# On the Relationship between the Thermal Properties of Modified Polyurethane Elastomers and the Efficiency of Antipyrens

K. TROEV, K. MARKOVA,* and G. BORISOV, *Central Laboratory for Polymers, Bulgarian Academy of Sciences, Sofia 1113, Bulgaria*, and * *Higher Institute of Chemical Technology, Burgas, Bulgaria*

## Synopsis

A study is made of the relationship between the thermal properties of polyurethane elastomers and the efficiencies of antipyrens containing phosphorus and some containing both phosphorus and chlorine. It is shown that a relationship exists between the thermal properties of polyurethane elastomers and the efficiencies of the antipyrens. It is also found that the presence of antipyrens in the molecules of the polyurethane elastomer effects the course of DTA, DTG, and TG curves. This permits antipyren efficiency to be qualitatively evaluated as well as the antipyren optimal concentration to be determined.

## INTRODUCTION

Organic polymers and polymeric materials undergo destructive processes on heating leading to low-molecular gaseous or liquid volatile as well as carbonized products. Some of the volatile compounds burn. Combustibility of the polymers and polymeric materials is mainly dependent on the ratio between the heat evolved from burning the pyrolysis products and the heat required for their formation and gasification.

The following factors characterize the combustibility of polymers:temperature of ignition and rate of combustion;[1] heat of combustion and temperature on the surface of the burning material.[2] It can be seen that decrease in combustibility should be associated with increasing the temperature of ignition and reducing the rate of combustion, heat of combustion, and surface temperature. It has been established that antipyrens, which most often are phosphorus-containing, or phosphorus- and chlorine-containing compounds, affect the factors in question.

The choice of antipyrens for polymers is always accompanied by an evaluation of their efficiency. The question of determining the combustibility of polymers is already resolved by employing methods such as oxygen index evaluation, fire tube procedure, gravimetric determinations, etc. Under laboratory conditions they all require considerable amounts of polymer. Studies conducted by van Krevelen,[3] Zabski and co-workers,[4] and Zeronian and co-workers[5] have attempted to find a method for evaluating the combustibility of polymers using very small amounts of material. The derived relationships are empirical in nature, since they are linked with the individual characteristics of the examined samples.

The aim of the present work is to consider the behavior of modified polyurethane elastomers as related to the efficiencies of antipyrens containing phosphorus or both phosphorus and chlorine.

## EXPERIMENTAL

Polyurethane elastomers[6] containing 0.8%, 1.4%, 2.8%, 3.8%, and 5.2% of phosphorus and 1.35% and 11.42%, 3.40% and 4.04%, and 4.80% and 5.51% of phosphorus and chlorine and also unmodified polyurethane elastomer were used for tests.
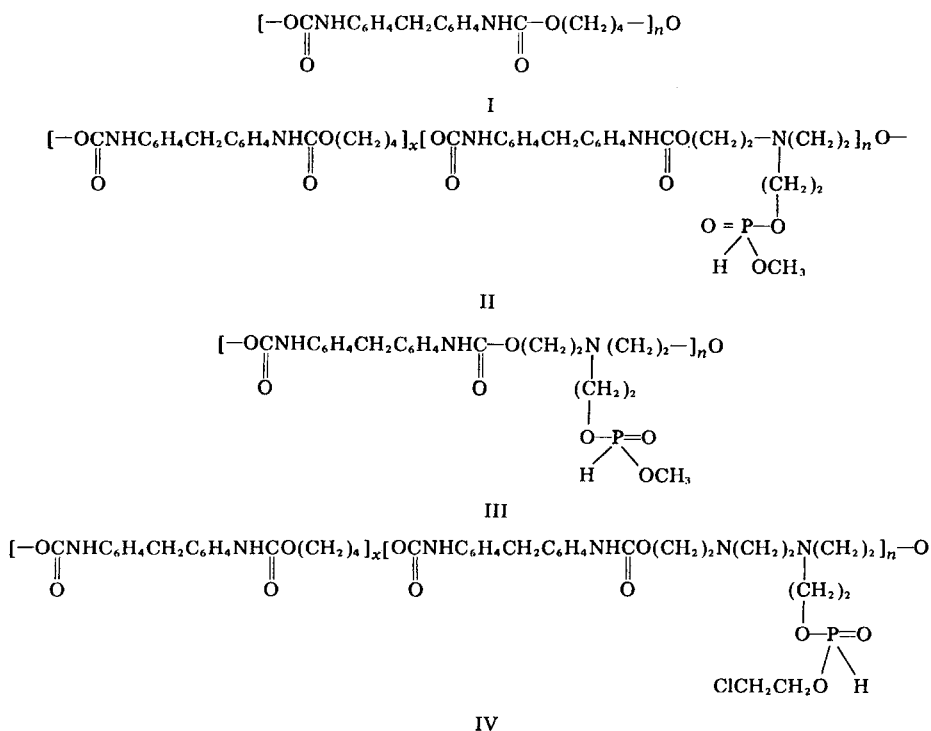
A derivatograph (Paulik, Paulik, Erdey-MOM) was used. The rate of heating was 6°/min, 9°/min, or 20°/min in air; the size of sample was 100 mg, and the temperature interval between 20°C and 900°C; sintered $Al_2O_3$ was used as standard; a Pt crucible was employed with a diameter of 9.5 mm.
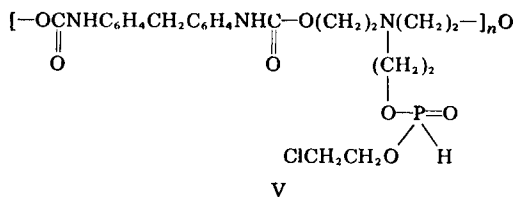
The oxygen index was determined on a Module FTA Instrument [Stanton Redcroft (Great Britain)] using samples with dimensions 80 mm × 6 mm and 0.15–0.20 mm thick.

## RESULTS AND DISCUSSION

It is established that phosphorus brings about a reduction in the rate of combustion of polymers and polymeric materials increasing the carbonized residue,[7,8] hindering the exothermic oxidation of carbon in the solid phase,[9,10] and absorbing heat as the result of the endothermic reduction of phosphoric acid.[11,12]

Elastomers of the following structure were examined with the view to establishing whether a relationship existed between their thermal properties and the efficiency of the antipyrens:

$$[-OCNHC_6H_4CH_2C_6H_4NHC-O(CH_2)_4-]_nO$$

I

$$[-OCNHC_6H_4CH_2C_6H_4NHCO(CH_2)_4]_x[OCNHC_6H_4CH_2C_6H_4NHCO(CH_2)_2-N(CH_2)_2]_nO-$$

with substituent $(CH_2)_2$, $O=P-O$, $H$, $OCH_3$

II

$$[-OCNHC_6H_4CH_2C_6H_4NHC-O(CH_2)_2N(CH_2)_2-]_nO$$

with substituent $(CH_2)_2$, $O-P=O$, $H$, $OCH_3$

III

$$[-OCNHC_6H_4CH_2C_6H_4NHCO(CH_2)_4]_x[OCNHC_6H_4CH_2C_6H_4NHCO(CH_2)_2N(CH_2)_2N(CH_2)_2]_n-O$$

with substituent $(CH_2)_2$, $O-P=O$, $ClCH_2CH_2O$, $H$

IV

$$[-\underset{\underset{O}{\|}}{O}CNHC_6H_4CH_2C_6H_4NH\underset{\underset{O}{\|}}{C}-O(CH_2)_2\underset{\underset{(CH_2)_2}{|}}{N}(CH_2)_2-]_nO$$

$$\underset{ClCH_2CH_2O \quad H}{\overset{O-P=O}{\diagup \diagdown}}$$
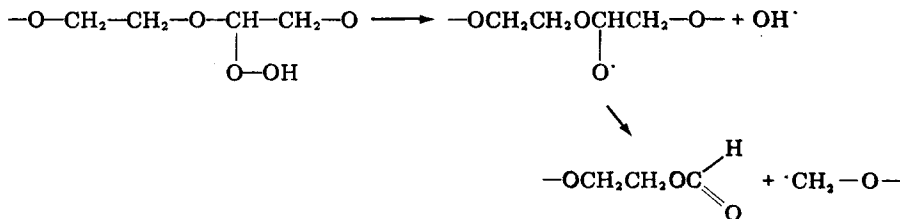
V

From the DTA curve in Figure 1 it can be seen that the polyurethane elastomers I (curve 1) exhibits at 205°C a well-defined exothermic effect accompanied by a slight increase in the mass of the sample by about 0.5%. Conducting the thermal degradation in an inert atmosphere confirmed that the exothermic effect was due to polyurethane oxidation according to the following scheme:[13]

$$-O-CH_2-CH_2-O-CH_2-CH_2-O- \xrightarrow{O_2} -O-CH_2-CH_2-O-\underset{\underset{O-OH}{|}}{CH}-CH_2-O-$$
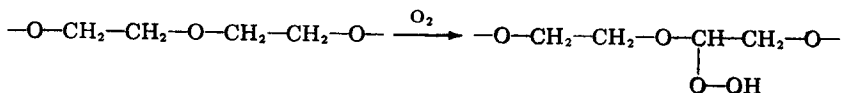
Hydroperoxides spontaneously increasing with time decompose[14] to highly reactive OH· radicals which govern the rate of combustion:

$$-O-CH_2-CH_2-O-\underset{\underset{O-OH}{|}}{CH}-CH_2-O \longrightarrow -OCH_2CH_2O\underset{\underset{O·}{|}}{C}HCH_2-O- \; + \; OH·$$

$$-OCH_2CH_2O\underset{\diagdown O}{\overset{\diagup H}{C}} \; + \; ·CH_2-O-$$

A wide endothermic region is observed from 250°C characterized by a slow degradation; the loss in mass is about 4%. From 315°C exothermic effects appear, accompanied by significant losses in mass (70%). The exothermic effect changes into an extremely strong endothermic effect at the maximum rate of decomposition (405°C) and at 500°C the endothermic effect changes into an exothermic effect, accompanied by increase in mass of about 25%. The latter effect is caused by the strongly exothermic reaction proceeding on the carbonized surface of the polyurethane after the degradation:

$$C + O_2 \to CO_2 + 94 \text{ kcal/mol}$$
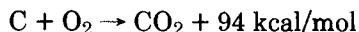
The thermal study of the polyurethane elastomers II containing 0.8% P (Fig. 1, curve 2) revealed that no exothermic effect occurred at 205°C. The first exothermic effect in this case appear at 300°C and can be explained with the presence of phosphorus since this was the sole difference between the compositions of the polyurethane elastomers I and II. This change in the course of the DTA curves of the modified samples was retained with increasing phosphorus content (curves 3, 4, and 5).

A difference in the intensities of the exo- and endothermic effects was also observed on comparing the DTA curves obtained with modified polyurethane elastomer II and unmodified elastomer I. The modified elastomer samples showed exothermic effect, which were reduced in intensity. These can be explained by the action of the antipyrens, which absorb heat as a result of the endothermic reduction of phosphoric acid and also hinder the oxidation of carbon thus directing the oxidation towards the formation of mono-oxides.
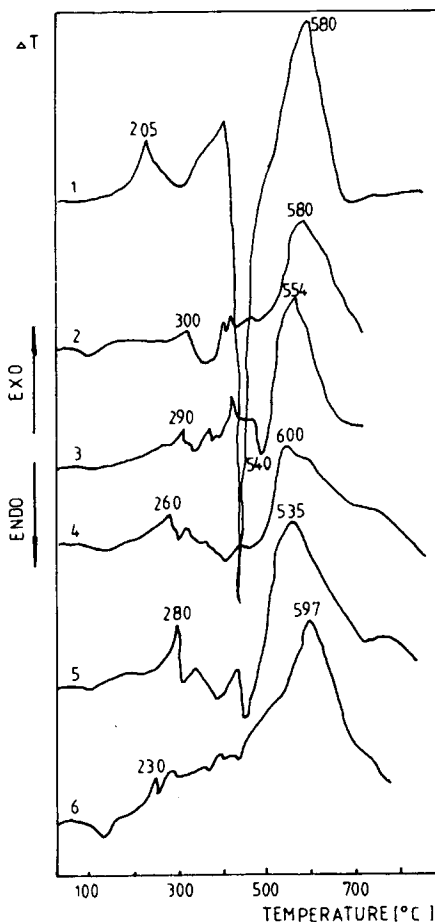
Fig. 1. DTA curves of modified polyurethane elastomers: (1) pure polyurethane elastomer; (2) 0.8% P; (3) 1.4% P; (4) 2.8% P; (5) 3.8% P; (6) 5.2% P.

An extremely pronounced endothermic effect accompanied by a significant loss in mass (70%) was observed for the unmodified polyurethane elastomer (Fig. 1, curve 1) in the region were the maximum degradation rate occured at 400°C, as observed on the DTA and DTG curves. It was found that this effect was caused by removal of heat with the products of degradation and that its intensity depended on the rate of degradation and on the speed at which gaseous products left the system. The higher the rate of degradation and diffusion the greater the endothermic effect. The modified polyurethane elastomers (Fig. 1, curves 2, 3, 4, and 5) exhibit a much reduced endothermic effect. This reduction is due to the presence of the phosphorus-containing antipyren which broadens the temperature interval in which the destructive processes take place and reduces the rate of degradation, as well as the quantity of the gaseous products evolved at a given temperature.

The DTG curves (Fig. 2) provide a means for evaluating the rate of decomposition. Comparison of the intensities of the minima at maxima rates of decomposition for the modified II and unmodified I polyurethane elastomers leads
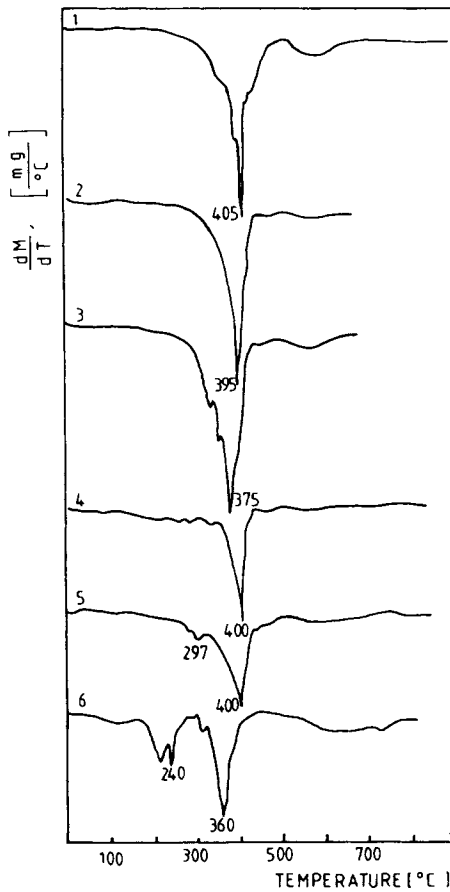
Fig. 2. DTG curves of modified polyurethane elastomers: (1) pure polyurethane elastomer; (2) 0.8% P; (3) 1.4% P; (4) 2.8% P; (5) 3.8% P; (6) 5.2% P.

one to the conclusion that the presence of phosphorus in the macromolecule of the polyurethane elastomer II reduces the rate of decomposition.

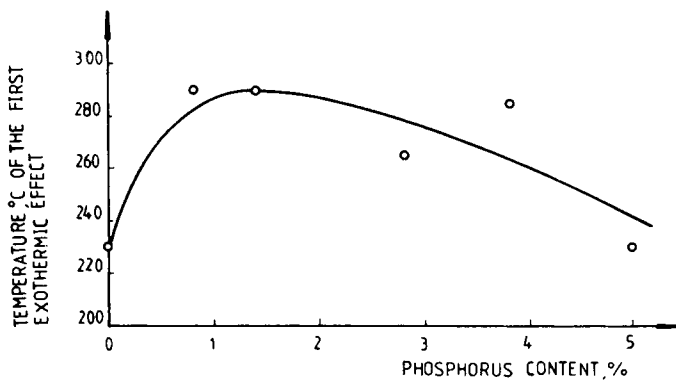The results show that the phosphorus-containing antipyren acts by shifting



Fig. 3. Relationship between the temperature of the first exothermic effect and phosphorus content ($V_h$ = 20°/min).

TABLE I

Values Obtained for Temperature of First Exothermic Effect ($T$), Solid Residue (R), and Oxygen Index (OI) by Rates of Heating ($V_h$) —6°, 9°, and 20°/min

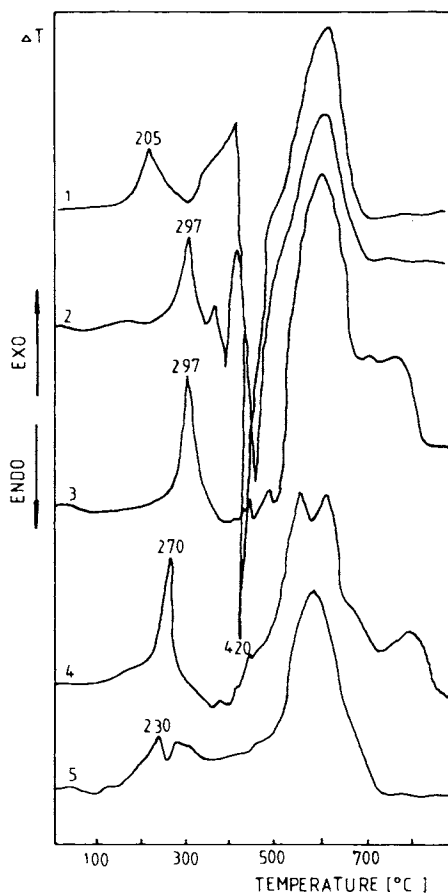| $P$ (%) $V_h$ | $T$ (°C) | | | $R^a$ (%) | | | OI calcd by (3) (%$O_2$) | | | Exptl OI (%$O_2$) |
|---|---|---|---|---|---|---|---|---|---|---|
| | 6 | 9 | 20 | 6 | 9 | 20 | 6 | 9 | 20 | |
| 0 | 205 | 205 | 230 | 0.5 | 0.5 | 1.0 | 17.7 | 17.7 | 17.9 | 19.0 |
| 0.8 | 275 | 300 | 290 | 0.0 | 0.0 | 0.5 | 17.5 | 17.5 | 17.7 | 21.5 |
| 1.4 | 280 | 290 | 290 | 0.0 | 0.0 | 1.0 | 17.5 | 17.5 | 17.9 | 21.4 |
| 2.8 | 240 | 260 | 265 | 2.5 | 2.5 | 1.0 | 18.5 | 18.5 | 17.9 | 16.8 |
| 3.8 | 265 | 280 | 285 | 2.0 | 2.0 | 1.5 | 18.3 | 18.3 | 18.1 | 16.4 |

$^a$ The heating is done in air at 800°C.

Fig. 4. DTA curves of modified polyurethane elastomers: (1) pure polyurethane elastomer; (2) 1.35% P and 1.42% Cl; (3) 2.20% P and 2.34% Cl; (4) 3.40% P and 4.04% Cl; (5) 4.80% P and 5.51% Cl.

the exothermic effect, in decreasing the intensities of the exothermic effects and in reducing the decomposition rates.

Investigation of the relationship between the degree of movement of the first exothermic effect and the amount of phosphorus present in the sample permitted the optimum concentration of the antipyren to be determined for its maximum efficiency (Fig. 3). This was corroborated by examining the relationship between the phosphorus content, oxygen index, and extent of shifting the first exothermic effect (Table I).

It can be seen that the greatest shift of the first exothermic effect parallels the oxygen index value. It should be also noted that phosphorus concentrations above 1.4% result in a decrease in both the oxygen index and the extent of the shift. This is probably due to the considerable changes in the structure of the polyurethane elastomer which occur at higher contents of the antipyren. This premice is also corroborated by the DTG curve for the polyurethane III (Fig. 2, curve 6).

Van Krevelen[3] has shown that there is a relationship between the oxygen index and the amount of the carbonized residue; this relationship can be described by

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| Content of | | $T$ (°C) of the first exothermic effect | Solid residue (%) | OI calcd by (3) (%$O_2$) | Exptl OI (%$O_2$) |
| --- | --- | --- | --- | --- | --- |
| P(%) | Cl(%) | | | | |
| 0.00 | 0.00 | 205 | 0.5 | 17.7 | 19.0 |
| 1.35 | 1.42 | 297 | 0.0 | 17.5 | 19.8 |
| 2.20 | 2.34 | 297 | 0.0 | 17.5 | 19.6 |
| 3.40 | 4.04 | 260 | 1.0 | 17.9 | 16.6 |

the following empirical formula:

$$OI \times 100 = 17.5 + 0.4\,CR^+ + \text{solid residue} \quad (\%)$$

The oxygen indices calculated on the basis of the solid residue were found to be considerably lower than the experimental values. Moreover, no relationship was found between the calculated oxygen indices and the extent of the shift of the first exothermic effect. These data therefore indicate that the application
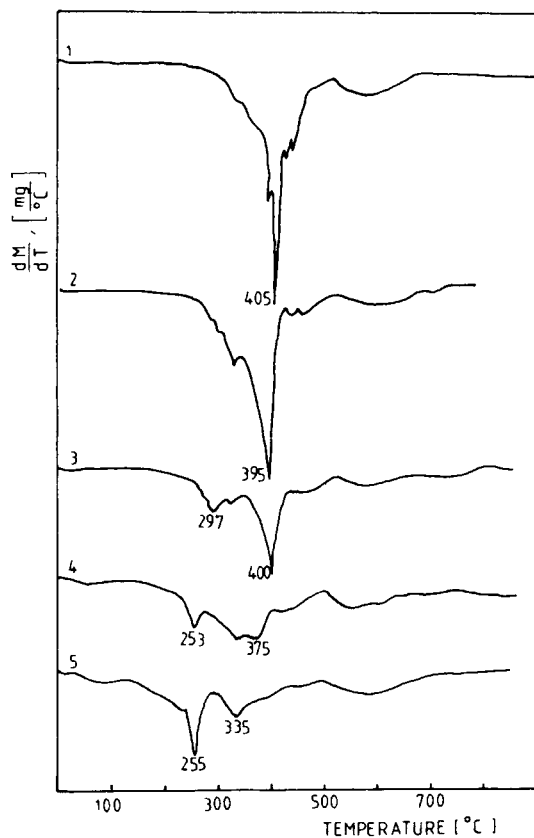


Fig. 5. DTG curves of modified polyurethane elastomers; (1) pure polyurethane elastomer; (2) 1.35% P and 1.42% Cl; (3) 2.20% P and 2.34% Cl; (4) 3.40% P and 4.04% Cl; (5) 4.80% P and 5.51% Cl.

of empirical formula for calculating the oxygen index is not suitable in this case. It is possible due to a difference in the experimental conditions.

Two theories have been proposed to explain the action of halogen-containing antipyrens. According to one, they dilute the volatile substances evolved during combustion[7,8] with noncombustible hydrogen halides and, according to the other, they inhibit the radical reactions.[15]

The thermal investigation of the polyurethane elastomer IV containing phosphorus and chlorine showed that the first exothermic effect (Fig. 4, curve 2) appeared at 297°C. A comparison of the DTA curves for the modified elastomer IV with that for the unmodified one revealed that, in addition to the shift towards higher temperatures of the first exothermic affect, a significant decrease in the intensity of the endothermic effect in the region of maximum destruction rates was also indicated. The differences were also observed with the samples containing higher amounts of phosphorus and chlorine (curves 3 and 4). The increase of antipyren content (curve 4) shifts the first exothermic peak towards lower temperatures—270°C. Similar behavior was also observed with the antipyren containing only phosphorus. We assumed that this was due to significant changes in the structure at high antipyren concentrations. This was corroborated by the course of the DTA curve for polyurethane V (curve 5) i.e., the exothermic effect which was observed at 230°C.

In this case also, a very good relationship was observed between the experimental values for the oxygen index and the temperature of the first exothermic effect (Table II). The optimum antipyren concentration, i.e., that at which the delay is most pronounced, can be determined from the temperatures at which the first exothermic effect appear.

Data on the antipyren efficiency can be deduced from the DTG curve (Fig. 5). It can be established by comparing the minima of the DTG curves at maximum decomposition rates for unmodified elastomer I and the modified ones IV that in the presence of antipyren the intensity significantly decreases.

The data show that there is a relationship between the thermal properties of the polyurethane elastomer and the efficiency of antipyrens containing phosphorus or phosphorus and chlorine, thus allowing the optimum antipyren concentration to be determined.

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