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THERMAL BEHAVIOUR OF RIGID POLYURETHANE FOAMS

II. A study of rigid polyurethane foam containing reactive antipyrenes

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The effects of P- and Cl-containing reactive antipyrenes with different compositions and structures on the mechanism and kinetics of the total thermal decomposition of rigid polyurethane foams, together with the possibility of evaluating their effectiveness as combustion inhibitors, were studied by means of a combined thermal analysis technique. It is shown that dynamic thermal analysis can register the changes resulting in the mechanisms and kinetics of the thermal decompositions of the investigated polyurethanes from comparatively low concentrations and differences in the concentrations and from differences in the chemical compositions and structures of the antipyrenes. The most sensitive characteristics associated with the influence of antipyrenes in this case were the coke residue determined at 850° in an inert medium and the areas of exothermic peaks I and II in the DTA curve in air medium.

Because of the increased tendency to burning and the requirements for their combustion stability, the problem of selecting optimum antipyrene compositions [1] for polyurethanes is becoming an urgent necessity. This requires the development of laboratory methods which are minimum time-, labour- and material-consuming and can provide the maximum insight into the mechanism of the inhibitory effect of antipyrenes [1–4].

Additive antipyrenes are not always efficient enough. The tendency is to search for reactivity modifiers which are introduced into the polymer molecule during synthesis. In the case of polyurethanes, it is the most convenient to introduce them in the polyol component. Systematic investigations on the thermal behaviour of substances of this type are still scarce.

The aim of the present work was to study the effects of reactive antipyrenes with different compositions and structures on the mechanism and kinetics of the total

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thermal decomposition reactions of rigid polyurethane foams (RPUF), and the possibility of evaluating their effectiveness as combustion inhibitors.

Experimental

Initial materials

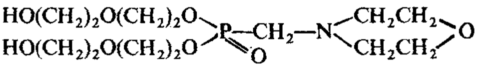
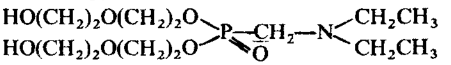
The initial rigid polyurethane foam (IRPUF) was based on a polyol component obtained from by-products of the synthesis of dimethyl terephthalate and polymeric diphenylmethanediisocyanate (MDI). The following reactive antipyrenes were used: I – N-morpholinylmethyl-bis(ω-hydroxyethoxyethyl) phosphonate; II – N,N-diethylaminomethyl-bis(ω-hydroxyethoxyethyl) phosphonate; and III – a reaction product of the reesterification of dimethyl phosphate with 1,3-dichloropropanol-2 treated with epichlorhydrin.

Some of the characteristics of the compositions under study are given in Table 1. All compounds were in the nascent state. The synthesis routes are reported in [5].

Methods

TG, DTG and DTA measurements were carried out with a Q-derivatograph under the following conditions: temperature range — 20–900°; heating rate — 10 deg/min; sample weight — 40 mg; error of weight loss allowed — ±0.5 mg; no inert substance; medium — air (static) of a continuous flow of nitrogen at a rate of 17 l/h; a platinum cone-like crucible with a diameter of 9.5 mm; the thermocouple was Pt/PtRh at the centre of the sample.

Table 1 Characteristics of rigid polyurethane foams containing reactive antipyrenes

Composition	Antipyrene	Weight		Density, kg/m^3	OI, % O_2
		P, %	Cl, %		
IRPUF	initial polymer	0.0	0.0	38	20.2
I-1		0.70	1.37	36	23.5
I-2	same antipyrene	0.85	1.97	35	24.3
II	 $[HO(CH_2)_2O(CH_2)_2O]_2P(O)-CH_2-N(CH_2CH_3)_2$	1.09	1.50	37	23.5
III-1	reaction product in the transesterification of dimethyl phosphite with 1,3-dichloropropanol-2, treated with epichlorohydrin	0.81	2.91	39	23.7
III-2	same antipyrene	1.24	4.11	38	24.9
III-3	same antipyrene	1.22	4.21	38	25.4

From consideration of the weight changes in the characteristic temperature interval, the apparent activation energy (E_a) of the thermal decomposition was calculated as in [6] by using a computer program. The areas of the exothermic peaks were measured planimetrically.

The coke residue (CR) was assessed after heating to 850° in air and the inert medium, from the TG curve of the dynamic thermal analysis.

The results of the thermal analysis are the average results from three consecutive experimental runs.

The oxygen index values (OI) were determined on an FTA apparatus, using a standard method and samples measuring 100 × 10 × 10 mm.

Results and discussion

Figure 1 shows DTA, TG and DTG curves of RPUF without antipyrene in air and in inert medium. In [1] it was shown that the total reactions of thermal decomposition in air are highly exothermic and proceed in two distinct stages. In nitrogen medium there is no definite step of temporary stabilization in the TG curve, and after separation of the unstable groups from the main structure the decomposition goes on at the same rate up to about 500°.

The results obtained for the activation energy of the thermal decomposition of IRPUF in Table 2 reveal the considerable catalytic role of oxygen in the decomposition reactions of RPUF at above 450°.

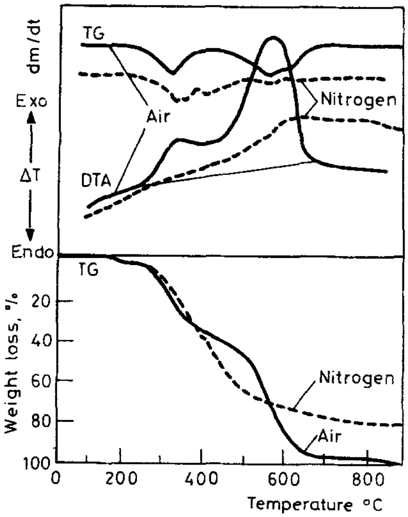


Fig. 1 DTA, TG and DTG curves of IRPUF

Table 2 Thermal analysis data on compositions I, II and IRPUF
(a) air medium

Composition	Stage	Temp. int., °C	Weight loss %	T_{max} dec. rate, °C	$CR_{850°}$, %	E_a, kJ	Correl. coeff.	Amplit. exo, cm	S_{I+II} cm^2
IRPUF	I	230–400	35.0	320		70.0	0.96	22.0	
	II	400–700	64.5	560	0.0	72.0	0.95	67.0	25.0
I–1	I	220–400	36.0	300		86.0	0.99	20.0	
I–2	I	200–400	33.0	295		77.0	0.97	18.0	20.9
	II	650–810	5.5	—	2.0	—	—	—	—
I–2	I	200–400	33.0	295		76.8	0.97	18.0	
	III	400–590	45.0	550		87.0	0.98	55.0	23.0
	III	590–690	13.0	—		—	—		
	IV	690–820	5.5	—	0.0	—	—		
II	I	220–400	30.0	300		55.0	0.98	15.0	
	II	400–600	38.0	555		80.0	0.96	48.0	19.8
	III	600–660	16.0	—		—	—		
	IV	660–770	4.0	—	8.5	—	—		
(b) nitrogen medium									
IRPUF	I	220–390	40.0	330		64.0	0.99	—	—
	II	390–650	36.0	420		277.0	0.90	—	—
	III	650–850	5.0	—	17.0	—	—	—	—
I–1	I	210–370	36.0	330		61.0	0.99	—	—
	II	370–435	19.0	400		92.0	0.94	—	—
	III	435–590	12.0	—		—	—	—	—
	IV	590–850	2.0	—	32.0	—	—	—	—
I–2	I	210–340	29.0	315		64.0	0.99	—	—
	II	340–430	24.0	385		78.8	0.98	—	—
	III	430–580	12.0	—	31.0	—	—	—	—
II	I	215–340	29.0	320		38.0	0.95	—	—
	II	340–440	30.0	395		59.0	0.93	—	—
	III	440–530	8.0	—	33.0	—	—	—	—

One of the decisive factors for the easy inflammability and increased combustibility of RPUF is the heat evolution during heating. Further stabilization of RPUF based on MDI may be achieved by thermooxidizing decomposition proceeding in two stages [7]. The results of the thermogravimetric analysis in Table 2 show that this fact may be used for the stabilization of the polymer structure if a suitable antipyrene is chosen.

Whereas additive antipyrenes decompose before the polymer, reactive antipyrenes take part in the polymer structure and decompose at the same time as the polymer. Part of the active fragments from the decomposition of P and Cl-containing antipyrenes may remain in the solid phase, helping to stabilize the structure, or, after evaporation, may affect the reactions in the gaseous phase in the combustion zone [8].

The compositions under study were chosen from among a number of increasing concentrations of antipyrenes on the basis of preliminary data concerning their OI values.

It can be seen from Table 1 that the antipyrenes relating to compositions I and II have similar compositions and structures, except for the oxygen-containing ring in antipyrene I. Table 2 presents a comparison between the thermogravimetric analysis data on compositions I and II, and the untreated composition.

The modified samples exhibit different thermal behaviour from that of the unmodified sample. The latter decomposes in two stages in the interval from 230 to 670°, while for compositions I and II 3 or 4 steps of decomposition are observed and the temperature intervals widen and shift mainly to higher temperatures: 820° in air, and 850° in nitrogen atmosphere. A similar tendency was found for polyurethane elastomers (PUE) modified with P and P/Cl-containing antipyrenes [9], and also for RPUF containing additive antipyrenes with the same active elements, P and Cl [1]. Unlike additive antipyrenes, the presence of reactive antipyrenes affects the initial temperature of polymer decomposition slightly, i.e. it does not decrease by more than 10 or 20°. A slight decrease is also observed in the temperature of the maximum rate of decomposition in each stage. In general, however, the decomposition in the presence of antipyrene is retarded and proceeds over a wide temperature interval, which means that the flow of potentially combustible products towards the combustion zone per unit time decreases. In nitrogen atmosphere (Table 2b) the modified samples form more CR than the untreated RPUF. Of the compositions presented in Table 2a, composition II forms the highest percentage of CR in air. For composition I, the exothermic oxidation probably increases because of the presence of oxygen in its own structure.

The E_a values for the thermal decompositions may also give an idea of the effects of antipyrene on the reactions. Table 2 shows that in stage I of decomposition the presence of low concentrations of antipyrene does not affect E_a substantially, while E_a for stage I of the decomposition of RPUF containing additive antipyrenes decreases in all cases with increase of the quantity of antipyrene, and increases in stage II. E_a for stage II of the decompositions of the investigated compositions containing antipyrene I and II changes slightly, its values in air being higher than those of IRPUF.

Analysis of the DTA curves (Fig. 2) shows that in the presence of antipyrenes I and II the exothermic peaks characteristic of the decomposition of IRPUF become less intensive and shift slightly towards lower temperatures. At temperatures above 700°, a slight third exothermic peak appears. The result is a general decrease in the

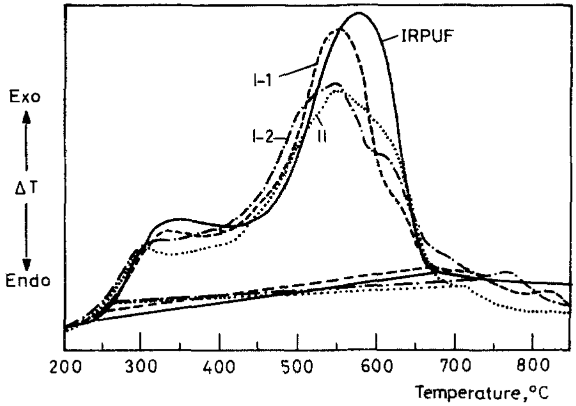


Fig. 2 DTA curves of IRPUF and compositions I and II

rate of heat evolution. Thus, in this case, the antipyrenes cause the distribution of both weight losses and heat evolution over a wide temperature interval, which is an important condition for reducing the heat flow towards the combustion zone during fire.

The total area of exothermic peaks I and II was determined. Figure 2 and Table 2 show that the compositions with the smallest area of the exothermic peaks give a higher percentage of CR, no matter that the OI values (Table 1) are not always the highest. For composition I it was found that the higher concentration of antipyrene results in an increase of the area of exothermic peaks I and II; while the CR is smaller than that for composition II. The values obtained for the areas of the exothermic peaks, the percentage of CR and the OI show that composition II is a better combustion retardant. This particular case illustrates the possibility of utilizing thermal analysis to register the effects of small differences in the chemical composition and structure of the antipyrene on the specific characteristics of the thermal curves.

The TG data for composition III are compared with the TG data for the untreated composition in Table 3. In the case of composition III, just like compositions I and II, more and better differentiated steps of decomposition are observed, the rate decreases and the interval of decomposition broadens towards higher temperatures. The effect of the antipyrene in composition III may be seen in the fact that, even at 350° in stage I, the modified compositions have higher thermostability than the unmodified RPUF. In this case, therefore, the conditions for decreasing the gasification are created at the very beginning of heating. A third stage of decomposition begins at temperatures above 670°, which indicates a change of mechanism towards the formation of more stable structures due to the effect of antipyrene. In nitrogen atmosphere this tendency leads to the preservation

Table 3 Thermal analysis data on compositions III and IRPUF
(a) air medium

Composition	Stage	Temp. int., °C	Weight loss %	T_{max} dec. rate, °C	$CR_{850°}$, %	E_a, kJ	Correl. coeff.	Amplit. exo, cm	S_{I+II} cm²
IRPUF	I	230–400	35.0	320		70.0	0.96	22.0	
	II	400–700	64.5	560	0.0	72.0	0.95	67.0	25.0
III–1	I	200–400	36.0	300		72.0	0.99	16.0	
	II	400–630	55.0	545		86.0	0.98	53.0	18.8
	III	630–750	7.0	—	0.0				
III–2	I	200–400	36.0	300		68.0	0.98	16.0	
	II	400–670	54.0	550		84.0	0.99	51.0	18.0
	III	670–800	9.0	—	1.0	—	—		
III–3	I	200–400	32.0	300		68.0	0.97	12.5	
	II	400–590	42.0	540		80.0	0.97	49.0	17.2
	III	590–670	12.0	750		—	—	—	—
	IV	670–780	10.0	—	4.0	—	—	—	—

(b) nitrogen medium

Composition	Stage	Temp. int., °C	Weight loss %	T_{max} dec. rate, °C	$CR_{850°}$, %	E_a, kJ	Correl. coeff.	Amplit. exo, cm	S_{I+II} cm²
IRPUF	I	220–390	40.0	330		64.0	0.99	—	—
	II	390–650	36.0	420		277.0	0.90	—	—
	III	650–850	6.0	—	17.0	—	—	—	—
III–1	I	220–390	33.0	340		41.0	0.98	—	—
	II	390–460	13.0	420		36.0	0.90	—	—
	III	460–530	12.0	510		—	—	—	—
	IV	530–850	10.0	—	33.0	—	—	—	—
III–2	I	210–340	26.0	300		34.0	0.92	—	—
	II	340–450	20.0	400		48.0	0.94	—	—
	III	450–570	9.0	490		—	—	—	—
	IV	570–850	1.0	—	43.0	—	—	—	—
III–3	I	210–340	26.0	300		32.0	0.98	—	—
	II	340–430	16.0	390		73.0	0.95	—	—
	III	430–570	10.0	480		—	—	—	—
	IV	570–850	3.0	—	45.0	—	—	—	—

of the structure and the formation of a high percentage of CR, which, in the case of composition III–3, is 45% larger than the CR of IRPUF.

The change of E_a is not a sensitive indicator, since the E_a of the exothermic decomposition is not affected by the presence of antipyrene. To a certain extent this proved true for compositions I and II, too. The important factors here are probably the type of chemical bonding of the antipyrene with the polymer chain, and also its composition and concentration.

Composition III clearly shows the tendency of decreasing intensity of exothermic peaks I and II in the presence of antipyrene, and their breaking up into three exothermic peaks which expand their area towards higher temperatures (Fig. 3). Their shift towards lower temperatures is not more than 10 deg, while towards higher temperatures it is about 150 deg.

The largest CR, and the greatest decrease in the rate and widening of the temperature interval of heat evolution and weight loss were obtained for composition III–3 without a decrease in the density of the sample in comparison with that of IRPUF (Table 1).

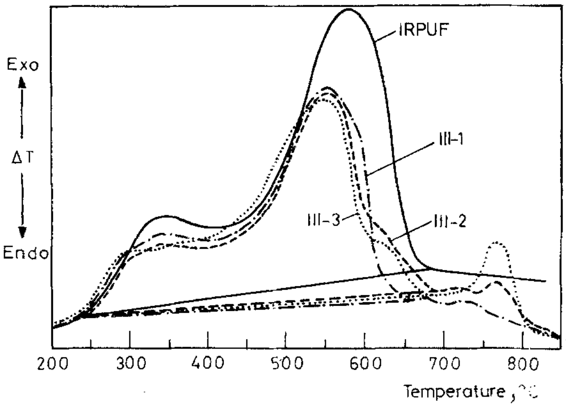


Fig. 3 DTA curves of IRPUF and compositions III

The data presented show that the direction and the degree of the effects of the various antipyrenes on the thermal decomposition of the polymer may be revealed more fully by studying the thermal decomposition of the polymer-antipyrene system in a wide temperature interval. The type of the thermal decomposition is indicative of the inhibitory effect of antipyrenes, and thus it is possible to predict the combustion stability of different polymer materials on the basis of the thermal analysis data. For this purpose, it is necessary to take into consideration the type of the thermal decomposition and to determine the sensitive thermal characteristics in each case. For example, the most sensitive parameter for polyurethane elastomers containing reactive antipyrenes [9] was the temperature of exothermic peak I, by means of which an idea of the optimum concentration of antipyrene was obtained. The present work shows that dynamic thermal analysis can register changes resulting in the mechanism and kinetics of the thermal decomposition of the investigated RPUF from comparatively low concentrations and differences in the concentrations, and from differences in the chemical compositions and structures of the antipyrenes.

The most sensitive characteristics associated with the influence of antipyrenes in this case were the CR determined at 850° in an inert medium, and the area of exothermic peaks I and II in the DTA curves in air medium.

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Zusammenfassung — Die Effekte von P und Cl enthaltenden reaktiven Antipyrenen unterschiedlicher Zusammensetzung und Struktur auf den Mechanismus und die Kinetik der vollständigen thermischen Zersetzung von festen Polyurethanschäumen wurden zusammen mit der Möglichkeit, ihre Wirksamkeit als Verbrennungsinhibitor zu beurteilen, mittels kombinierter thermoanalytischer Techniken untersucht. Es wird gezeigt, daß mit dynamischer thermischer Analyse die Veränderungen im Mechanismus und in der Kinetik der thermischen Zersetzung der untersuchten Polyurethane erfaßt werden können, die durch vergleichsweise niedrige Konzentrationen und kleine Konzentrationsunterschiede sowie auf Unterschiede in der chemischen Zusammensetzung und der Struktur der Antipyrene bedingt sind. Die im gegebenen Fall für den Einfluß der Antipyrene charakteristischsten Kenndaten sind der in einem inerten Medium bei 850° bestimmte Koksrückstand und die Flächen der exothermen Peaks I und II in der in Luftatmosphäre aufgenommenen DTA-Kurve.

Резюме — Методом комбинированного термического анализа изучено влияние фосфор- и хлорсодержащих антипиренов различного состава и структуры на механизм и кинетику общего термического разложения жестких полиуретановых пен. Наряду с этим проведена оценка их эффективности как ингибиторов горения. Показано, что динамический термический анализ позволяет регистрировать изменения механизма и кинетики термического разложения полиуретанов в зависимости от концентрации, химического состава и структуры антипиренов. Наиболее чувствительными характеристиками влияния антипиренов были коксовый остаток, определяемый при 850° в какой-либо инертной атмосфере, и площади экзотермических пиков I и II на кривой ДТА, измеренной в атмосфере воздуха.