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## PROPERTIES OF POLYURETHANE FOAMS WITH OXAMIDE AND BORATE GROUPS

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**Abstract.** The conditions of polyurethane foams preparation with the use of new bororganic compounds as polyols have been presented. The new polyols have been obtained by two methods: in reactions of N,N'-bis(2-hydroxyethyl)oxamide (BHEOD) and boric acid (BA) with excess of ethylene carbonate (EC) and in reactions of BHEOD esterified with BA with excess of EC. The results of determination of foaming process parameters as well as of investigation of the foams properties have been given.

**Keywords:** rigid polyurethane foams, oxamide, boric acid, hydroxyalkylation, modification of structure, thermal stability, compressive strength.

### 1. Introduction

In the seventies of the twentieth century oxamide (OD) was used in many branches of industry [1-3]. Its derivative N,N'-bis(2-hydroxyethyl)oxamide (BHEOD) has also found application in industry, the synthesis of polymers including BHEOD was used for manufacturing of the flame-retardant polyurethanes [4], amido-urethanes [5], and tension-resistant flexible fibers [6]. BHEOD was also used as a component in the flame-retardant polyurethane foams. The presence of BHEOD not only decreased flammability but at the same time did not deteriorate any mechanical properties of the foamed polyurethane plastics [7].

Nowadays literature data indicate that boric acid and organic boron compounds are used in the production of polymeric materials increasingly. Their role is to reduce flammability and to improve some of physical and mainly mechanical properties of plastics such as enhancing compressive strength and reducing brittleness [8-10].

In this work hydroxyethyl derivatives of OD and boric acid (BA) as a mixture or bonded chemically was used in order to obtain foamed polyurethane materials. It was expected that polyurethane foams should be

characterized by high thermal stability due to the presence of oxamide group and good compressive strength due to boron and oxamide groups presence.

Boron was introduced into the structure of polyurethane foams *via* the modification of polyol component by boric acid. The modification of polyol was made according to two ways. In the first method a homogenous mixture of BHEOD and BA was hydroxyalkylated with excess of ethylene carbonate (EC), so the polyol was a mixture of hydroxyethyl derivatives of OD and BA. In the second method borate groups were incorporated into the structure of hydroxyethyl derivatives of OD.

With the participation of the mentioned polyol components the rigid foamed polyurethane plastics have been obtained, and then their properties have been determined and compared.

### 2. Experimental

#### 2.1. Syntheses

##### 2.1.1. Homogenization of BHEOD and BA

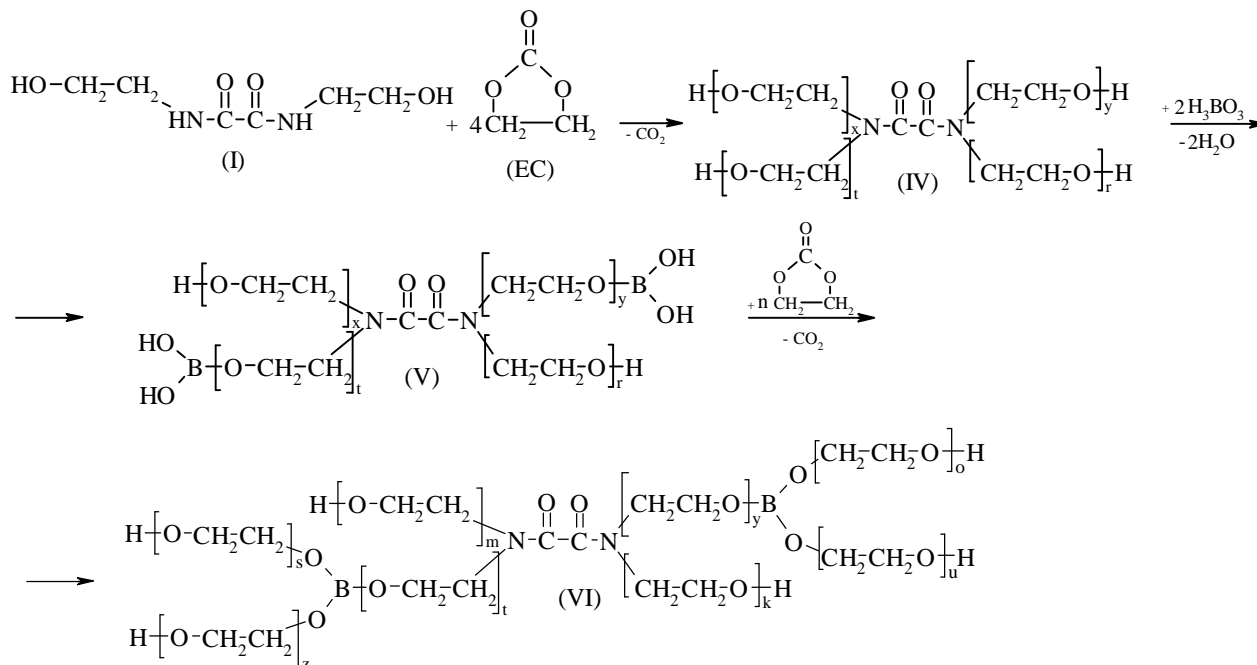
In a round bottom flask 44 g (0.25 mol) BHEOD (obtained according to [11]) and 31 g (0.50 mol) BA (pure, POCH, Poland) were placed. The reaction mixture was stirred mechanically at temperature 423 K to until getting a homogenous mixture (5 min).

##### 2.1.2. Reactions of the mixture of BHEOD and BA with excess of EC

In a 250 cm<sup>3</sup> three-necked round bottom flask 75 g mixture consisting of 44 g (0.25 mol) BHEOD and 31 g (0.50 mol) BA and the appropriate amount of EC (pure, Fluka, Switzerland) were placed to reach the molar ratio of reagents of 1:10 or 1:14 and 3.1 or 4.1 g potassium carbonate (pure for analysis, POCH, Poland) (12.42 or



In the second method BHEOD was reacted with 4-molar excess of EC and then this derivative (IV, THEOD) was esterified with BA. Borate (V, EBOD) was reacted with excess of EC (Table 1, synth. 3 and 4):



where:  $m + t + y + k + s + z + u + o \leq 12$  or  $16$

Table 1

Conditions of polyols obtaining

Synth.	Initial molar ratio BHEOD:EC:BA:EC	Amount of $\text{K}_2\text{CO}_3$ , mol/mol BHEOD	T, K	Reaction time, h	Molar ratio BHEOD:x in post-reaction mixture
1	1:0:2:10	0.09	433	24	1:9.50
2	1:0:2:14	0.12	433	20	1:13.32
3	1:4:2:6	0.09	433	3+1.5+12	1:9.48
4	1:4:2:10	0.12	433	3+1.5+10	1:13.31

Note: x – oxyethylene unite.

Table 2

Parameters of foaming process

Molar ratio BHEOD:EC:BA:EC in polyol	Comp.	Composition, g/100 g polyol			Course of foaming time, s		
		isocyanate*	water	catalyst**	creaming <sup>a</sup>	expanding <sup>b</sup>	drying <sup>c</sup>
1:0:2:10	F1(10)	208	6	1.87	54	82	40
1:0:2:14	F1(14)	248	6	7.48	43	15	20
1:4:2:6	F2(10)	268	6	6.23	38	36	1
1:4:2:10	F2(14)	248	6	3.46	22	16	1

Notes: \* 4,4'-diphenylmethane diisocyanate; \*\* triethylamine; <sup>a</sup> creaming time: the time elapsed from the moment of mixing to the start of volume expansion; <sup>b</sup> expanding time: the time from the start of expansion to the moment of reaching the sample final volume; <sup>c</sup> drying time: the time from reaching by the sample its final volume to the moment of losing its surface adhesion to powdered substances.

In both methods the same initial molar excess of EC was used thus the oxyethylene units excess in relation to OD was identical (1:12 and 1:16). Furthermore in both methods 2-molar excess of BA in relation to OD was applied.

New polyols obtained (mixture II and III as well as VI) were used for polyurethane foams preparation. Parameters of foaming process and foams compositions were given in Table 2.

It has been stated that apparent density of all foams was within the range of 33–60 kg/m<sup>3</sup> (Fig. 1). The foams prepared with the participation of polyols obtained at larger excess of EC (that means with lower boron content) were characterized by lower apparent density (33–40 kg/m<sup>3</sup>), whereas density of foams with higher boron content was of 58–60 kg/m<sup>3</sup>.

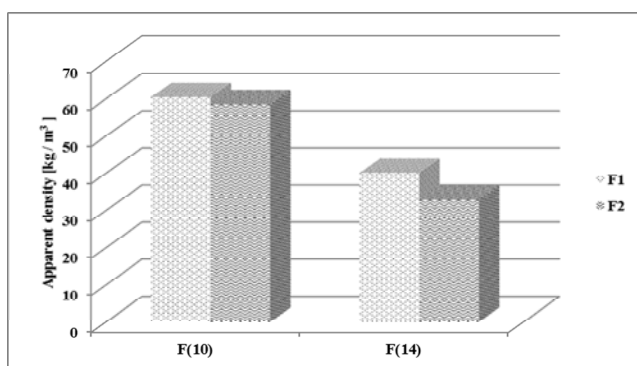


Fig. 1. Apparent density of obtained polyurethane foams

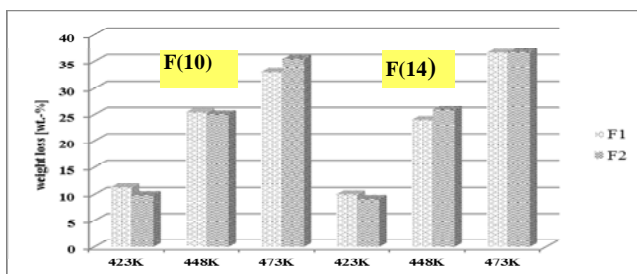


Fig. 2. Thermal stability of foams measured by weight loss after annealing for 30 days

The glass transition temperature of all foams was in the range of 370–390 K (Table 3). However, the glass transition temperature of the obtained foams was higher than room temperature; these foams were classified as rigid ones [15].

Thermogravimetric analysis demonstrated high thermal stability of the obtained polyurethane foams (Table 3). 5% weight loss occurs only at about 483 to 493 K and the temperature of maximum decomposition was in the range of 538–693 K (Table 3). To essential influence of polyol type on thermal stability of the obtained foams has been stated.

Table 3

### Thermal stability and glass transition temperature of the polyurethane foams

Comp.	$T_{5\%}$ , K	$T_{10\%}$ , K	$T_{20\%}$ , K	$T_{50\%}$ , K	$T_{max}$ , K	$T_g$ , K
F1(10)	493	513	533	598	538, 583 and 673	380.5
F1(14)	483	513	533	578	568	370.3
F2(10)	483	503	528	578	563 and 678	370.0
F2(14)	488	508	518	573	553 and 693	390.1

Note:  $T_{x\%}$  – temperature at which the weight loss is  $x\%$ .

In order to investigate the possibility of work of the foams at the temperature 423 K and higher the weight loss was measured during the foams heating for 30 days at 423, 448 and 473 K (Fig. 2). The foams heated at 423 K showed the lowest value of weight loss (9.2–11.3 wt %). Weight losses were comparable for the foams obtained from both types of polyols, but in case of foams from polyols synthesized by the first method weight losses were slightly lower (lower than 10 wt %, Fig. 2).

The foams were also subjected to strength tests by investigating compressive strength before temperature exposition and after heating at 423 K. The direction of foams compression was in line with the direction of foams growth. The foams were characterized by the compressive strength within the range of 0.17–0.27 MPa (Table 4). The foams obtained with participation of the polyols synthesized in the second method were characterized by a bit higher compressive strength (Table 4).

Table 4

### Compressive strength of polyurethane foams

Comp.	Compressive strength* ( $sM$ ), MPa	
	without heating	after exposition at 423 K
F1(10)	0.25 ± 0.02	0.28 ± 0.02
F1(14)	0.17 ± 0.01	0.24 ± 0.01
F2(10)	0.27 ± 0.02	0.27 ± 0.02
F2(14)	0.22 ± 0.02	0.24 ± 0.01

Note: \*measured by 10% deformation.

The compressive strength of foams with higher boron content was higher (Table 4, comp. F1(10) and F2(10)) than in foams with lower boron content, as the result of their higher apparent density. The compressive strength of foams increased after their heating at 423 K and larger changes was observed in case of foams obtained from polyols synthesized by the first method (Table 4, comp. F1(10) and F1(14)).

The properties of the obtained polyurethane foams were compared with the properties of other rigid polyurethane foams, *i.e.* properties of foams prepared with participation of Rokopl RF-55 [9, 10]. The density of the

reference foams is about  $36.9 \text{ kg/m}^3$  and is comparable with the density of foams obtained from both polyols containing lower boron content ( $33\text{--}40 \text{ kg/m}^3$ , Fig. 1, F1(14) and F2(14)).

It was noticed that the compressive strength of reference foams was 0.24 MPa whereas compressive strength of foams modified with boron was comparable or slightly lower (0.22 and 0.17 MPa). In turn, reference foams had lower thermal stability; their 5% weight loss occurred at 458 K, while that for the foams modified with boron - at 483 K. Furthermore, the temperature of the maximum decomposition of these foams was higher than 553 K and that of the reference foams was 483 K.

#### 4. Conclusions

Most of the properties, *i.e.* apparent density and thermal stability, of polyurethane foams with oxamide and borate groups obtained from polyols synthesized by two different methods are similar.

The foams exhibit some differences in thermal resistance and compressive strength. The foams obtained from polyols synthesized by the second method show slightly lower weight loss after annealing to constant weight at the temperature of 423 K and slightly higher compressive strength.

Polyurethane foams obtained from both types of polyols are characterized by higher thermal stability while slightly lower compressive strength as compared with the reference foams.

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#### ВЛАСТИВОСТІ ПІНОПОЛІУРЕТАНІВ З ОКСАМІДНИМИ І БОРАТНИМИ ГРУПАМИ

**Анотація.** *Визначено умови приготування пінополіуретанів з використанням нових бороорганічних сполук, таких як полііоли. Показано, що нові полііоли отримані двома способами: реакцією N,N'-біс (2-гідроксіетил)оксаміду (ВГЕОД) і борної кислоти (БК) з надлишком етиленкарбонату (ЕК) і реакцією етерифікації ВГЕОД з БК з надлишком ЕК. Приведено результати визначення параметрів процесу спінювання і дослідження властивостей піни.*

**Ключові слова:** *жорсткі пінополіуретани, оксамід, борна кислота, гідроксіалкілювання, модифікація структури, термостійкість, міцність на стиснення.*