

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

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ABSTRACT: The effect of selected borates [i.e., tri(hydroxypropyl) borate (BTHP), tri[(3-chloro-2-hydroxy-1-propoxy)propyl] borate (BTCIHPP), and tri[(3-chloro-2-hydroxy-1-propoxy)-1-methylethyl] borate (BTCIHPE)] on the heat and thermal properties of the rigid polyurethane–polyisocyanurate foams was investigated. Increasing amounts of BTHP and BTCIHPP in the foam composition, from 0.1 to 0.4 of chemical equivalent, caused increases in the softening point, the temperature of the first decrement of foam mass, the extrapolated temperature of the main decre-

ment of the foam mass, and temperature of the highest rate of the mass decrement. In the case when BTCIHPE was added to the foam compositions, the softening point decreased but temperatures characterizing their thermal resistance were higher compared to that of standard foam. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 95: 400–403, 2005

Key words: foams; heat resistance; thermal properties; thermogravimetric analysis (TGA); chemical equivalent

INTRODUCTION

Rigid polyurethane foams are thermoinsulating materials, characterized by better technological parameters than those of foamed polystyrene and mineral wool.^{1,2} Their overall heat-transfer coefficient is very low, that is, about $0.025 \text{ W m}^{-1} \text{ K}^{-1}$.³ The heat and thermal resistance parameters, however, limit their application in thermal insulation. Heat resistance is associated with 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 of its determination. During the changes, the molecular weight of polymer is unchanged.

The thermal resistance of polyurethane foams is associated mainly with 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, the ester, ether, alophaniane, urea, biuret, carboimide, isocyanurate, and other bonds can be formed in foams, depending on the raw materials applied and the equilibrium ratio NCO:OH. Their temperatures of dissociation are about 200, 260, 350, 106, and 250°C, from 130 to 145, 240, and 300°C, respectively.^{4–8}

The aim of our studies was to determine the effect of tri(hydroxypropyl) borate (BTHP), tri[(3-chloro-2-hy-

droxy-1-propoxy)propyl] borate (BTCIHPP), and tri[(3-chloro-2-hydroxy-1-propoxy)-1-methylethyl] borate (BTCIHPE) on the heat and thermal resistances of the rigid polyurethane–polyisocyanurate (PUR–PIR) foams.

EXPERIMENTAL

Characteristics of raw materials

Polyethers with trade name Rokopol RF-55 (product of oxypropylation of sorbitol; L_{OH} (hydroxyl number) = 495.0 mg KOH/g, produced by NZPO “Rokita,” Brzeg Dolny, Poland) and Ongromat CR 30-20 (technical polyisocyanate whose main component is diphenylmethane 4,4'-diisocyanate, made in Hungary) were used to prepare the rigid PUR–PIR foams. The density of Ongromat CR 30-20 at 25°C was 1.23 g/cm^3 , its viscosity was 200 mPa·s, and the content of NCO groups was 31.0%. Polyether and polyisocyanate mentioned above were characterized according to ASTM D 2849-69 and ASTM D 1638-70 standards.

An anhydrous potassium acetate (POCh, Gliwice, Poland), applied in the form of 33% solution in diethylene glycol (Catalyst-12), and DABCO (triethylenediamine, Hüls, Germany), applied in the form of 33% solution in dipropylene glycol, were applied as catalysts in the process. The polysiloxanepolyoxyalkylene surface active agent (Silicone L-6900, Witco Chemical Co., Gothenburg, Sweden) was used as a stabilizer of foam structures.

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

Type	Abbreviation	Density at 20°C (g/cm ³)	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	Yellow-straw colored
Tri[(3-chloro-2-hydroxy-1-propoxy)1-methylethyl] borate	BTCIHPME	1.040	177.9	429.6	Liquid	Pale yellow
Tri[(3-chloro-2-hydroxy-1-propoxy)propyl] borate	BTCIHPP	1.047	122.4	491.3	Liquid	Yellow

The porophor was CO₂ formed in reaction of isocyanate groups with distilled water. Moreover, tri(2-chloro-1-methylethyl) phosphate (Antiblaze TMCP, Albright & Wilson, Oldbury, UK) was introduced into the foams.

BTHP, BTCIHPME,⁹ and BTCIHPP were applied to prepare the foams studied. All the borates mentioned above 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 ($d = 1.84 \text{ g/cm}^3$, in the amount of 3% w/w with respect to the total mass of boric acid and diol) were introduced, at room temperature, into a three-neck flask (250 cm³) equipped with a Dean-Stark head for azeotropic distillation, thermometer, and mechanical stirrer. Then, xylene in the amount of 75 cm³ was added.

The content of the flask was heated to boiling temperature (120°C) with continuous stirring for 150 min, after which water (13.5 cm³) was azeotropically distilled off. The liquid straw-yellow product was obtained and its main component was BTHP.

Preparation of BTCIHPP

Tri(hydroxypropyl) borate (47.2 g, 0.2 mol), epichlorohydrin (55.5 g, 0.6 mol), and BF₃(Et)₂O catalyst (2.68 g) were introduced, at 50°C and continuous stirring, into a three-neck flask (250 cm³) equipped with a reflux condenser, thermometer, and stirrer. The temperature was increased to 90°C and the reaction run for 90 min. After that time, the temperature was increased to 128°C and the reaction run for a further 20 min. A liquid transparent yellow product was obtained whose main component was BTCIHPP.

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

Synthesis of rigid polyurethane-polyisocyanurate foams

The rigid PUR-PIR foams were obtained on a laboratory scale by a one-stage method from a two-compo-

nent 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 (1800 rpm, 10 s) in a suitable mass ratio and poured into an open rectangular metal mold. The expanded foams, after their removal from the mold, were thermostated at a temperature of 120°C for 4 h.

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

Heat resistance of foams was determined according to standard DIN 53424 using a Vicat apparatus. The foams were analyzed by IR spectroscopy (KBr technique; Vector spectrometer, range: 400–4000 cm⁻¹; Bruker, Darmstadt, Germany).

RESULTS AND DISCUSSION

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

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

The first decrement of mass is probably caused by diffusion of carbon dioxide, which plays the role of a blowing agent in the foams studied. Carbon dioxide is formed as a result of reaction between the excess of

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

No. of foam	Raw materials						
	Rokopol RF-55 (g)	BTHP		BTC1HPME		BTC1HPP	
		(g)	(ch.e.)	(g)	(ch.e.)	(g)	(ch.e.)
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

^a ch.e., chemical equivalent; $R = \frac{56,100}{L_{OH}}$ (L_{OH} , hydroxyl number). Moreover, each receipt contained as follows: silicone L-6900, 4.6 g; catalyst DABCO, 2.8 g; catalyst 12, 6.5 g; antiblaze TMCP, 46.1 g; water, 3.1 g; and Ongromat 30-20, 250.1 g.

isocyanate groups (–NCO) and water. Moreover, the diffusion of triethylenediamine from the foam can occur within the range from 85 to 110°C. Triethylenediamine (DABCO), in the form of 33% solution in dipropylene glycol, was 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 of chemical equivalent, the extrapolated temperature of the main decrement of mass increased from 240°C (standard foam, no. 0) to 290°C (foams with BTHP added, nos. 1–7) and 280°C (foams with BTCIMP added, nos. 8–14). In the case of BTCIHPME, the increase in the temperature was very slight and was 5°C for the foam containing 0.4 of chemical equivalent of the borate.

Probably, the extrapolated temperature of the mass main decrement is associated with decomposition of urea formed as a result of reaction of polyisocyanate, water, and urethane groups. Borates behave in foam composition similarly to a typical polymer crosslinking agent, causing the structure of foam to be more ordered. As the amount of boroorganic compounds is increased in foam composition, the growth of flexible segments occurs, which in turn results in an increase in the thermal resistance. The highest increase in extrapolated temperature of the mass main decrement was observed in the case when 0.4 of chemical equivalent of BTHP and BTCIHP were added to the foams (i.e., 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 of chemical equivalent, it increased to

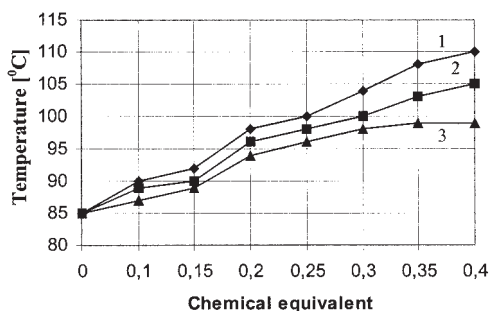


Figure 1 Dependency between temperature of the first increment of the foam mass and content of the selected boroorganic compounds: (1) tri(hydroxypropyl) borate (BTHP); (2) tri[(3-chloro-2-hydroxy-1-propoxy)propyl] borate (BTCIHP); (3) tri[(3-chloro-2-hydroxy-1-propoxy)-1-methyl-ethyl] borate (BTCIHPME).

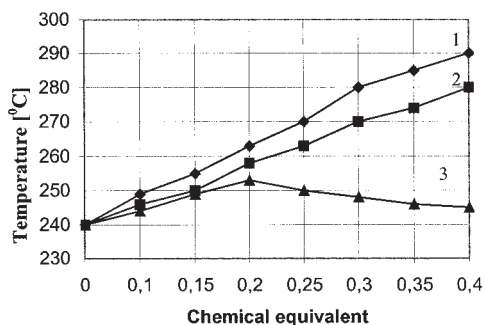


Figure 2 Dependency between extrapolated temperature of the main decrement of the foam mass and content of the selected bororganic compounds: (1) BTHP; (2) BTCIHPP; (3) BTCIHPME.

310°C (foam with BTHP added, no. 7), 305°C (foam with BTCIHPP added, no. 14), and 295°C (foam with BTCIHPME added, no. 21), respectively (Fig. 3).

Dependency between the softening point and content of borates in foam compositions is presented in Figure 4.

The softening point for standard foam was 200°C. The highest increase in softening point (to 230°C) was obtained as the amount of BTHP was increased in foams from 0.1 to 0.4 of chemical equivalent. The minimum increase (to 210°C) was observed in the case when BTCIHPP was added to foam composition. Addition of BTCIHPME 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 (1710–1690 and 1410 cm^{-1}) and urethane (1740–1700 cm^{-1}) bonds.

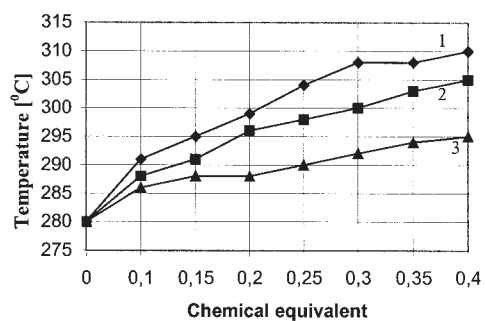


Figure 3 Dependency between temperature characterized by the highest rate of foam mass decrement and content of the selected bororganic compounds: (1) BTHP; (2) BTCIHPP; (3) BTCIHPME.

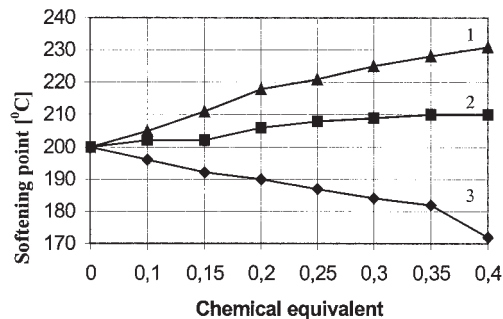


Figure 4 Dependency between softening point and content of the selected bororganic compounds: (1) BTHP; (2) BTCIHPP; (3) BTCIHPME.

CONCLUSIONS

BTHP, BTCIHPP, and BTCIHPME, in foam composition, behaved similarly to a typical chain extender, favoring the improvement of heat and thermal properties of foams. That is, it was found that the softening point, the temperature of the first decrement of foam mass, the extrapolated temperature of the main decrement of mass, and the temperature of the highest rate of mass decrement (compared 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 tri(hydroxypropyl) borate, which is the compound with straight chains without branching.

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