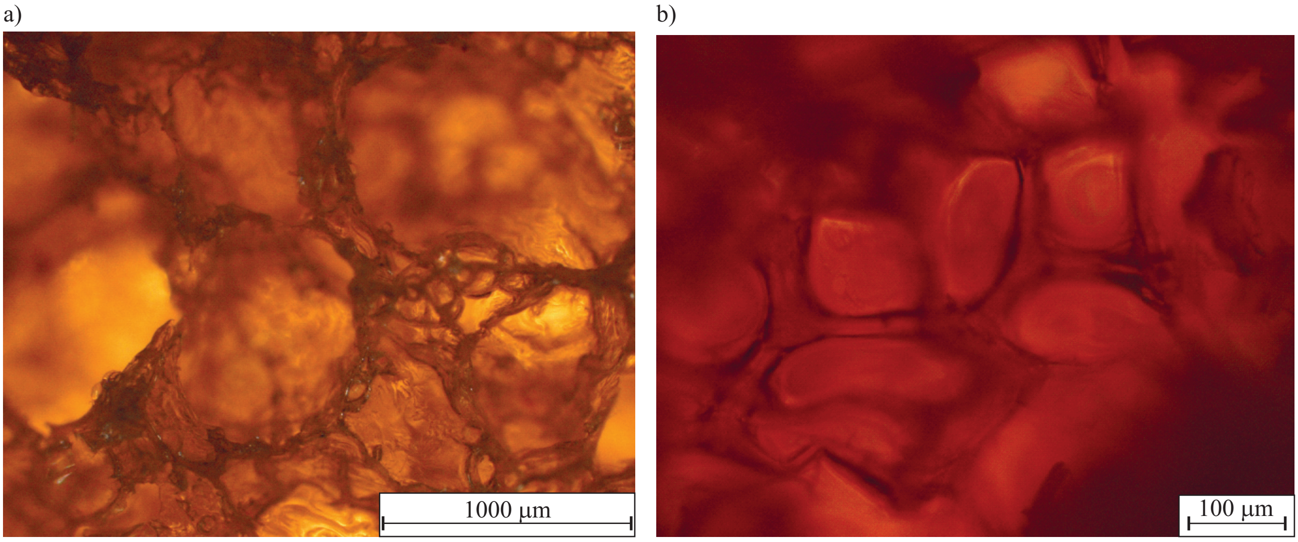


Fig. 7. Morphology of the foam derived from polyols obtained as a product of reaction of mixture of BHEOD and boric acid and: a) 10-, b) 14-molar excess of EC, magnification: a) 2.5×, b) 10×

ticipation of hydroxyethyl derivatives of OD but unmodified with boric acid [1]. These weight losses are still too high to foams to be able to find practical application.

T a b l e 7. Thermal stability of foams measured by weight loss during temperature exposition for 30 days

Comp. No.*)	Weight loss (wt. %) of foams after exposition in temperature (°C)		
	150	175	200
6.	11.30 ± 0.57	25.40 ± 0.52	32.90 ± 0.70
9.	10.00 ± 0.60	24.00 ± 0.47	36.60 ± 0.67

*) Comp. No. according Table 4.

The foams were also subject of strength tests, by investigating compressive strength before the temperature exposition and after heating at 150, 175 and 200 °C. The direction of compression of the foam was in line with the direction of foams growth. The foams were characterized by the compressive strength within the range of 0.17—0.25 MPa (Table 8), that is higher than in case of traditional foams (0.10—0.20 MPa), which are characterized by similar apparent density [2]. After temperature exposition the compressive strength of the foams was higher, especially for the foams obtained from polyols obtained with higher EC excess, that is with lower boron content. The compressive strength increased gradually with the increase in the heating temperature, so that the foams heated at 200 °C showed 114 % higher compressive strength in comparison to the starting foam (Table 8, comp. 9). The compressive strength of foams with higher boron content was higher than for foams with lower boron content, but this also results from higher apparent density. After heating these foams at 150 °C theirs compressive strength slightly increased. At 175 °C the compressive strength did not change but it decreases after heating at 200 °C (Table 8, comp. 6).

T a b l e 8. Compressive strength of polyurethane foams

Comp.*) No.	Compressive strength**) σ_M MPa	Compressive strength σ_M (MPa) after exposition in temperature (°C)			Increase of compressive strength (in %) after exposition in temperature (°C)		
		150	175	200	150	175	200
6.	0.25 ± 0.02	0.28 ± 0.02	0.25 ± 0.02	0.08 ± 0.01	11	0	-68
9.	0.17 ± 0.01	0.24 ± 0.02	0.28 ± 0.02	0.30 ± 0.03	41	65	114

*) Comp. No. according to Table 4. **) Measured at 10 % deformation.

Comparing the properties of polyurethane foams obtained with the participation of BHEOD and EC reaction products [1] with those of OD hydroxyethyl derivatives modified with boric acid, it was stated that the foams obtained with the addition of boric acid were characterized by higher dimensions and thermal stability, lower weight losses during the temperature exposition and higher compressive strength, which increased with an increase in the heating temperature.

The properties of obtained polyurethane foams were compared with properties of other rigid polyurethane foams modified with boron [13], for example, foams obtained with boron-modified with derivatives of urea as an additive to polyol component, which compressive strength is slightly higher and depending on the amount of additive is in the range 0.23—0.39 MPa. Similarly, these foams have lower water absorption, compared to the foams obtained from hydroxyethyl derivatives of oxamide modified boron. The foams obtained in this work show higher thermal stability, 5 % weight loss occurs only at 210 °C, while in the case of comparable foams it occurs at 164 °C [14].

CONCLUSIONS

— The homogenization conditions of *N,N*'-bis(2-hydroxyethyl)oxamide and boric acid were developed.

— Obtained with *N,N*'-bis(2-hydroxyethyl)oxamide, boric acid and with of excess ethylene carbonate, hydroxyalkyl derivatives are characterized by high thermal stability, and they exhibit the typical changes of properties of polyols used for the preparation of polyurethane foams.

— Obtained from participation of hydroxyethyl derivatives oxamide modified with boric acid rigid polyurethane foams have good dimension stability, high thermal stability, small weight loss during exposition in high temperature and good compressive strength, which is associated with the presence of boron.

— The introduction of boron into the structure of polyurethane foams makes that they have higher thermal stability and compressive strength compared to the foams obtained with hydroxyethyl derivatives of oxamide without presence of boron.

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