

# Effect of Selected Boroorganic Compounds on Thermal and Heat Properties of Rigid Polyurethane–Polyisocyanurate Foams

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**ABSTRACT:** The effects of three selected borates {tri(hydroxypropyl), tri[(3-chloro-2-hydroxy-1-propoxy)-1-methylethyl], tri[(3-chloro-2-hydroxy-1-propoxy)propyl]} on the heat and thermal properties of rigid polyurethane–polyisocyanurate foams was studied. Increasing the amount of tri(hydroxypropyl) borate and tri[(3-chloro-2-hydroxy-1-propoxy)propyl] borate in the foam composition from 0.1 to 0.4 chemical equivalents caused an increase in the softening point, the temperature of the first decrement of foam mass, the extrapolated temperature of the main decrement of the

foam mass, and the temperature of the highest rate of the mass decrement. When tri[(3-chloro-2-hydroxy-1-propoxy)-1-methylethyl] borate was added to the foam compositions, the softening point decreased but the temperatures characterizing their thermal resistance were higher in comparison with the standard foam. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 768–771, 2006

**Key words:** rigid polyurethane–polyisocyanurate foam; heat resistance; thermal resistance; thermogravimetric analysis

## INTRODUCTION

Rigid polyurethane (PU) foams are thermoinsulating materials characterized by better technological parameters than foamed polystyrene and mineral wool.<sup>1,2</sup> Their overall heat-transfer coefficient is very low (i.e.,  $\sim 0.025$  W/m K).<sup>3</sup> The heat and thermal resistances are the parameters limiting their application as thermal insulation. Heat resistance is connected to the physical changes in foams occurring under the action of temperature and applied forces. Most often, it is characterized by a softening point and a method for its determination. During the changes, the molecular weight of the polymer is unchanged.

The thermal resistance of PU foams is connected mainly with the temperature of thermal dissociation of the weakest bonds occurring in foams, and it is accompanied by a decrease in weight. In addition to the urethane bond, ester, ether, aliphatic, urea, biuret, carbamide, isocyanurate, and other bonds can be formed in foams, depending on the raw materials applied and the equilibrium ratio of NCO/OH. Their temperatures of dissociation are approximately 200, 260, 350, 106, 250, 130–145, 240, and 300°C, respectively.<sup>4–8</sup>

The aim of our studies was to determine the effect of tri(hydroxypropyl) borate (BTHP), tri[(3-chloro-2-hydroxy-1-propoxy)propyl] borate (BTCIHP), and tri[(3-chloro-2-hydroxy-1-propoxy)-1-methylethyl] borate (BTCIHPME) on the heat and thermal resistances of rigid PU (PUR)–polyisocyanurate (PIR) foams.

## EXPERIMENTAL

### Characteristics of raw materials

A polyether with the trade name Rokopol RF-55 [product of oxypropylation of sorbitol, hydroxyl number ( $L_{OH}$ ) = 495.0 mg KOH/g, NZPO Rokita, Brzeg Dolny, Poland] and Ongromat CR 30-20 (technical polyisocyanate whose main component is diphenylmethane 4,4'-diisocyanate) were used to prepare the PUR–PIR foams. The density of Ongromat CR 30-20 at 25°C was 1.23 g/cm<sup>3</sup>, the viscosity was 200 mPa s, and the content of NCO groups was 31.0%. The polyether and polyisocyanate were characterized according to ASTM D 2849-69 and ASTM D 1638-70 standards.

Anhydrous potassium acetate (POCh, Gliwice) applied in the form of a 33% solution in diethylene glycol (Catalyst-12) and triethylenediamine (DABCO, Hüls) applied in the form of a 33% solution in dipropylene glycol were used as catalysts in the process. A polysiloxanepolyoxyalkylene surface active agent (Silicone L-6900, Witco) was used to stabilize the foam structure.

The porophor was CO<sub>2</sub> formed in a reaction of isocyanate groups with distilled water. Moreover, tri(2-chloro-1-methyl-ethyl) phosphate (Antiblaze

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TABLE I  
Characteristics of Selected Borates Applied to Obtain Rigid PUR-PIR Foams

Type	Abbreviation	Density at 20°C (g/cm <sup>3</sup> )	Viscosity at 20°C (mPa s)	Hydroxyl number (mg KOH/g)	State of aggregation	Color
Tri(hydroxypropyl) borate	BTHP	1.072	41.0	437.4	Liquid	Straw yellow
Tri[(3-chloro-2-hydroxy-1-propoxy)1-methylethyl] borate	BTCIH PME	1.040	177.9	429.6	Liquid	Pale yellow
Tri[(3-chloro-2-hydroxy-1-propoxy)propyl] borate	BTCIH PP	1.047	122.4	491.3	Liquid	Yellow

TMCP, Albright and Wilson) was introduced into the foams.

BTHP, BTCIH PME,<sup>9</sup> and BTCIH PP were applied to prepare the foams under study. All borates were obtained from the Department of Chemistry and Technology of Polymers and Ecotechnology, Casimir the Great Academy of Bydgoszcz.

#### Preparation of BTHP

Boric acid (15.5 g, 0.25 mol), 1,3-propanediol (57.0 g, 0.75 mol), and sulfuric acid ( $d = 1.84 \text{ g/cm}^3$ , 3% w/w total mass of boric acid and diol) were introduced at room temperature into a three-necked flask (250 cm<sup>3</sup>) equipped with a Dean-Stark head for azeotropic distillation, a thermometer, and a mechanical stirrer. Then, 75 cm<sup>3</sup> of xylene was added.

The content of the flask was heated to boiling (120°C) with continuous stirring for 150 min. Then, the water (13.5 cm<sup>3</sup>) was distilled off azeotropically. A liquid straw-yellow product was obtained, the main component of which was BTHP.

#### Preparation of BTCIH PP

BTHP (47.2g, 0.2 mol), epichlorohydrin (55.5 g, 0.6 mol), and BF<sub>3</sub>(Et)<sub>2</sub>O catalyst (2.68 g) were introduced at 50°C with continuous stirring into a three-necked flask (250 cm<sup>3</sup>) equipped with a reflux condenser, thermometer, and stirrer. Then, the temperature was raised to 90°C and the reaction run for 90 min. After that time, the temperature was raised to 128°C and the reaction was run for a consecutive 20 min. A liquid transparent-yellow product was obtained whose main component was BTCIH PP.

The properties of the borates applied to prepare rigid PUR-PIR foams are presented in Table I.

#### Synthesis of rigid PUR-PIR foams

The rigid PUR-PIR foams were obtained on a laboratory scale by a one-stage method from a two-component system. The equivalent ratio of —NCO and OH groups was 3 : 1. Component A was obtained by precise mixing (1800 rpm, 10 s) of the respective amounts

of Rokopol RF-55, borates, catalysts, flame retardant, and surfactant. Component B was Ongromat 30-20 (Table II). Both components were mixed at 1800 rpm for 10 s in a suitable mass ratio and poured into an open rectangular metal mold. After the expanded foams were removed from the mold, they were thermostated at 120°C for 4 h.

The foams were milled in an Ianetzki agate mortar and subjected to thermogravimetric (TG) analysis at temperatures from 20 to 800°C. The thermal resistance of the foams was determined under dynamic conditions in an air atmosphere at a heating rate of 5°C/min. Tests were carried out using a derivatograph produced by MOM Budapest (Paulik-Paulik-Erdey).

The heat resistance of the foams was determined according to DIN 53424 using a Vicat apparatus. The foams were analyzed by IR spectroscopy with the KBr technique on a Vector spectrometer (Bruker) in a range from 400 to 4000 cm<sup>-1</sup>.

## RESULTS AND DISCUSSION

On the basis of TG (change of mass) and derivative TG (DTG, derivative of the mass change) curves, the following characteristic values were determined<sup>7,8,10</sup>: the temperature of the first change of the sample mass, the extrapolated temperature of the main decrement of the mass, and the temperature of the highest rate of the foam mass decrement (corresponding to the extreme on the DTG curve).

The first decrement of the standard foam mass (without the addition of borates, foam no. 0) occurs at 85°C (Fig. 1). As the amount of borates was increased in foams from 0.1 to 0.4 chemical equivalents, the temperature increased to 110, 105, and 99°C for foams with BTHP added (nos. 1–7), foams with BTCIH PP added (nos. 8–14), and foams with BTCIH PME added (nos. 15–21), respectively.

The first decrement of mass is probably caused by diffusion of carbon dioxide, which plays the role of blowing agent in the foams we studied. Carbon dioxide is formed as a result of the reaction between the excess of isocyanate groups (—NCO) and water. Moreover, the diffusion of DABCO from the foam can occur within the temperature range from 85 to 110°C.

TABLE II  
Compositions of Reaction Mixtures Applied to Prepare Rigid PUR-PIR Foams

Foam no.	Raw materials						
	Rokopol RF-55 (g)	BTHP		BTCIHPME		BTCIHPP	
		(g)	(g)	(ch.e.)	(g)	(ch.e.)	(g)
0	55.6	0.0	0.0	0.0	0.0	0.0	0.0
1	51.0	5.2	0.10	—	—	—	—
2	48.1	7.8	0.15	—	—	—	—
3	45.3	10.4	0.20	—	—	—	—
4	42.3	13.0	0.25	—	—	—	—
5	39.7	15.7	0.25	—	—	—	—
6	36.8	18.3	0.30	—	—	—	—
7	34.0	20.9	0.35	—	—	—	—
8	51.0	—	—	5.7	0.10	—	—
9	48.1	—	—	8.6	0.15	—	—
10	45.3	—	—	11.4	0.20	—	—
11	42.3	—	—	14.3	0.25	—	—
12	39.7	—	—	17.1	0.25	—	—
13	36.8	—	—	20.0	0.30	—	—
14	34.0	—	—	22.8	0.35	—	—
15	51.0	—	—	—	—	7.0	0.10
16	48.1	—	—	—	—	10.5	0.15
17	45.3	—	—	—	—	14.0	0.20
18	42.3	—	—	—	—	17.5	0.25
19	39.7	—	—	—	—	21.0	0.25
20	36.8	—	—	—	—	24.5	0.30
21	34.0	—	—	—	—	28.0	0.35

ch.e., chemical equivalent;  $R = 56,100/L_{OH}$ , where  $L_{OH}$  is the hydroxyl number. Each receipt contained the following: 4.6g Silicone L-6900, 2.8g DABCO catalyst, 6.5g catalyst 12, 46.1g Antiblaze TMCP, 3.1g water, and 250.1g Ongromat 30-20.

DABCO in the form of a 33% solution in dipropylene glycol is applied as a catalyst in the reaction of polyisocyanates with polyols.

The extrapolated temperature of the main decrement of the standard foam mass was 240°C. As the amount of the selected boroorganic compounds was increased from 0.1 to 0.4 chemical equivalents, the extrapolated temperature of the main decrement of

mass increased from 240°C for the standard foam (no. 0) to 290°C for foams with BTHP added (nos. 1–7) to 280°C for foams with BTCIMPP added (nos. 8–14). In the case of BTCIHPME, the increase in the temperature was very slight and was equal to 5°C for the foam containing 0.4 chemical equivalents of borate.

The extrapolated temperature of the mass main decrement is probably connected with the decomposition of urea formed as a result of the reaction of polyisocyanate, water, and urethane groups. The borates in the foam composition behave similarly to a typical polymer crosslinking agent, causing the structure of the foam to be more ordered. As the amount of boroorganic compounds is increased in the foam composition, the growth of flexible segments occurs, which in turn results in an increase in the thermal resistance. The highest increases in the extrapolated temperature of the mass main decrement were observed when 0.4 chemical equivalents of BTHP and BTCIHPP were added to the foams, that is, increases to 290 and 280°C, respectively (Fig. 2).

The temperature of the highest rate of mass decrement for the standard foam was 280°C. As the content of boroorganic compounds was increased in the foams from 0.1 to 0.4 chemical equivalents, they increased to 310, 305, and 295°C for the foam with BTHP added (no. 7), the foam with BCIHPP added (no. 14), and the

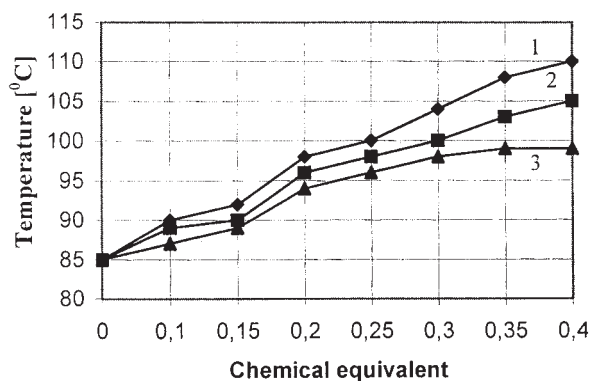
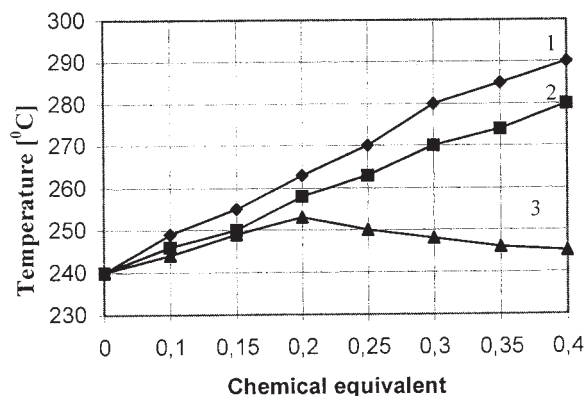


Figure 1 The dependence between the temperature of the first decrement of the foam mass and the content of the selected boroorganic compounds: 1-tri(hydroxypropyl) borate, 2-tri[[3-chloro-2-hydroxy-1-propoxy]propyl] borate, and 3-tri[[3-chloro-2-hydroxy-1-propoxy]-1-methylethyl] borate.



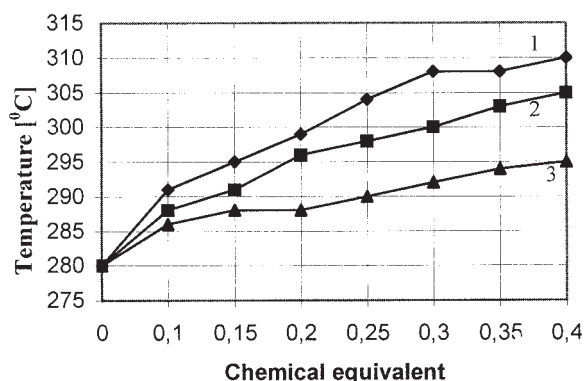
**Figure 2** The dependence between the extrapolated temperature of the main decrement of the foam mass and the content of the selected boroorganic compounds: 1-tri(hydroxypropyl) borate, 2-tri[(3-chloro-2-hydroxy-1-propoxy)propyl] borate, and 3-tri[(3-chloro-2-hydroxy-1-propoxy)-1-methylethyl] borate.

foam with BTCIHPPME added (no. 21), respectively (Fig. 3).

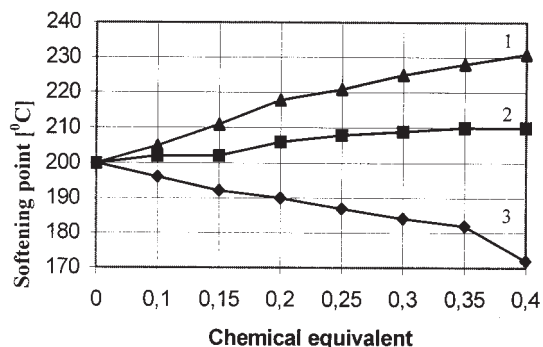
The dependences between the softening point and content of borates in the foam compositions are presented in Figure 4.

The softening point for the standard foam was 200°C. The highest increase in the softening point (to 230°C) was obtained as the amount of BTHP was increased from 0.1 to 0.4 chemical equivalents in the foams. A minimum increase (to 210°C) was observed when BTCIHPP was added to the foam composition. Addition of BTCIHPPME caused a decrease in the softening point to 172°C (foam no. 21).

IR spectroscopy of PUR-PIR foams confirmed the presence of the bands characteristic for isocyanurate



**Figure 3** The dependence between the temperature characterized by the highest rate of foam mass decrement and the content of the selected boroorganic compounds: 1-tri(hydroxypropyl) borate, 2-tri[(3-chloro-2-hydroxy-1-propoxy)propyl] borate, and 3-tri[(3-chloro-2-hydroxy-1-propoxy)-1-methylethyl] borate.



**Figure 4** The dependence between the softening point and content of the selected boroorganic compounds: 1-tri(hydroxypropyl) borate, 2-tri[(3-chloro-2-hydroxy-1-propoxy)propyl] borate, and 3-tri[(3-chloro-2-hydroxy-1-propoxy)-1-methylethyl] borate.

(1710–1690 and 1410  $\text{cm}^{-1}$ ) and urethane (1740–1700  $\text{cm}^{-1}$ ) bonds.

## CONCLUSIONS

The BTHP, BTCIHPP, and BTCIHPPME in the foam composition behaved in a similar manner to a typical chain extender, favoring the improvement of the heat and thermal properties of foams. Namely, we found that the softening point, the temperature of the first decrement of the foam mass, the extrapolated temperature of the main decrement of the mass, and the temperature of the highest rate of mass decrement (in comparison to foams without the additives) increased.

The obtained results confirmed the practicability of the applied borates as additives to improve the heat and thermal properties of foams, particularly BTHP (i.e., the compound with straight chains without branching).

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