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The effect of tri(1-chloro-3-etoxy-propane-2-ol) borate on the properties of rigid polyurethane-polyisocyanurate foams

RAPID COMMUNICATION

Summary — Tri(1-chloro-3-etoxy-propane-2-ol) borate (I) was obtained by reaction of tri(hydroxyethyl) borate and epichlorohydrin. Reaction product was applied as fire retardant for preparation of rigid polyurethane-polyisocyanurate foams. As the (I) content was increased from 0.1 to 0.4 of the chemical equivalent, the compressive strength, oxygen index, residue after combustion and content of closed cells rose but brittleness, softening point and water absorption decreased. However, (I) presence does not influence explicitly on the foam apparent density. The results of our studies showed that chloroboroorganic compound [ChBOC, (I)] is generally useful as an additive to improve the properties of rigid PUR-PIR foams.

Key words: rigid PUR-PIR foams, fire retardancy, tri(1-chloro-3-etoxy-propane-2-ol) borate, properties of foams.

The rigid polyurethane foams are the best heat-insulating materials. Thermal conductivity, in $W/m^{\circ}C$, for polyurethane foam is within the range 0.019–0.026, while for mineral wool it is 0.042–0.052 and for foamed polystyrene 0.031–0.036 [1]. Increasing demand for polyurethane foams is the reason why many research works are undertaken with the aim to improve foams' properties. The present studies are concentrated mainly on flammability reduction and increasing the mechanical strength and thermal resistance of these plastics.

Modification of the foam properties aiming at reduction of its flammability affects the functional properties of the foam. The attempts are undertaken to find such a composition of substrates, which would allow to obtain the foams with reduced flammability while their mechanical and other properties should be unchanged in comparison to the foams without fire retardant [1–7].

One of the ways to reduce polyurethane foam flammability consists in increasing its cyclic structures and cross-linking density. More and more interest is focused on multi-hydroxyl fire retardants containing chlorine, fluorine and nitrogen. Chlorine is applied for quenching the radicals responsible for polymer burning. The detailed mechanism of borate action as a fire retardant is unknown but it is supposed that it forms borate glass during melting at high temperatures. This borate glass acts as insulating layer protecting the contact of an air

with the burning plastic [8–11]. The aim of our work was to obtain boronorganic compound containing chlorine and to study an effect of its various amounts on the properties of PUR-PIR foams.

Tri(1-chloro-3-etoxy-propane-2-ol) borate $[B(OCH_2CH_2OCH_2CHOHCH_2Cl)_3, (I)]$ *i.e.* reaction product of tri(hydroxyethyl) borate with epichlorohydrin was used for foam preparation.

EXPERIMENTAL

Preparation of tri(1-chloro-3-etoxy-propane-2-ol) borate

38.8 g (0.2 mole) of tri(hydroxyethyl) borate and catalyst BF_3 in ethylene ether in amount of 2.5% w/w with respect to the total amount of the rest of components were introduced into a three-necked flask (250 cm^3) equipped with stirrer, reflux condenser and thermometer. Epichlorohydrin in amount of 55.5 g (0.6 mole) was introduced into the flask under conditions of continuous stirring at temperature of $50^{\circ}C$. Then, temperature of reaction was risen to $105^{\circ}C$ and synthesis was led at this temperature for 2 hours. After this time, temperature was risen again to $120^{\circ}C$ and reaction was led for 1 hour more. The initial turbid and creamy solution became transparent and pale-yellow during the reaction. 86.23 g of product (I) was obtained and a compound with for-

mula: $B(OCH_2CH_2OCH_2CHOHCH_2Cl)_3$ was identified as its main component.

The borate obtained was characterized by the following properties: density at 20°C — 1033 kg/m³ (ISO 845:1988); viscosity at 20°C — 165 mPa · s (ISO 2555:1989, Brookfield DV-III reometer); hydroxyl number — 503 mg KOH/g (xylene method [12]); molecular weight — 469 (by ebulliometry) [13–15].

The product was analyzed by IR spectroscopy (KBr technique, range from 400 cm⁻¹ to 4000 cm⁻¹, a Vector spectrophotometer produced by Bruker) and by ¹H NMR (Gemini 2000 spectrophotometer, Varian, 200 MHz).

IR spectroscopy confirmed the presence of the bands characteristic for B-O (1325–1315 cm⁻¹), ether (1270–1200 cm⁻¹) and hydroxyl (3600–3000 cm⁻¹) groups as well as for C-Cl (750–700 cm⁻¹) bond.

¹H NMR analysis showed the following chemical shifts of protons with respect to HDMS as standard (in

ppm): 2.480–2.516 (6 atoms -CH₂), 4.521–4.589 (3 atoms -OH), 4.035–4.188 (3 atoms -CH), 3.384–3.632 (6 atoms -CH₂), 3.650–3.853 (12 atoms -CH₂).

Experimentally determined properties slightly vary from theoretical ones since the obtained chloroboroorganic compound was not purified. The compound contained small amounts of unreacted substrates.

Preparation of rigid PUR-PIR foams

The foams were obtained in laboratory scale by one-step method from the two-component (A–B) system at the equilibrium ratio of NCO to OH groups equal to 3:1. The component A was obtained by precise mixing (1800 rpm) of Rokopol RF-55, catalysts, fire retardant — Antiblaze TMCP, surface active agent, water and chloroboroorganic compound. The component B was Ongromat 20-30 (Table 1). The two components were mixed and poured onto an open metal tray. The resulting foams

Table 1. The compositions of the reaction mixtures used to prepare rigid PUR-PIR foams

No	Materials	Characteristics, procedure	Unit	No of foam				
				1	2	3	4	5
1	Rokopol RF-55	Product of oxypropylation of sorbitol $L_{OH}=495$ mg KOH/g (NZPO "Rokita", Brzeg Dolny, Poland) ASTM D 2849-69	Chemical equivalent	1.0	0.9	0.8	0.7	0.6
2	Tri(1-chloro-3-etoxypropane-2-ol) borate	Product of tri(hydroxyethyl) borate reaction with epichlorohydrin (Academy of Bydgoszcz, Poland)	Chemical equivalent	0.0	0.1	0.2	0.3	0.4
3	Silikone L-6900	Polysiloxyalkylene copolymer (Union Carbide Corporation, USA)	g	4.6	4.6	4.6	4.6	4.6
4	Dabco 33 LV	33% solution of triethylenediamine in dipropylene glycol (Hondry Process, USA)	g	2.8	2.8	2.8	2.8	2.8
5	Catalyst-12	33% solution of potassium acetate in diethylene glycol (Academy of Bydgoszcz, Poland)	g	6.5	6.5	6.5	6.5	6.5
6	Antiblaze TMCP	Tri(2-chloro-1-methylethyl) phosphate (Albright and Wilson, Great Britain)	g	34.6	34.6	34.6	34.6	34.6
7	Distilled water		Chemical equivalent	0.7	0.7	0.7	0.7	0.7
8	Ongromat 20-30	Polyisocyanate NCO groups, 31% (Hungary), ASTM D 1638-70	Chemical equivalent	3.7	3.7	3.7	3.7	3.7

Table 2. Basic functional properties of rigid PUR-PIR foams

Foam No	Apparent density ^{a)}	Retention residue, % after combustion ^{b)}	Oxygen index ^{c)}	Vicat softening temperature ^{d)}	Foam mass decrement after 48 h at 120°C	Change of linear dimensions in direction of foam expansion after 48 h at 120°C ^{e)}	Change of foam volume after 48 h at 120°C	Content of closed cells (pores) ^{d)}	Water absorption ^{e)}
	kg · m ⁻³	%	%	°C	%	%	%	% v/v	% v/v
1	60.1	78.7	24.7	192.1	1.12	0.10	-1.13	83.4	1.80
2	61.3	81.1	24.9	184.0	1.23	0.10	-1.08	93.4	0.74
3	60.6	84.9	25.1	181.0	1.37	0.15	-0.99	93.3	0.75
4	59.9	90.5	26.5	172.0	1.49	0.16	-0.77	93.5	0.76
5	60.2	93.8	27.1	169.0	1.63	0.15	-0.78	93.4	0.75

^{a)} According to ISO 845:1988; ^{b)} According to ASTM D 3014-73; ^{c)} According to ASTM D 1692-59T; ^{d)} According to DIN 53424; ^{e)} According to ISO 1923:1981; ^{f)} According to PN-ISO 4590:1994; ^{g)} According to DIN 53433.

were thermostated for 4 hours at temperature 120°C and seasoned for 48 hours at room temperature. Then the foams were cut and their basic functional properties were determined according to: brittleness — ASTM C 421-61 and compressive strength — ISO 844:1993. Each type of foam was subjected to a double control of foaming. PUR-PIR foams were analyzed by IR spectroscopy (KBr technique) by using a Vector instrument (Brucker).

RESULTS AND DISCUSSION

The compositions of the rigid PUR-PIR foams are presented in Table 1. The trade polyol Rokopol RF-55 was partially replaced by (I) and the properties of resulting foams are presented in Table 2 and Fig. 1. The processing parameters of these foams became longer as the amount of borate was increased. The starting, foaming and gelation times became longer from, respectively, 15 s, 18 s and 35 s (foam No 1 with no borate added) to 29 s, 37 s and 64 s (foam No 5 containing 0.4 of the chemical equivalent of borate).

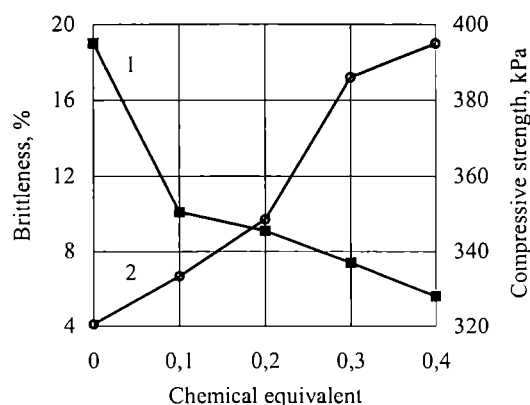


Fig. 1. Influence of the amount of borate added to foam on: 1 — brittleness, 2 — compressive strength of the foam

An addition of borate to the foams has no effect, within the limits of measurement error, on apparent density value ($60.6 \pm 0.7 \text{ kg/m}^3$) in comparison with a standard foam. No changes in foaming process of these foams were also observed. Pores both in foams with no borate added (standard foam) and with its addition have the same size what proves, among others, that surfactant was selected properly and (I) had no effect on the size and shape of pores.

ChBOC in the foam behaves similarly as a typical cross-linking compound causing the structure to become ordered. It favors the reduction of brittleness. As the borate content was increased the compressive strength of the foam increased from 320.5 kPa (standard foam No 1) to 394.9 kPa (foam with 0.4 of chemical equivalent of borate added); however the brittleness decreased from 19% to 5.6% and softening point did so from 192.1°C to

169.0°C (foam No 5). Increasing the borate amount in the foam from 0.1 to 0.4 of chemical equivalent caused reduction of foam flammability: the oxygen index rose from 24.7% (foam No. 1) to 27.1 (foam No 5) and retention rose from 78.7 to 93.8%. Addition of (I) caused decrease of water absorption from 1.8% v/v (foam No 1) to approx. $0.75 \pm 0.1\%$ v/v (foams Nos 2—5) and the amount of closed cells increased from 83.4% v/v to $93.4 \pm 0.1\%$ v/v, respectively.

Changes in linear dimensions and the volume and mass decrement after 48 hours of thermostating at 120°C remained practically unaffected (taking into account small absolute values) by the borate content in PUR-PIR foams.

IR spectroscopy of PUR-PIR foams confirmed the presence of the bands characteristic for isocyanurate ($1710\text{--}1690 \text{ cm}^{-1}$ and 1410 cm^{-1}) and urethane ($1740\text{--}1700 \text{ cm}^{-1}$) bonds.

Our studies have shown that (I) is useful as an additive improving the rigid PUR-PIR foams properties, in spite of the softening point decrease.

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