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THERMAL BEHAVIOUR OF RIGID POLYURETHANE FOAMS

I. A study of rigid polyurethane foam containing additive antipyrenes

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By means of a combined thermal analysis technique, the thermal behaviour of rigid polyurethane foams containing additive antipyrenes was studied. The presence of phosphorus— and phosphorus/chlorine-containing antipyrenes based on phosphate and phosphonate and a combination of them led to decreases in the rates of heat and weight loss during heating. More steps of decomposition were formed and the interval of decomposition was widened and shifted to higher temperatures. Some thermal characteristics make it possible to predict the optimum antipyrene compositions and concentrations with minimum time, labour and material consumption under laboratory conditions.

Rigid polyurethane foam (RPUF) is an organic material with a high tendency to burn. Its combustibility depends essentially on the thermal stability of the structural chemical bonds and the products of decomposition. As with other types of polyurethanes, its flammability is reduced by the addition of antipyrenes. The problem of selecting optimum antipyrene compositions for polymers is becoming an urgent necessity. It requires the development of laboratory methods which are minimum time-, labour- and material-consuming and can provide maximum insight into the inhibiting effect of antipyrenes, thereby allowing a comparative evaluation of their efficiency. A major shortcoming of the available flammability tests is their failure to meet these requirements. Directly proportional relationships between polymer flammability tests and thermal analysis data have, recently been found [1–5]. Systematic studies [6–9] in this field, however, are still scarce.

The aim of this work was to study the effect of additive antipyrenes with different compositions and structures on the mechanism and kinetics of the total thermal decomposition reactions of RPUF, and the possibility of evaluating their effectiveness as combustion inhibitors.

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Experimental

Initial materials

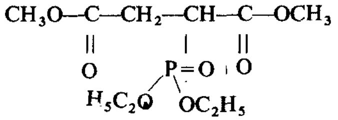
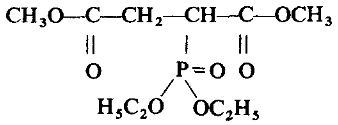
The initial rigid polyurethane foam (IRPUF) without antipyrene was based on the polyol component, a reaction product of the synthesis of dimethyl terephthalate, and polymeric diphenylmethanediisocyanate (MDI). The following antipyrenes were used: composition *A*–0,0-diethyl-1,2-dicarbomethoxyethylphosphonate; composition *B*–tris-(β-chloroethyl)-phosphate; composition *C*–consisting of *A* and *B*. Some characteristics of antipyrene-containing RPUF are shown in Table 1.

All compounds were in the nascent state. The way they were synthesized is reported in ref. [11].

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; initial weight of samples—40 mg; error for weight loss allowed—±0.5 mg; no inert substance; medium—air (static) or a continuous flow of

Table 1 Characteristics of rigid polyurethane foams containing additive antipyrenes

Composition	Antipyrene	P, % weight	Cl, % weight	Density kg/m^3	OI % O_2
IRPUF	without antipyrene	0.0	0.0	38	20.2
A_1	 $CH_3O-C(=O)-CH_2-CH(P(=O)(OC_2H_5)_2)-C(=O)-OCH_3$	0.51	0.0	38	23.0
A_2	same antipyrene	1.02	0.0	38	24.1
A_3	same antipyrene	1.50	0.0	36	24.4
B_1	$(ClCH_2CH_2O)_2P=O$	0.51	1.83	35	22.0
B_2	same antipyrene	0.78	2.69	35	23.0
B_3	same antipyrene	1.01	3.50	34	24.5
C_1	 $CH_3O-C(=O)-CH_2-CH(P(=O)(OC_2H_5)_2)-C(=O)-OCH_3$ $(ClCH_2CH_2O)_3P=O$	1.04	1.77	39	23.7
C_2	same antipyrenes	1.38	1.57	39	24.4
C_3	same antipyrenes	1.93	1.37	43	25.0

nitrogen at 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.

Taking into consideration the weight changes in the characteristic temperature intervals, the effective activation energy (E_a) of the thermal decomposition was calculated as in ref. [12] by using a computer program.

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

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

Results and discussion

Figure 1 shows DTA, TG and DTG curves of RPUF without antipyrene in air and in inert medium. The total reactions of the thermal decomposition in air are highly exothermic and proceed in two stages. Stage I, up to about 370°, is characterized by the same rate of decomposition in air and nitrogen.

Backus *et al.* [13], who studied the thermal decomposition and combustibility of polyurethanes based on MDI, also noted the similarity of the TG decomposition curves in air and in inert medium in stage I. IR spectroscopy revealed that weight stabilization in the interval 360–500° in air the step in the TG curve does not indicate preservation of the main functional groups of the initial structure. Probably, after their separation and the destruction of hydroxide structures, the

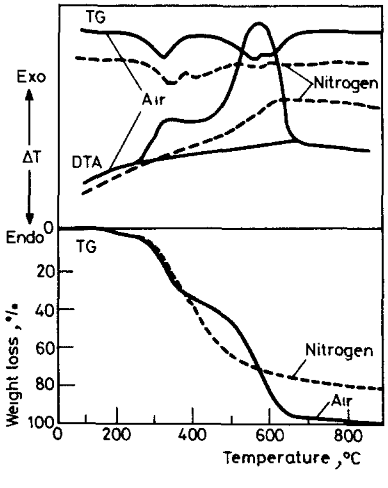


Fig. 1 DTA, TG and DTG—plots of IRPUF

weight is retained owing to stabilization of the main structure due to the formation of C = C bonds, with an absorption band at 1650 cm^{-1} in the IR spectrum [14]. In nitrogen medium, there is no such step 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 500°. In air, stage II of the decomposition is accompanied by intense heat evolution in the interval 500–650°, resulting in combustion. In nitrogen atmosphere, above 500°, the decomposition abates and 17% CR is formed. Therefore, stage II of decomposition is definitely affected by atmospheric oxygen.

The results obtained for the activation energy of thermal decomposition agree well with the slope of the thermal curves. For stage I of the decomposition in air and nitrogen, they are comparatively low and similar: 70.4 and 63.2 kJ/mol, respectively. For stage II, the E_a value in air is much lower than that in nitrogen: 71.6 and 227.2 kJ/mol, respectively. These results confirm the substantial catalytic role of oxygen in the decomposition of RPUF above 450°.

It may be assumed that one of the decisive factors concerning the easy inflammability and increased combustibility of RPUF is the heat evolution during heating. It is well known that the two-stage thermooxidizing decomposition allows the further stabilization of RPUF based on MDI [15]. The TG analysis data presented in Table 2 also show that this factor may be used for further stabilization of the polymer structure, provided the antipyrene composition is properly chosen.

In principle, additive antipyrenes should decompose just before the temperature at which decomposition of the main polymer material begins. The particles resulting from the decomposition of antipyrene may remain in the solid phase or affect the gas-phase reactions in the combustion region. In the solid phase, they can even affect the whole mechanism and kinetics of the polymer thermal decomposition. Phosphorus-containing antipyrenes are known to be effective mainly in the solid phase, as catalysts of coking and inhibitors of exothermic reactions in combustion, owing to the dehydrating effect of the phosphoric acids formed at given stages [16]. This fact may be related to the tendency shown in Table 2, namely that the thermal decomposition of RPUF containing antipyrene A with increasing quantities of phosphorus is characterized by the formation of more steps in the TG and DTG curves. There are two decomposition stages for the untreated sample in the interval 230–700°, while in the case of A_2 and A_3 three steps can be seen. The interval widens as the quantity of antipyrene increases, and it is 160–780° for A_3. The lowered thermostability is due to the decomposition of antipyrene. The shift in the maximum rate of decomposition towards lower temperatures, and the shift in decomposition towards higher temperatures show that the interaction of the active antipyrene fragments with the polymer structure slows down the decomposition of the polymer as a whole. A similar tendency was observed for polyurethane elastomers based on MDI [17]. In terms of combustion, this means a decrease in the

Table 2 TG analysis data for compositions A and IRPUF a) air medium; b) nitrogen medium

a)

Composit.	Stage	Temp. int. °C	Weight loss, %	T_{max} decomp. rate, °C	$CR_{850°}$ %	E_a kJ/mol	Correlat. coeffic.
IRPUF	I	230–400	35.0	320		70.0	0.96
	II	400–700	64.5	560	0	72.0	0.95
A_1	I	220–400	36.0	310		48.0	0.97
	II	400–700	63.5	590	0	76.0	0.97
A_2	I	190–400	38.0	300		44.0	0.95
	II	400–650	56.0	560		68.0	0.98
	III	650–770	4.0	—	2.0	—	—
A_3	I	160–400	39.0	300		32.0	0.94
	II	400–650	56.0	540		103.0	0.99
	III	650–720	5.0	—	0	—	—

b)

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	—	—
A_1	I	200–300	12.5	250		28.0	0.90
	II	300–370	19.0	340		54.0	0.90
	III	370–450	31.0	410		—	—
	IV	450–600	15.0	500		—	—
	V	600–850	3.0	—	29.5	—	—
A_2	I	190–300	13.0	240		—	—
	II	300–360	17.0	330		23.6	0.90
	III	360–430	19.0	400		65.6	0.97
	IV	430–600	10.0	480		—	—
	V	600–850	5.0	—	34.0	—	—
A_3	I	150–270	13.0	240		36.0	0.97
	II	270–340	14.0	335		115.0	0.99
	III	340–430	19.0	390		96.0	0.97
	IV	430–600	9.0	—		—	—
	V	600–850	3.0	—	33.5	—	—

flow of potentially combustible products towards the zone of burning. In nitrogen atmosphere, there are as many as 5 steps in the TG curve and the interval of decomposition widens to about 850°. What is more, for sample A_2 CR is formed in twice the quantity for the untreated sample (Table 2).

An idea of the effect of antipyrene on the mechanism and kinetics of the reactions during heating is also obtained from the E_a values for the thermal decomposition. Table 2 shows that in stage I of the decomposition E_a decreases with increasing quantities of antipyrene in both air and the inert atmosphere. The E_a values for stage II are higher than those in stage I of the decomposition.

Further tests on the residue after heating at 400° were performed by IR and emission spectroscopy. No P or P-containing fragments were found for composition A_2 in nitrogen atmosphere. According to the data presented above, the mechanism of action of antipyrene here is probably connected with its interaction with RPUF in stage I of the decomposition and the ensuing evolution in the gas phase. The residue after heating in air does show traces of phosphorus.

Analysis of the DTA curves for compositions A (Fig. 2) shows that in the presence of antipyrene the intensities of the exothermic peaks I and II decrease and, in most cases, they are shifted slightly towards lower temperatures. Only for sample A_2 does exothermic peak I shift to higher temperatures by about 10°, while its intensity decreases. The intensity of exothermic peak II also decreases greatly. At the same time, at temperatures above 700° the treated samples exhibit a slight exothermic peak III. This is associated with the differentiation of stage III of decomposition (Table 2), resulting from the decomposition of more thermostable structures formed in the earlier stages of heating under the influence of antipyrene. Therefore, antipyrene acts as a retardant by distributing both weight losses and heat evolution in wider temperature ranges. This effect is very important for reducing the total heat flow towards the combustion zone during fire (according to Kamenetzky's combustion stability diagram) [15].

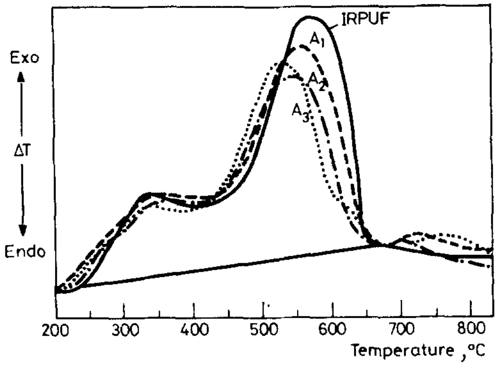


Fig. 2 DTA—plots of IRPUF and compositions A_1, A_2, A_3

The TG curve for compositions B (Table 1) containing Cl and P in the form of phosphates shows more steps and widening of the interval of decomposition. Because of the higher total concentration of antipyrene and the presence of Cl in the structure, the beginning of decomposition is shifted towards lower temperatures as early as composition B_1, because of the volatilization of antipyrene. As noted earlier, the activity of additive antipyrenes is attributed to their volatility.

With compositions *B*, CR is obtained in air too, though in a small quantity proportional to the quantity of the additive. In nitrogen, the quantity of CR obtained is greatest for composition B_1. This fact is probably related to the high concentration of Cl in compositions B_2 and B_3; it is known that in some cases Cl hinders the formation of stable coke. Its effect might be expected mainly in the gas phase of the sample [16], due to the liberation of noncombustible HCl, while coke formation is catalyzed to a greater degree by P.

The tendency for E_a to change in the presence of composition *B* in stages I and II of the decomposition is analogous to that for composition *A*. It is most probable that antipyrene interacts with the polymer; in this case, the IR and emission spectra data confirmed the presence of P after stage I of the decomposition (at 400° in air and in nitrogen atmosphere). The P found is in the form of P = O bonds (the adsorption band in the IR spectrum is at 1240 cm^{-1}) [18] and it comprises more than 10% of the initial quantity. Therefore, the chemical structure of antipyrene conditions its preservation in the structure of a given polymer, since the antipyrenes used are volatile substances. In this case it is possible for Cl to take part in common P/Cl-containing active fragments [16].

Figure 3 presents DTA curves for compositions *B* compared with the untreated polymer. Both a reduction and a shift in exothermic peaks I and II are observed. The reduction in exothermic peak I for sample B_2 is greatest, without its being shifted to lower temperatures. This is not the case with composition B_3, which is probably due to the antipyrene concentration in B_3 exceeding the optimum. An increase in exothermic peak I and a decrease in thermostability was established for Cl-containing polyurethane elastomers [19], suggesting a change in the polymer structure at Cl-containing antipyrene concentrations higher than the optimum. It

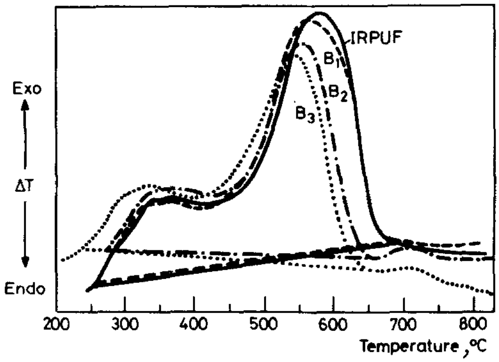


Fig. 3 DTA—plot of IRPUF and compositions B_1, B_2, B_3

may be seen from Table 1 that in the case of B_3 the density of the sample does decrease. This makes oxygen access easier and shifts the oxidation reactions to lower temperature, thereby deteriorating the fireproof characteristics of the polyurethane. In this case too, the appearance of a third, small exothermic peak corresponds to the third step in the TG curves, resulting from decomposition of the products of coking formed in the earlier stages of heating.

Compositions *C* contain antipyrenes *A* and *B* with increasing concentrations of P and decreasing concentrations of Cl (Table 1). Figure 4 shows the DTA curves for compositions *C*. With compositions *C*, the tendency for the antipyrenes from compositions *A* and *B* to influence mass and heat transfers is not only similar, but also sharply increased. For example, the steps in the TG curves are better differentiated, the CR is substantially increased and the exothermic peaks are sharply reduced. With composition C_3, the CR is 2.5 times as much as that for the initial composition, and the exothermic area of exothermic peaks I and II is more than twice as low as for the untreated sample. At the same time, the temperature interval of heat evolution widens to above 850° and the first exothermic peak disappears. Thus, the polymer is prevented from rapid heating and its decomposition shifts to higher temperatures. The importance of this shifting and of the intensity reduction in exothermic peak I as concerns the fireproof characteristics of the polymers is in agreement with the studies of other authors [2, 3].

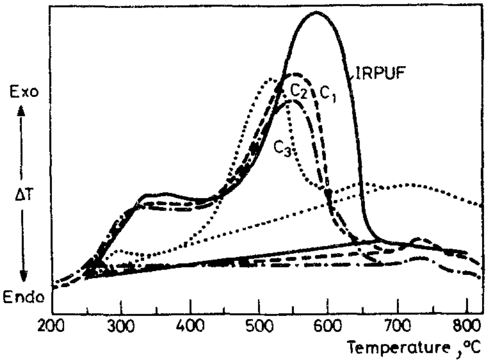


Fig. 4 DTA—plots of IRPUF and compositions C_1, C_2, C_3

Figures 5–8 present the dependences of the most important characteristics of the thermal curves (CR, E_a, area of exothermic peaks I and II (S_{I+II})) and the OI values on the concentrations of P and Cl for antipyrenes with different chemical compositions.

It can be seen from Fig. 5 that the OI values are in all cases directly proportional to the quantity of antipyrene introduced. These values do not express the

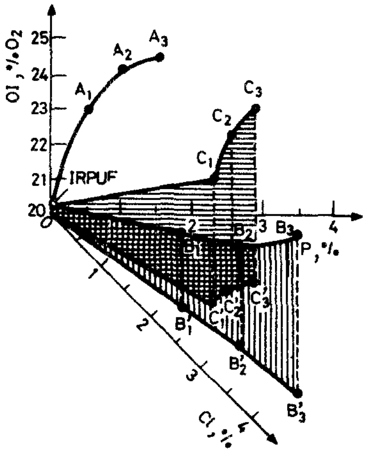


Fig. 5 Relationship between the OI values and the content of P and Cl in the investigated compositions

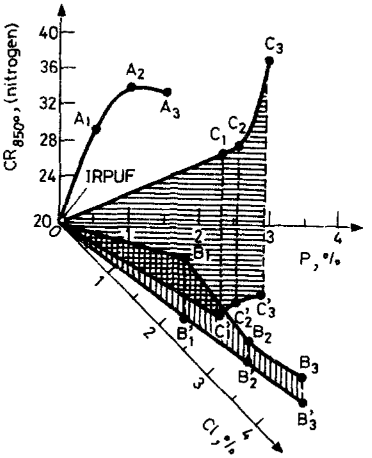


Fig. 6 Relationship between the $CR_{850°}$ (nitrogen) and the content of P and Cl in the investigated compositions

dependence of the combustibility on the structure of antipyrene nor the way in which the latter affects the elements of combustion [1, 15]. For example, the OI is almost the same for compositions A_3, B_3 and C_3 (Table 1), while the CR differs in absolute value. The dependences for the other thermal characteristics are similar, too. The latter, however, can show clearly in which stage, in what direction and to what extent the presence of antipyrene influences heat and weight losses during heating. What is more, a clearer picture of the action of each antipyrene may be obtained, this providing a wider basis for comparison and preference of one composition to another, depending on the conditions of exploitation of a given

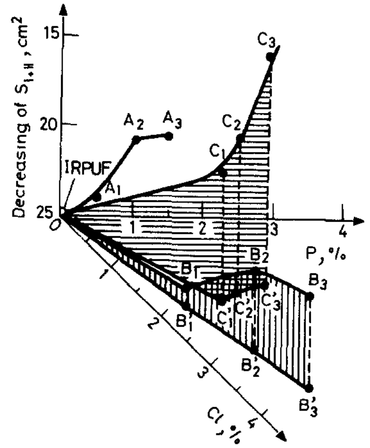


Fig. 7 Relationship between the sum of the intensities of the first and the second exothermal peaks (S_{I+II}) and the content of P and Cl in the investigated compositions

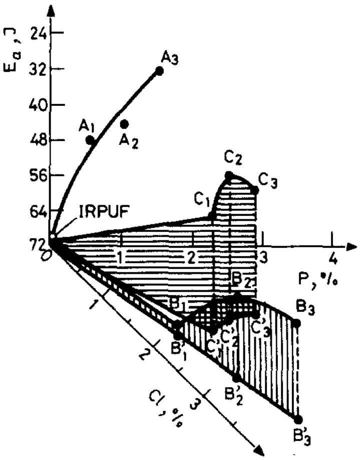


Fig. 8 Relationship between the E_a of the first stage of decomposition in air and the content of P and Cl in the investigated compositions

material. All this is achieved with minimum time and material consumption, with laboratory conditions and equipment.

It is well known that a high quantity of antipyrene does not always lead to optimum results, particularly with polyurethanes (PU) [20, 21]. As can be seen from the Figures presented, there is a maximum in some cases. The maxima for the compositions under study are exhibited best for composition *A*. The reason may be that the retarding effect in this case is conditioned mainly by P, which acts predominantly in the solid phase (the object of this study). As our previous studies of PU elasomers showed [19], increase of the concentration of P above 1% does not lead to a substantial improvement in thermal behaviour. This concentration may be presumed to be the optimum for PU because of the catalytic effect of P on dehydrogenation and coking, which retards gasification and hinders the exothermic reactions of the solid phase of the polymer [16].

On the other hand, the chemical compositions and structures of antipyrenes also affect the mechanism of their action, which accounts for the fact that the simultaneous presence of P and Cl in composition *C* helps to form a high CR and to inhibit exothermic reactions. This tendency for the combination of antipyrenes from phosphate and phosphonate is strongest when the quantity of P increases (1.9%) and the quantity of Cl decreases (1.37%).

It was shown that thermal analysis is able to register the change resulting in the mechanism and kinetics of the thermal decomposition of the RPUF under study from comparatively low concentrations and concentration differences of antipyrene.

The most sensitive characteristics of the thermal curves proved to be the CR at 850° in nitrogen atmosphere, the exothermic peaks (particularly the first exothermic peak), their intensity, shifting and widening, and the values of the effective activation energy of thermal decomposition. It was found that the protective effect of these antipyrenes on RPUF is due to decreases in the rates of heat and weight loss by distribution of the decomposition processes in a wider temperature interval and their shifting to higher temperatures.

Thermal analysis makes it possible to predict the optimum antipyrene composition and optimum minimum concentrations of antipyrenes for the polymers with a low consumption of time, labour and material.

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Zusammenfassung — Mittels einer kombinierten Technik wurde das thermische Verhalten eines starren, Antipyrene als Additiv enthaltenden Polyurethanschaumes untersucht. Phosphor und Phosphor/Chlor enthaltende Antipyrene auf Phosphat- und Phosphonatbasis und eine Kombination dieser Substanzen vermindern die Geschwindigkeit der Wärmeentwicklung und des Gewichtsverlustes während des Aufheizvorganges. Es treten mehr Zersetzungsschritte auf und das Temperaturintervall der Zersetzung ist größer und nach höheren Temperaturen hin verschoben. Einige thermische Kennwerte ermöglichen die Voraussage der optimalen Zusammensetzung und Konzentration des Antipyren-Additivs für minimalen Zeit-, Arbeits- und Materialaufwand unter Laboratoriumsbedingungen.

Резюме — Посредством комбинированных методов термического анализа изучено термическое поведение твердых полиуретановых пенопластов, содержащих антипирены в качестве добавок. Присутствие фосфора и фосфор/хлор-содержащих антипиренов на основе фосфатов и фосфонатов и комбинация их, приводит к уменьшению скорости потери тепла и веса. При этом происходит многостадийность процесса разложения, а интервал разложения расширяется и сдвигается в сторону более высоких температур. Некоторые термические характеристики предоставили возможность установить оптимальный состав антипиренов и их концентрацию при минимальных затратах времени и веществ для получения пенопластов в лабораторных условиях.