

Solid Foam-Polyurethanes with a Lowered Combustibility

K. TROEV, K. TODOROV,* and G. BORISOV, *Central Laboratory of Polymers, Bulgarian Academy of Sciences, Sofia 1113, Bulgaria and *Center for Development and Implementation at the Chemical State Enterprise "D. Dimov," Yambol, Bulgaria*

Synopsis

A composition of solid foam-polyurethane is developed, the polyol component of which is a mixture of oligoestercohols obtained as waste products in the production of dimethylterephthalate, and is modified with phosphorus or phosphorus plus chlorine-containing antipyrenes. It is demonstrated that the introduction of antipyrenes into the foam-polyurethanes substantially enhances the combustion resistance of the composition, without impairing its physical and mechanical properties.

INTRODUCTION

Foam-polyurethanes find an increasing application in the production of consumer goods and in construction. In some cases their applicability, however, is restricted because of their high flammability.

The ignition resistance of these polymers can be substantially reduced by the introduction of reactive or nonreactive antipyrenes, which in most cases are phosphorus or phosphorus plus chlorine-containing compounds.

The aim of this paper is to study the modification of a solid foam-polyurethane,¹ the polyol component of which is a mixture of oligoestercohols, obtained as waste products in the production of dimethylterephthalate, and which polyurethanes are modified with phosphorus and phosphorus plus chlorine-containing antipyrenes.


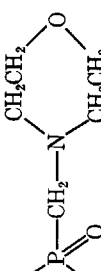
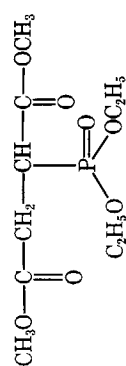
EXPERIMENTAL

The starting composition of the solid foam-polyurethane¹ (parts per weight): oligoestercohol A (9); oligoestercohol B (14); oligoestercohol C (9); oligoestercohol D (15); polyethyleneglycol (MW 200) (11.2); glycerol (3.9), surfactant "Tegostab B 1903" (1.3); tin dibutyldilaureate (0.09); water (1.2), polymeric diphenylmethanediisocyanate (112.0).

The polyol component, comprising all compounds with the exception of the polymeric diphenylmethanediisocyanate, has the following characteristics: hydroxyl number (mg KOH/g), 310.8; acid number (mgKOH/g), 8.1; water (%), 1.88; density at 20°C, 1.0962 g/cm³; viscosity at 20°C (cP), 1887.

The foam-polyurethanes are synthesized in a 250-mL beaker by mixing the components and stirring with a propeller (3500 rpm) for 10 s. The reaction

TABLE I
 Characteristics of Solid Foam-Polyurethanes, Modified with Various Antipyrenes

No.	Antipyrene	P (%)	Cl (%)	Density (kg/m ³)	Oxygen index (% O ₂)	Temp of first exotherm (°C)
FPU-1	No antipyrene	0.0	0.0	38	20.2	295
FPU-2	(ClCH ₂ CH ₂ O) ₃ P=O	0.51	1.83	35	22.0	340
FPU-3	Same antipyrene	0.78	2.69	35	23.0	320
FPU-4	Same antipyrene	1.01	3.50	34	24.5	330
FPU-5	HO(CH ₂) ₂ O(CH ₂) ₂ O 					
FPU-6	HO(CH ₂) ₂ O(CH ₂) ₂ O 	1.09	1.50	37	23.5	305
FPU-7	HO(CH ₂) ₂ O(CH ₂) ₂ O 	0.85	1.97	35	24.3	318
FPU-8	Same antipyrene	0.51	0.0	38	23.0	330
FPU-9	Same antipyrene	1.02	0.0	38	24.1	320
FPU-9	Same antipyrene	1.50	0.0	36	24.4	320

mixture is then poured on a foil. The foaming characteristics are: initiation time, 20 s, time for crosslinking, 58 s; rise time, 105 s.

The following antipyrenes were used: tris(β -chloroethyl)phosphate*¹; bis(hydroxyethoxyethyl)-*N*-methylmorpholinphosphonate²; *O,O*-diethyl-1,2-dicarbomethoxyethylphosphonate³; biphosphite of diphenylsilanediol⁴; a reaction product of the transesterification of dimethylphosphite with 1,3-dichloropropanol-2, treated with epichlorohydrin, with the following characteristics: hydroxyl number (mg KOH/g), 155; acid number (mg KOH/g) 6.82.⁵

The physical and mechanical properties of the solid foam-polyurethanes were assessed by the following methods: density (kg/m³), TGL 14370; compressive strength (kg/cm²), DIN 53421; bending strength (kg/cm²), DIN 53423; tensile strength (kg/cm²), 52365; water vapor resistance (m), SVS 0300, p. 3.

The oxygen index was determined by a FTA apparatus using samples 100 × 10 × 10 mm. The thermal characteristics were studied by a MOM derivatograph at a rate of the temperature rise of 10°C/min in air atmosphere.

The content of carbon monoxide (CO) was determined by a Perkin-Elmer gas chromatograph under the following conditions: pyrolysis temperature, 900°C; weight of sample, 0.0025 g; time of pyrolysis, 90 s; rate of temperature rise, 7.5°C/min; nitrogen flux rate, 60 mL/min; height of column, 2 m; phase, 10% polyethyleneglycol adipate on Chromosorb P, 60–80 mesh.

RESULTS AND DISCUSSION

The solid foam-polyurethanes, synthesized on the basis of polyolic component, representing a mixture of oligoesteralcohols, obtained by transesterification of waste products in the production of dimethylterephthalate with various hydroxyl compounds, has an unsatisfactory combustion resistance—oxygen index, 20.2% O₂.¹

Several syntheses were performed with the aim of improving the combustion resistance of the foam-polyurethane using phosphorus and phosphorus plus chlorine antipyrenes.

The study of the synthesized materials revealed (Table I), that irrespective of the type of antipyrene used—reactive or nonreactive, phosphorus or phosphorus plus chlorine-containing—the technical parameters of the foaming process were similar to those of the starting compound. The modified solid foam-polyurethanes were studied with respect to combustion resistance, thermooxidative resistance, and physical and mechanical characteristics.

Combustion Resistance

The oxygen index values of solid foam-polyurethanes modified with tris(β -chloroethyl)phosphate (FPU-2, -3, and -4 in Table I), an antipyrene which has found practical application, demonstrate that the increase in the antipyrene concentration enhances the combustion resistance. The latter reaches 24.5% O₂ (FPU 4) at a content of 1.01% of phosphorus and 3.50% of chlorine. The further increase in the antipyrene concentration has but insignificant effect on the combustion resistance.

The use of the reactive bis(hydroxyethoxyethyl)-*N,N*-methylaminoalkylphosphonate enhances the value of the oxygen index by 3–4% O₂. It is note-

* Tris(β -chloroethyl)phosphate was introduced in samples FPU nos. 5, 6, 10, 11, 12, 13, 14, and 15 as a component improving the compatibility of the oligoesteralcohols with Freon 11 in concentrations as in sample FPU-2.

worthy that bis(hydroxyethoxyethyl)-*N*-methylmorpholinephosphonate combined with tris(β -chloroethyl) phosphate with a considerably lower content of phosphorus and chlorine in comparison with FPU-2, -3, and -4 [modified only with tris(β -chloroethyl)phosphate] enhances the oxygen index to 24.3%, i.e., in this case there is a synergistic effect of the two antipyrenes.

The investigation of the foam-polyurethanes, modified with *O,O*-diethyl-1,2-dicarbomethoxyethylphosphonate, showed that this antipyrene has the advantage over the rest of the antipyrenes, that it can be used without the introduction of tris(β -chloroethyl)phosphate as a component used to improve the compatibility of the oligoesteralcohols with Freon 11. This antipyrene appeared more efficient than tris(β -chloroethyl)phosphate. The oxygen index of FPU-7 is 23.0% O₂ at a phosphorus content of 0.5%. With tris(β -chloroethyl)phosphate as modifier, this index is achieved at a content of 0.78% phosphorus and 2.69% chlorine (FPU-3). The synthesis with various amounts of this antipyrene revealed that the optimum content of phosphorus is ca. 1% (FPU-8), corresponding to an oxygen index of 24.1% O₂. The increase of phosphorus above this value brings about but an insignificant increase in the combustion resistance (e.g., FPU-9 with 1.5% phosphorus and oxygen index 24.4% O₂).

The compositions comprising both tris(β -chloroethyl) phosphate and *O,O*-diethyl-1,2-dicarbomethoxyethylphosphonate (FPU-10, -11, and -12) were also tested for combustion resistance. In this case the antipyrene was introduced in the composition FPU-2. The values of the oxygen index of these compositions show that the introduction of tris(β -chloroethyl)phosphate (FPU-10, -11, and -12) does not improve the combustion resistance, i.e., there is no synergistic effect of these two antipyrenes.

The biphosphite, synthesized by the transesterification of dimethylphosphite with diphenylsilanediol, was also tested as antipyrene (FPU-13). The maximum combustion resistance was attained at 0.89% phosphorus and 2.03% chlorine.

The highest combustion resistance was achieved by the foam-polyurethane modified with an antipyrene, obtained by the transesterification of dimethylphosphite with 1,3-dichloropropanol-2, subsequently treated with epichlorohydrin. At a content of 1.22% phosphorus with 4.21% chlorine, the oxygen index was 25.4% O₂.

It was established that the increase in the concentration of this antipyrene above this value leads to a considerable decrease in the technological time of foaming. This result could be associated with the higher acid number.

The present results of the combustion resistance of modified solid foam-polyurethanes demonstrate that the efficiency of the antipyrenes is related to their structure. The most efficient antipyrenes are: *O,O*-diethyl-1,2-dicarbomethoxyethylphosphonate (FPU-8 and -12) and the reaction product obtained in the transesterification of dimethylphosphite with 1,3-dichloropropanol-2, subsequently treated with epichlorohydrin (FPU-15).

Thermooxidative Resistance

It was shown⁶ that the service characteristics of foam-polyurethanes are to a high degree determined by their thermooxidative resistance.

The investigation of the modified foam-polyurethanes revealed that the introduction of antipyrenes does not affect their thermooxidative resistance. This

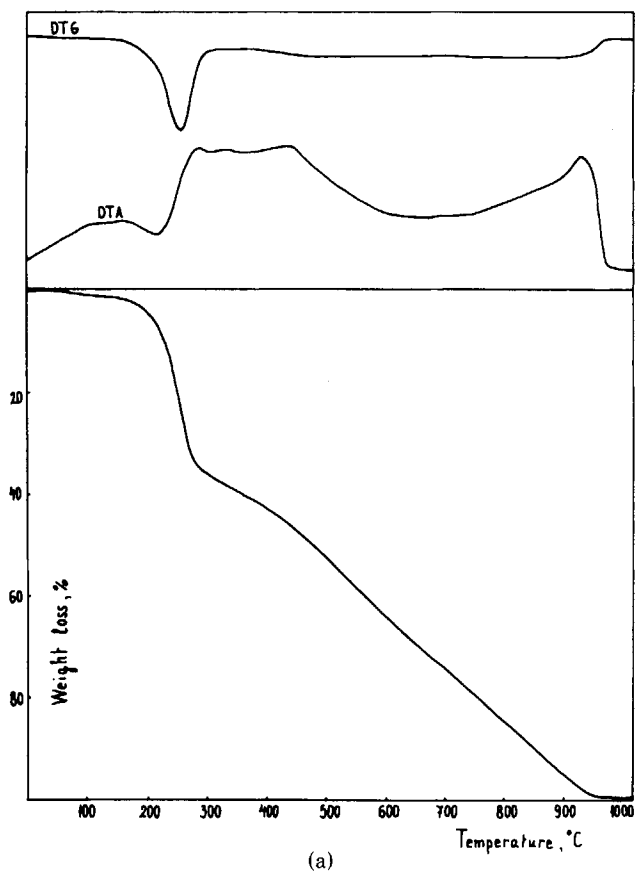
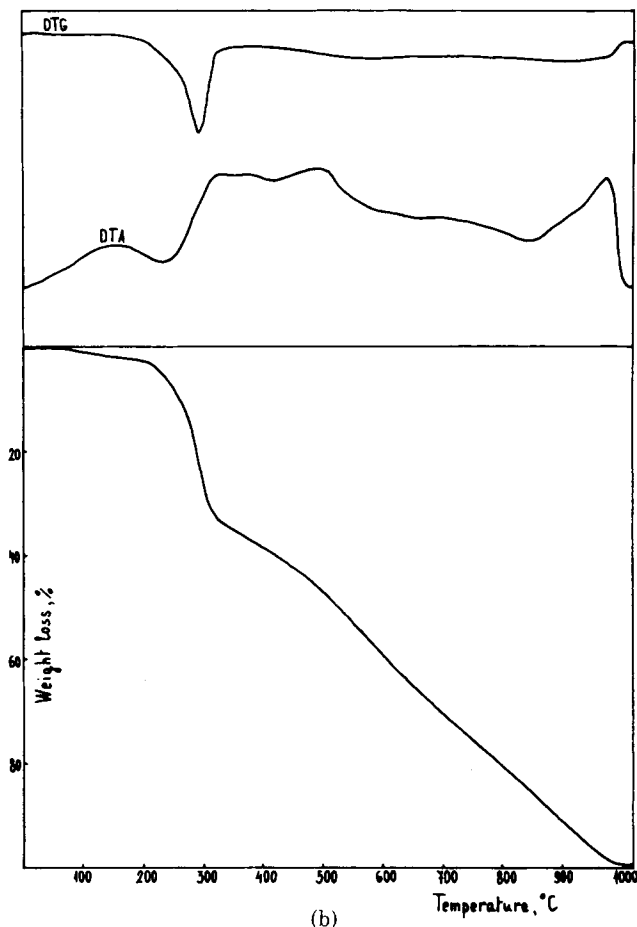


Fig. 1. (a) DTA plots for sample FPU-1; (b) DTA plots for sample FPU-8.

conclusion is corroborated by the DTA plots in Figures 1(a) and 1(b) pertaining to compositions FPU-1 and FPU-8, respectively. The DTA diagrams of the rest of the foam-polyurethanes investigated are quite similar.

The examination of the thermogravimetric curves exhibits that the foam-polyurethanes studied decompose on three stages: the first stage from 200°C to 330°C corresponds to the maximum rate of decomposition. From the shape of the DTA plots it can be seen that the destruction at this stage has a clearly expressed exothermic character. During this stage the foam-polyurethanes lose ca. 35% of their weight. During the second stage from 330°C to 500°C the weight losses reach ca. 15%, and in the third stage from 500°C to 1000°C, the samples lose all their weight. These three stages are distinctly observed for all solid foam-polyurethanes.

In the DTA plots of all foam-polyurethanes, both modified and nonmodified, there is a slight exotherm in the 130–140°C range, which according to Stirna et al.⁶ is due to isocyanate groups which have not reacted. In the 295–330°C range a strong exothermic effect is observed, which corresponds to the maximum rate of decomposition. This exotherm is due to the intensive oxidation of the foam-polyurethanes⁷ and the products of their decomposition.⁸ In the non-modified samples this exotherm appears at 295°C (Table I), while in the modified



(b)
Fig. 1 (Continued from the previous page.)

ones it is shifted to higher temperatures. According to Zeronyan et al.,⁹ this shift is due to the antipyrène and is in agreement with the finding¹⁰ that phosphorus retards burning and hinders the exothermal oxidation of carbon to CO₂.

One of the main obstacles for the wide application of foam-polyurethanes is the toxicity of their decomposition products, namely, hydrogen cyanide and carbon monoxide. The analysis for HCN by the method described by Bulygin et al.¹¹ did not give positive results.

The concentration of carbon monoxide was determined during pyrolysis of the samples at 900°C. The results demonstrate that the introduction of antipyrènes in the compositions of solid foam-polyurethanes does not affect noticeably the CO concentration. Thus for nonmodified samples it was 0.97% CO. For FPU-2 and -9, the CO concentration is lower than that for FPU-1. The highest CO concentration, 1.13%, was found for FPU-10.

Physical and Mechanical Properties

The results from the determinations of the combustion resistance, thermooxidative resistance, and CO concentration exhibited that the best compo-

TABLE II
Physical and Mechanical Properties of Modified Foam-Polyurethanes

No. of FPU	Density (kg/m ³)	Tensile strength to foaming direction (kg/cm ²)		Bending strength (kg/cm ²)	Compressive strength (kg/cm ²)	Model of elasticity (N/m ²)	Resistance to water vapor (m)	Cellular structure (%)
		Parallel	Perpendicular					
FPU-1	39	2.0	1.4	2.8	2.6	4.51	40	91
FPU-8	38	2.2	1.6	2.4	2.6	4.51	39	92
FPU-12	43	1.8	1.4	2.6	2.0	4.50	45	97
FPU-15	42	1.7	1.0	1.8	1.5	4.50	40	94

sitions are FPU-8, -12, and -15. Consequently, some of the physical and mechanical properties of these compositions were also studied (Table II). From the experimental data on the compressive strength, bending strength, tensile strength, modulus of elasticity, and water vapor resistance it can be concluded that the introduction of *O,O*-diethyl-1,2-dicarbomethoxyethylphosphonate does not affect the mechanical properties of the foam-polyurethanes. The slight decrease in the mechanical properties of sample FPU-15 does not go beyond the limits of the standard requirements.

The present results demonstrate that it is possible, by the introduction of phosphorus and phosphorus plus chlorine containing antipyrenes, to diminish the combustability of the solid foam-polyurethanes, having as a polyol component oligoesteralcohols, obtained from the waste products in the production of dimethylterephthalate. The introduction of these antipyrenes does not affect the thermal stability of the foam-polyurethanes, and, in the case of samples FPU-8, -12, and -15, the service characteristics are also retained.

References

1. K. Troev, K. Todorov, and G. Borisov, *J. Appl. Polym. Sci.*, **29**, 577 (1984).
2. Bulg. Pat. 55176 (1982).
3. A. N. Pudovik, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 926 (1952).
4. Bulg. Pat. 56743 (1982).
5. Bulg. Pat. 56826 (1982).
6. U. K. Stirna, R. Ya. Pernikis, and Ya. A. Surna, *Izv. Akad. Nauk Latv. SSR, Khim. Ser.* **6**, 696 (1971).
7. J. K. Backus, W. C. Darr, P. Q. Gemeinhardt, and J. H. Saunders, *J. Cell. Plast.*, **11**, 178 (1965).
8. V. A. Orlov, O. G. Tarakanov, *Vysokomol. Soed.*, **6**, 1157 (1964).
9. S. A. Zeronyan, M. S. Ellison, and K. Alger, *J. Appl. Polym. Sci.*, **25**, 311 (1980).
10. J. R. Van Wezzer, *Phosphorus and Its Compounds*, Vol. II, New York, (1961), p. 195.
11. B. M. Bulygin, E. A. Bulygina, and A. A. Karnishin, *Plast. Massy*, **8**, 49 (1973).

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