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Influence of different phosphorus flame retardants on fire behaviour of rigid polyurethane foams blown with pentane

Summary — The thermal stability and fire behaviour of a series of modified polyurethane foams has been studied by means of small-scale tests (spread of flame, oxygen index), thermogravimetric analyses and with the help of a cone calorimetr. These foams were prepared with three different flame retardants: poly(ammonium phosphate), diethyl *N,N*-bis(2-hydroxyethyl)aminomethyl phosphonate and triethyl phosphate. The addition of the flame retardants was limited because of worsening of the physical properties of the foams. The effect of flammability reducing is discussed with respect to the content of phosphorus in the flame retardants.

Key words: polyurethane foams, flame retardants, fire behaviour, thermal stability.

The replacement of chlorofluorocarbon compounds with blowing agents having zero environmental impact changes several properties of foamed polyurethanes including the worsening of their fire behaviour [1—4]. Rigid polyurethane foams are heterogeneous materials made with gas enclosed in polymer matrix. The necessity of hydrochlorofluorocarbons (HCFCs) phasing-out in the 21st century has promoted the use of hydrocarbons in polyurethanes (PUR) production. The flammable blowing agents like pentanes evidently influence the fire behaviour of the foams. As it was presented [3], the compounds with a higher phosphorus content are more effective than halogenated products in protecting against small flame ignition and combustion process, when flammable blowing agents are used.

The aim of this work is to compare the influence of various additives and reactive phosphorous flame retardants on the flammability characteristics and physical properties of polyurethane foams blown with *n*-pentane.

EXPERIMENTAL

Raw materials

The materials used for foam preparation are listed below with the characteristics of the various components:

— D-24 (ICSO Blachownia): polyetherpolyol ethylene oxide based; hydroxyl number 260 mg KOH/g;

— Rokopol TD-34 (Interrokita Brzeg Dolny): polyol-based oxyalkylated *o*-tolylenediamine; hydroxyl number 420 mg KOH/g;

— Suprasec DNR (ICI): oligomeric diisocyanatodiphenylmethane;

— SR-321 (Union Carbide): silicone surfactant;

— DMCHA (Texaco): dimethylcyclohexylamine catalyst;

— *n*-Pentane (P.K.S.): blowing agent;

— PFA — poly(ammonium phosphate): $(NH_4PO_3)_n$ where n = 1000;

— Fyrol-6 (Stauffer Chem.): diethyl *N,N*-bis(2-hydroxyethyl)aminomethyl phosphonate;

— Levagard TEP (Bayer AG): triethyl phosphate.

Nitrogen and phosphorus contents in the examined flame retardants are reported in Table 1.

Table 1. Characteristics of the flame retardants

Flame retardant	Content of, wt. %	
	P	N
Levagard TEP	17	—
PFA	31.5	14.5
Fyrol-6	12.2	5.5

Foams preparation and characterization

Formulations based on different ratios between polyols were used for the preparation of polyurethane foams made by a manual mixing and free expansion technique. In these formulations a constant amount of *n*-pentane as a physical blowing agent and water as a co-blowing agent were used. The quantity of blowing agents was chosen as to obtain polyurethane foams

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with comparable densities of about 35—45 kg/m^3. One standard foam was also prepared without flame retardant for comparison. Flame retardants were applied as a polyol component in an amount up to 3 wt. % of phosphorus. The formulations of obtained polyurethane foams are shown in Table 2.

T a b l e 2. **Formulations of polyurethane foams**

Foam No.	Flame retardant	Phosphorus content	Component									NCO index
			D-24	Rokopol TD	H_2O	DMCHA	SR-321	TEP	PFA	Fyrol-6	*n*-pentane	
1	Reference foam	—	63.4	42,3	0.8	1.2	2	—	—	—	10	105
2	TEP	0.5	59.8	39.2	0.8	1.2	2	5.6	—	—	10	105
3		1	57.9	38.6	0.8	1.2	2	11.2	—	—	10	105
4		1.5	55.9	37.3	0.8	0.8	2	17.4	—	—	10	105
5	PFA	1	59.6	39.7	0.8	0.6	2	—	6.2	—	10	105
6		2	57.6	38.4	0.8	0.6	2	—	12.5	—	10	105
7		3	55.4	36.9	0.8	0.6	2	—	18.7	—	10	105
8	Fyrol-6	1	48.3	32	0.8	0.8	2	—	—	16.6	10	105
9		2	36.6	24.4	0.8	0.8	2	—	—	33	10	105
10		3	24.8	16.5	0.8	0.8	2	—	—	49.6	10	105

The foams were conditioned at 20°C and 65% relative humidity for 48 hours, before being cut to test their physical properties in accordance with the Standard ISO tests:

ISO 845 — apparent density, kg/m^3;
ISO 844 — compressive strength 10%, kPa;
ISO 4590 — closed cells, %;
ISO 3582 — spread of flame, mm/s;
ISO 3216 — oxygen index, %.

Thermal stability was evaluated by thermogravimetric analyses (TGA) carried out using a Netzsch system analyzer interfaced with computer. Samples of about 1.2 mg finely ground foam were examined at temperatures ranging from 30°C to 450°C with heating rate of 10°C/min in an argon atmosphere.

Fire behaviour was also investigated by using a cone calorimeter according to ISO 5660 [5]. The cone calorimeter exposes a small square horizontal test specimen of 100 x 100 mm and 25 mm thick to a preset heat flux (in our case 50 kW/m^2), then ignites it with electric spark. The fire effluent passes through a duct containing a sensor which permits the determination of the heat release rate (by oxygen consumption), while CO and CO_2 production is determined by infrared spectroscopic techniques. Weight loss was determined gravimetrically. For statistical reasons, at least 5 samples for each foam were tested. Each test was stopped when the flame was extinguished.

RESULTS AND DISCUSSION

In our research we have taken into account the need to obtain materials with suitable physical properties and only then their flammability behaviour was evaluated. Therefore, the foams with Levagard TEP content of maximum 1.5 wt. % phosphorus were investigated.

Characteristics of physical properties of foams is given in Table 3.

T a b l e 3. **Physical properties of foams**

Foam No.	Flame retardant	Amount of phosphorus, %	Density, kg/m^3	Compression strength 10%, parallel, kPa	Compression strength 10%, perpendicular, kPa	Closed cell content, %	OI, %	Flame spread mm/s
1	—	—	36.2	219.0	128.9	92.1	17.9	2.0
2	TEP	0.5	37.1	166.9	104.3	94.0	21.5	s*
3		1.0	43.2	216.5	120.0	94.2	22.9	s*
4		1.5	48.3	136.0	77.0	93.8	24.0	nf**
5	PFA	1.0	39.8	194.7	147.7	91.5	19.7	1.7
6		2.0	40.8	236.8	121.8	90.4	20.9	1.4
7		3.0	38.9	197.9	116.4	89.8	21.4	s*
8	Fyrol-6	1.0	34.5	208.2	128.5	90.4	22.5	s*
9		2.0	35.7	216.7	107.3	90.6	23.0	s*
10		3.0	36.2	169.2	71.3	89.7	26.6	nf**

s* — self-extinguishing: the flame front along the upper surface of the specimen does not reach the final line;
nf** — non-flammable: the flame front along the upper surface of the specimen does not reach the starting line.

The compressive strength was measured along directions parallel and perpendicular to those of foams rising. The addition of flame retardants in the formulations caused a decrease in PUR foam compression strength by less than 25% except of foams with 1.5% of phosphorus as TEP and of 3.0% as Fyrol. For these foams the decrease of compression strength exceeded 40%. The best results were obtained for samples with PFA.

Moreover, it was observed that the flame retardant additive practically did not influence the closed cells percentage in the investigated PUR foams.

Two types of tests were carried out for studying PUR foam fire behaviour. The ISO 3582 is a small-scale test applied to cellular plastics. This test evaluates the flammability of a horizontal sample ignited at one end by a burner flame. Measurements of flame spread and burning extension were made; the results are reported in Table 3. Among the flame retardants examined, the most effective (with respect to the amount of phosphorus) in reducing flame spread was Levagard TEP. Preparation of formulation with only 0.5 wt. % phosphorus as Levagard TEP made it possible to obtain "self-extinguishing" foams. The foams with 1.5 wt. % phosphorus as Levagard TEP were non-flammable according to ISO test.

The oxygen index (OI) test measures the minimum oxygen concentration in a gaseous oxygen-nitrogen mixture necessary to support the combustion of a vertical sample burning downward. The changes of oxygen index versus the amount of additive for different flame retardants are given in Fig. 1.

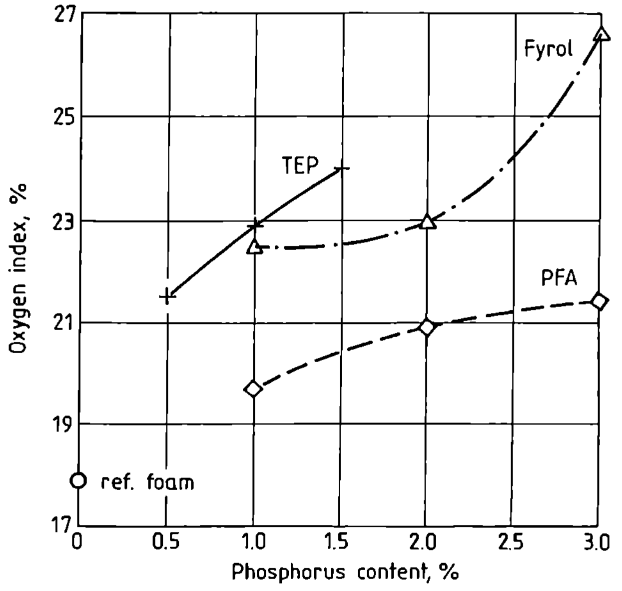

Fig. 1. Oxygen index of PUR foam versus phosphorus content various flame retardant additives

The increase in oxygen index to a value higher than 23% was caused by addition of Levagard TEP (1.5 wt. % phosphorus) and Fyrol-6 (twice higher amount of phosphorus). Like in the test for the flame spread, the most effective was Levagard TEP again.

The dimensional stability of polyurethane foams is also very important, particularly at low temperature. Therefore, the investigations of dimensional stability at -27°C and at ambient temperature (22°C) were carried out and the results are presented in Tables 4 and 5. It was observed that the addition of flame retardants caused small, less than 1% shrinkage of foams. Important changes of linear dimensions took place only at temperature of -27°C for the foams with a high content of Fyrol-6.

Table 4. Dimensional stability of polyurethane foams at -27°C

Foam No.	Type of foam	Phosphorus content, % w	Changes of width %	Changes of length %	Changes of thickness %
1	Ref. foam	0	-0.03	0.00	-0.04
2	with TEP	0.5	-0.07	-0.02	-0.10
3		1.0	-0.12	-0.30	-0.15
4		1.5	-0.06	-0.15	-0.23
5	with PFA	1.0	-0.03	-0.07	-0.07
6		2.0	-0.02	-0.06	-0.07
7		3.0	-0.04	-0.07	-0.03
8	with Fyrol-6	1.0	-0.07	-0.06	-0.02
9		2.0	-0.22	-0.28	-1.22
10		3.0	-1.08	-6.22	-4.92

Table 5. Dimensional stability of poluurethane foams at 22°C

Foam No.	Type of foam	Phosphorus content, % w	Changes of width %	Changes of length %	Changes of thickness %
1	Ref. foam	0	-0.03	0.00	-0.03
2	with TEP	0.5	-0.03	-0.05	-0.07
3		1.0	-0.04	-0.05	-0.16
4		1.5	-0.27	-0.12	-0.16
5	with PFA	1.0	-0.02	-0.03	-0.03
6		2.0	-0.04	-0.07	-0.06
7		3.0	-0.08	-0.03	-0.11
8	with Fyrol-6	1.0	-0.09	-0.11	-0.46
9		2.0	-0.11	-0.27	-0.34
10		3.0	-1.12	-1.11	-0.26

The thermal stability of the foams (ref. foam No. 1, the foams No. 4, 7 and 10 with maximum addition of various flame retardants) were compared by using TGA profiles reported in Fig. 2 for the tests performed in an inert argon atmosphere.

The TGA profiles of the PUR foams show two steps of polymer degradation for the products with flame retardants. A single step for reference foam corresponds to the second step for foams with phosphorus additives which takes place at the temperatures over 300°C. It is caused by degradation of polyurethane polymer; this

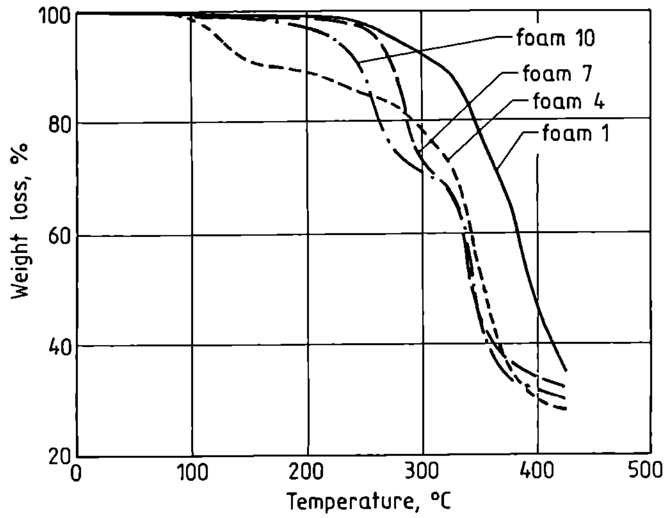

Fig. 2. TGA profiles (in argon) of PUR foams

mechanism has been already investigated in [6]. The decomposition or volatilization of flame retardants is the first step at a temperature between 110°C and 260°C. Among the investigated polyurethane foams, the product with the Levagard TEP decomposed at the earliest while the sample with PFA seems to be more stable. As was reported [6], the catalytic action of the polyphosphoric acid is possible only in the presence of an oxidative atmosphere to modify the degradation mechanisms of the polymer and to form more thermally stable structures.

The flammability properties of the foams were also investigated by the use of a cone calorimeter. The results for the foams without and with maximum addition of various flame retardants were compared (foams No. 1, 4, 7, 10). In these trials, the ignition time was always very low (about 1 s) because of the cellular structure of the samples and the presence of flammable, hydrocarbon blowing agent.

The weight loss of foams during the combustion is shown in Fig. 3. It was observed that the weight loss of reference foam and that of PUR with flame retardant TEP were considerably higher than of those modified by flame retardants like Fyrol and PFA. This result is unexpectedly high for the foam with Levagard TEP but it must be taken into account that the foam comprises only 1.5 wt. % of phosphorus and so the catalytic action to improve char formation was lower. Moreover, the thermal stability of the flame retardant is lower as shown by TGA analysis.

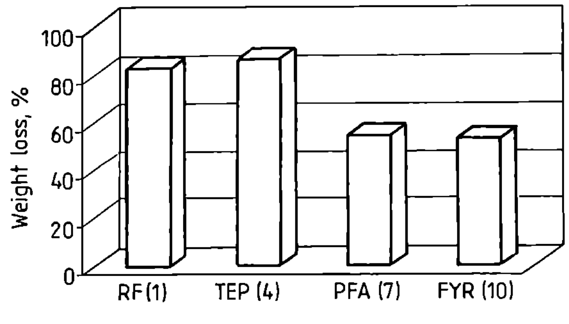

Fig. 3. Weight loss of PUR foams during combustion

Other results are shown in Table 6 as a peak and in Table 7 as average values of the Mass Loss Rate (MLR), Rate of Heat Release (RHR), Effective Heat Combustion (EHC), Carbon Monoxide Yield (CMY), and Carbon Dioxide Yield (CDY).

Table 6. Cone calorimeter peak values

Foam No.	1	4	7	10
Type of foam	Ref. foam	TEP	PFA	Fyrol
Phosphorus content	—	1.5	3	3
Mass loss rate, g/s	0.21	0.26	0.34	0.40
Heat release rate, kW/m^2	296.5	231.0	165.8	109.5
Effective heat of combustion, MJ/kg	25.9	27.7	39.1	14.1
Carbon monoxide yield, kg/kg	0.50	0.39	0.32	0.25
Carbon dioxide yield, kg/kg	3.93	4.00	4.29	2.87

Table 7. Cone calorimeter average values

Foam No.	1	4	7	10
Type of foam	Ref. foam	TEP	PFA	Fyrol
Phosphorus content	—	1.5	3	3
Mass loss rate, g/s	0.034	0.037	0.017	0.011
Heat release rate, kW/m^2	45.0	47.0	26.3	6.5
Effective heat of combustion, MJ/kg of burnt material	13.2	13.1	16.8	5.6
Carbon monoxide yield, kg/kg	0.065	0.105	0.060	0.075
Carbon dioxide yield, kg/kg	1.81	1.19	2.08	1.51
CO_2/CO yield	27.8	11.3	34.7	20.1

The peak of heat release rate (P-RHR) is believed by many fire scientists to be the most critical parameter, because it is responsible for the "flashover" phenomena in a real fire situation. Second important factor is the time interval before P-RHR. An empirical parameter that can be used to compare the critical fire behavior of different foams is the ratio between P-RHR and the time to reach this value. The lower this ratio, the safer is the material. The results of this ratio for various foams are presented in Fig. 4. Among the compared materials the best results were obtained for the foams with the addition of Levagard TEP and Fyrol which are correlated to the oxygen index and the flame spread even if the foams with TEP showed higher mean values of MLR and RHR. This can be due to a fast loss of the flame retardant with a longer time to reach the RHR peak.

From the data reported in Table 7 it is possible to note

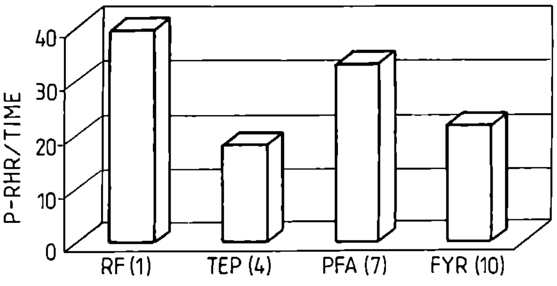

Fig. 4. P-RHR/time data from cone calorimeter test

that the average values of EHC are lowest for the foam with Fyrol. The high value of EHC for foam with PFA can be surprising if we consider the low amount of burnt material during the test. As can be expected, the flame retardant TEP which acts mainly in the gas phase, gives the worst CO_2/CO gas ratio.

CONCLUSIONS

— Among the flame retardants examined, the most effective in reducing flame spread was Levagard TEP. Nevertheless the maximum possible amount of this compound which can be added to formulations is 8.6 wt. % (1.5 wt. % with respect to the amount of phosphorus) due to dimensional stability of the foams.

— The addition of reactive Fyrol-6 to standard formulation (3 wt. % with respect to the amount of phosphorus) makes it possible to obtain nonflammable foams with good physical characteristics and fire performance.

— The content of ammonium polyphosphate in an amount of up to 9.3 wt. % (3 wt. % of phosphorus) in formulation assures foam properties similar to those of standard material but the effect of reducing of flame spread is small in comparison with the other investigated flame retardants. A higher amount of this flame retardant is necessary to accomplish its catalytic action in the solid phase [6].

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