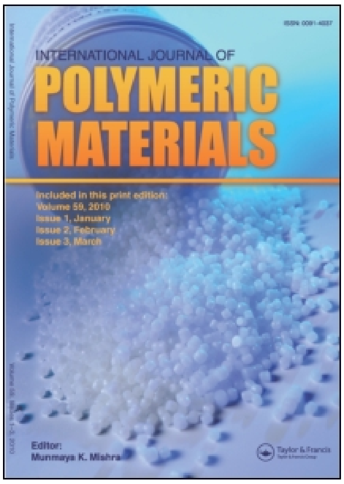

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Influence of Phosphorous-containing Antipyrenes on Thermolysis and Combustion of Epoxy Compounds

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The influence of the composition, mass correlation of its components and their chemical nature on thermolysis and combustion of the polymeric materials such as epoxy resins with phosphorous-contained fire retardant additions is studied. The investigations are carried out by thermal gravimetric analyses and high temperature pyrolysis which allow us to estimate the macro-kinetic characteristics of the processes at different heating rates.

Keywords: Epoxy compounds; combustion; antipyrenes; phosphorous

INTRODUCTION

An epoxy matrix hardened by low molecular polyamid with the trade mark PO-300, is characterized by high flammability. During combustion, a strong melt dropping is observed and mass loss amounts to about 76%. Besides, the oligomers which contain 35 and 45 m. u. of PO-300 (in comparison with pure epoxy oligomer), have large viscosity. This renders the filling of spaces and cavities difficult. Therefore, for decreasing of flammability of the material and improvement of its technological properties, the fire retardant addition (FR) containing dibutyl-phosphate, polybutyl-methacrylate and organic dye-stuff, is

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*Corresponding author.

used. Preliminary experimental data allow us to conclude that this FR is the most effective for decreasing the flammability of epoxy polymers.

An important stage of the combustion process is thermal and thermo-oxidizing destructive conversion of the polymer material in condensed phase, because basically these processes determine total quantity of volatile products which come into the gas phase and become a ⟨⟨fuel⟩⟩ for a combustion process. In addition, these combustion products affect the intensity of smoke- and soot-formation.

Thus, the influence of polymer composition, mass correlation of its components and their chemical nature on processes taking place in thermolysis and combustion of the polymer materials, is studied. The investigations are carried out by the method of thermal gravimetric analyses and high temperature pyrolysis, which allow us to estimate the macro-kinetic characteristics of the processes at different heating rates. The flammability and combustion of polymeric materials has been the subject of numerous studies [1–5].

RESULTS AND DISCUSSION

The method of thermal gravimetric analyses (TGA) gives a possibility to estimate thermal destruction of the polymer at low heating rates. According to TGA data, obtained with the derivatograph (system of Paulic-Paulic-Erday) with the rate 10°C/min, initial temperature of thermal degradation of an epoxy composition is between 200–210°C depending on the quantity of hardener (see Tab. I). An addition of FR changes the material structure and behavior under action of high temperature.

Independently on hardener quantity, compounds containing 10, 20 and 30% of FR, are more thermo-stable, since their initial destruction temperature (see Tab. I) is 20° higher than the temperatures of destruction for non-modified compositions. It is important, that they have low mass loss rates under thermal degradation (Fig. 1, Fig. 2). This allows us to assume that there is an interaction between a fraction of FR and the epoxy polymer. With increasing of the fire retardant content (phosphorous), the thermal stability decreases and mass thermal degradation rates increase, that may be related to surplus of FR in the composition.

TABLE I Data of TGA and combustion of epoxy resin

	TGA			
Composition, mass fraction/100 m.f. of ER	*Initial temperature of destruction, °C*	*Yield of coke residue at* $T = 500°C$, *%*	*Mass losses during combustion in air, %*	*OI, %(vol)*
PO-25	200	37	76	20
PO-35	210	39.5	74.2	20
PO-45	210	39.5	72.8	19.5
PO-35 FR-10	235	46	42.4	22
PO-35 FR-20	225	45.5	24.7	24.5
PO-35 FR-30	210	44.5	0.3	28
PO-45 FR-10	230	46	70	21
PO-45 FR-20	210	42.5	27.6	23.5
PO-45 FR-30	210	43.5	4.4	26.5

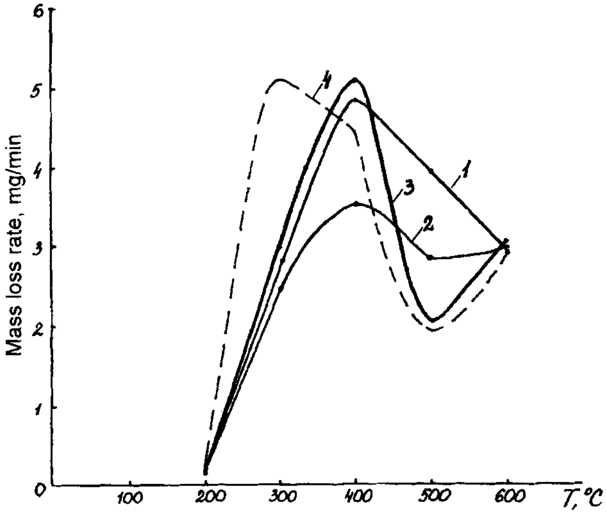

FIGURE 1 Dependences of mass loss rate on temperature: 1 – ER + PO(35%), 2 – ER +PO(35%) + FR(10%), 3 – ER + PO(35%) + FR(20%), 4 – ER + PO(35%) + FR(30%).

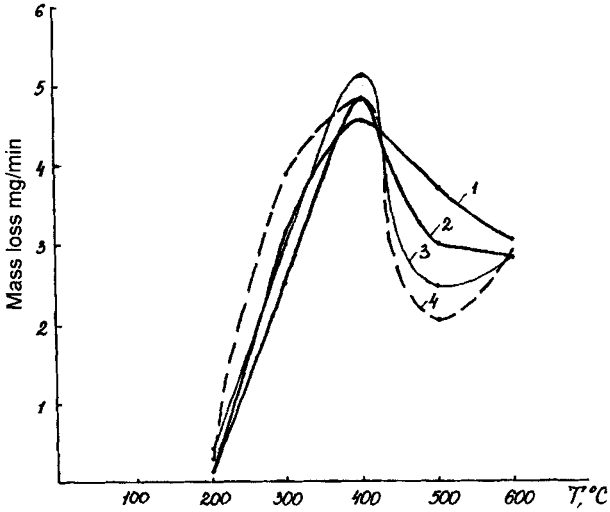

FIGURE 2 Dependences of mass loss rate on temperature: 1 – ER + PO(45%), 2 – ER + PO(45%) + FR(10%), 3 – ER + PO(45%) + FR(20%), 4 – ER + PO(45%) + FR(30%).

Yield of carbonized residue for phosphorous-containing compounds is significantly larger, than that for compositions without antipyrene. Therefore, the former compounds have higher fire retardancy.

Under a combustion, heating rate of polymer surface can exceed 300°C/min, so that to describe the polymer thermal degradation processes taking place in the combustion, it is not enough to have data obtained during degradation of polymer materials under low heating rates (*i.e.*, TGA data). Thus, we use the method of high temperature pyrolysis. The device for study of high temperature pyrolysis allows us to carry out the process with small quantity of polymers ($2-5*10^{-3}$ g) at high power of heat flow, synchronously registering both variation of polymer mass in time and the temperature of the polymer surface at the temperature of experiment 700°C. The data of the tests are processed by a special computer program and represented in Figures 3 – 5.

The plots of the mass and temperature variations (curves 1 and 1′) of an epoxy resin sample, hardened by 35 m. u. PO-300, are represented in Figure 3. There we see that the polymer composition degradation occurs in a few stages. The first stage of heating up to temperature 390°C corresponds to polymer heating until destruction temperature T_{destr}. The small peak of the temperature plot corresponds to beginning of the destruction. The second heating interval is related to particular polymer destruction and cross-linked structure formation. The inflection of the temperature plot (at 500°C) is connected with the end of formation of volatile products and coke residue. The plateau of the

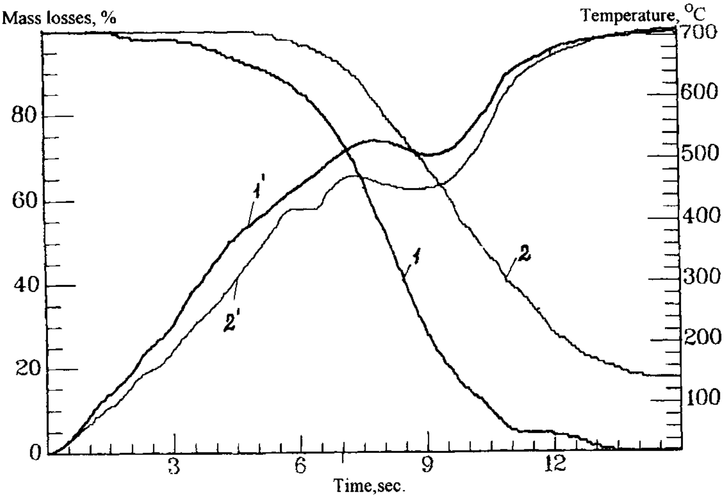

FIGURE 3 High temperature pyrolysis: 1 – ER + 35%PO(Δ*m*, %), 1′ – ER + 35% PO(*T*, °C), 2 – ER + 35%PO + 30%FR(Δ*m*, %), 2′ – ER + 35%PO + 30%FR(*T*, °C).

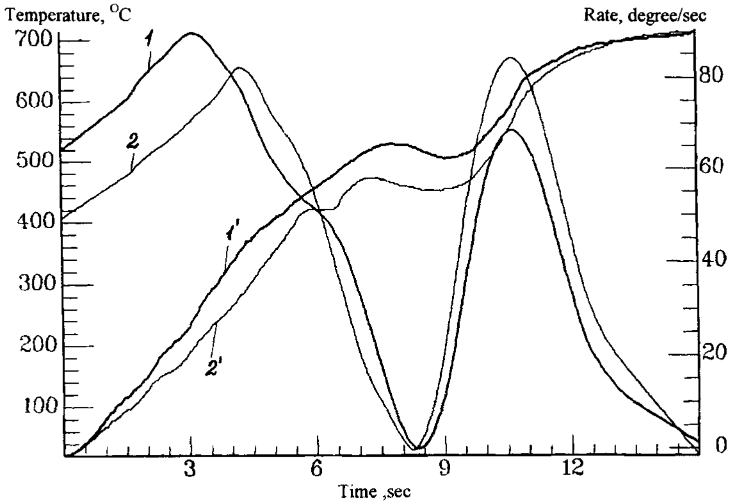

FIGURE 4 High temperature pyrolysis: 1 – ER + 35%PO(ν, °C), 1′ – ER + 35% PO(T, °C), 2 – ER + 35%PO + 30%FR(ν, °C), 2′ – ER + 35%PO + 30%FT(T, °C).

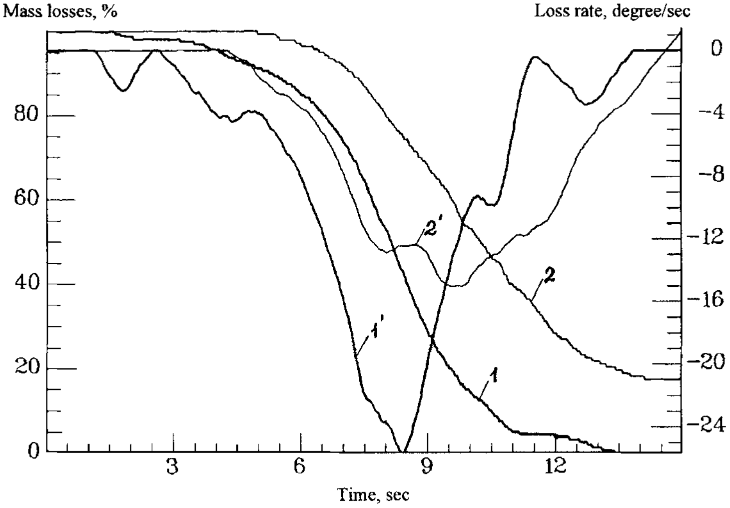

FIGURE 5 High temperature pyrolysis: 1 – ER + 35%PO(Δm, %), 1′ – ER + 35% PO(ν, °C), 2 – ER + 35%PO + 30%FR(Δm, %), 2′ – ER + 35%PO + 30%FR(ν, °C).

temperature curve showes that in this time interval the energetics of destruction reactions (endothermal) coincide with the reaction of carbonization (exothermal reaction). Further temperature increasing corresponds to oxidizing of formed coke. The very plateau describes total polymer degradation.

Influence of antipyrene on degradation of the epoxy composition under the condition of high temperature pyrolysis is studied. Plots of mass and temperature variations of a sample of epoxy resin, hardened by PO-300, contained FR (curves 2 and 2′) are represented in Figure 3. Obviously, FR exerts significant influence on high temperature pyrolysis of epoxy compositions. The inflection of the temperature plot at the beginning of destruction indicates the earlier formation of cross-linked structures of epoxy compound in the presence of antipyrene.

A comparison of the plots 1 and 2 shows, that in the presence of antipyrene the compound degradation occurs with larger amount of coke. On the basis of the obtained data (Figs. 3, 4, 5) we found the dependence of mass loss of sample (%) on time (sec.) under the experiment temperature 700°C (Fig. 6), the dependence of variation of polymer surface temperature (°C) on time (sec.) under experiment temperature 700°C (Fig. 7) and the dependence of polymer mass loss rate (%/sec.) on polymer temperature (Fig. 8).

Figures 6, 7 and 8 show, that during the same period a compound containing antipyrene FR has smaller mass losses (Fig. 6, curve 2) and lower temperature of surface (Fig. 7, curve 2) in comparison with

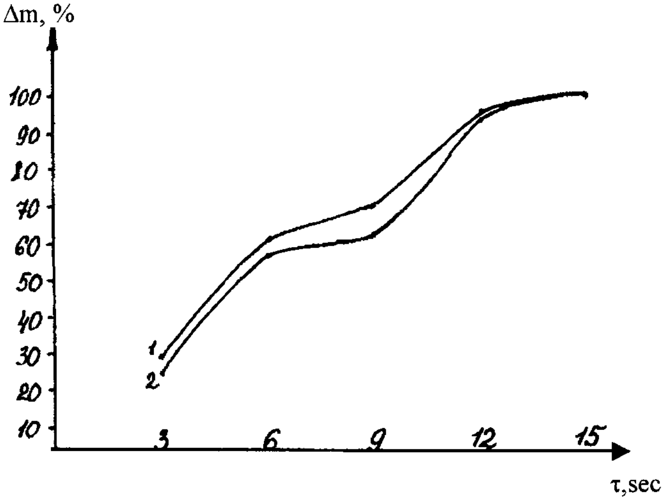

FIGURE 6 Dependence of mass loss (%) on time (sec.): Experiment temperature = 700°C. Curve 1 (no FR), curve 2 (with FR).

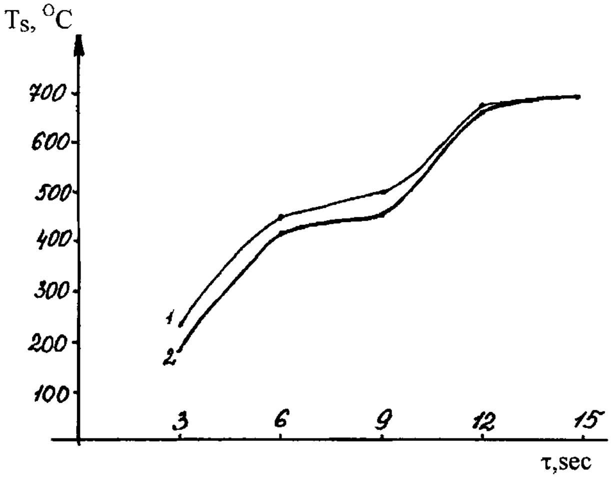

FIGURE 7 Dependence of polymer surface temperature (τ) on time (sec.): Experiment temperature = 700°C. Curve 1 (no FR), curve 2 (with FR).

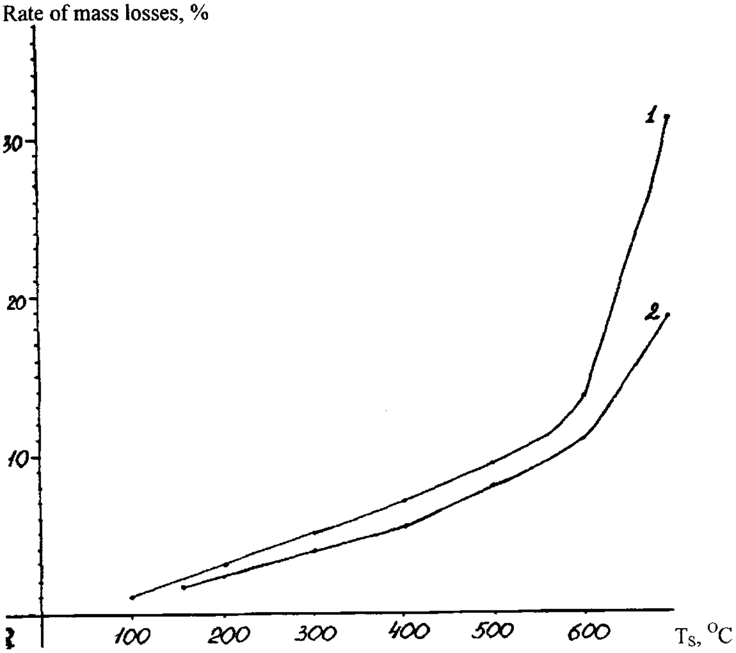

FIGURE 8 Dependence of mass loss rate (%/sec.) on polymer temperature: 1 – ER + PO – 35 m.f., 2 – ER + PO – 35 m.f. + FR – 35 m.f.

compound without antipyrene. Thus, we can conclude that the compound which has in its content a phosphorous-containing antipyrene, is more stable in combustion.

A comparative analysis of thermogravimetric and high temperature pyrolysis data has revealed considerable difference in mass losses and in mass loss rate under the same conditions (*i.e.*, temperatures on the polymer surface). However, in both types of experimental study we noticed an essential influence of the antipyrene FR.

In combustion of polymeric materials, there appears a carbonized layer on their surfaces, which reduces power of the heat flow directed onto degrading surface of the polymer material, changing heat exchange between the flame and the polymer and prevents yield of pyrolysis products into combustion zone. As a result, this decreases polymer flammability.

Epoxy materials are typical carbonizing polymers. To decrease their flammability it is important to study thermo-protection properties of cokes and influence on them of FR phosphorous-containing additions. Thermo-protection properties of cokes are investigated by laser techniques. CO_2-laser with wave length 10,6 nm, beam diameter 12 mm and radiation power 10 Wt/sm_2 has been used.

Figure 9 shows the plot of variation of the temperature on the back side of a sample with time for epoxy resin, hardened by 35 m. u. of lowmolecular polyamid PO-300 and containing 10, 20 and 30 m. u. of FR.

Comparison of the plots reveals the significant difference in thermoprotection properties (TPP) of cokes in the moment of formation. The plots have complicated shapes, each fragment of the curves corresponding to definite state of the system. Sharp increasing of temperature at the initial moment corresponds heating of the composition before a coke layer is formed. Following this moment inflection of the curve is related to the beginning of formation and growing of the coke on the polymer surface. Slow temperature increase up to the stationary value at the end of the plots 1 – 4 indicates that the coke formation process has finished by this time and the whole sample has turned into a coke. The shape of the curve 1 for epoxy resin composition, hardened by 35 m. u. of PO-300 without FR, shows that the coke formation goes very slowly, and the very coke forming during the reaction has low TPP (117°C in 150 sec.).

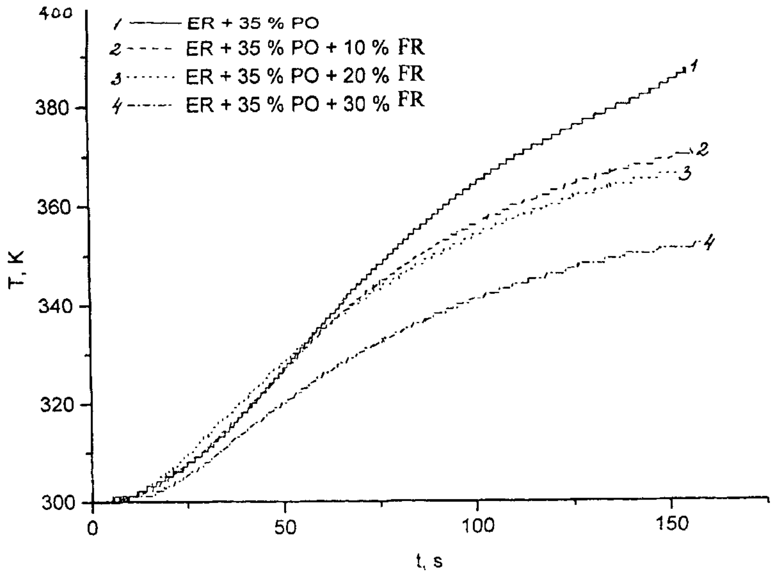

FIGURE 9 Variation of back side sample temperature with time.

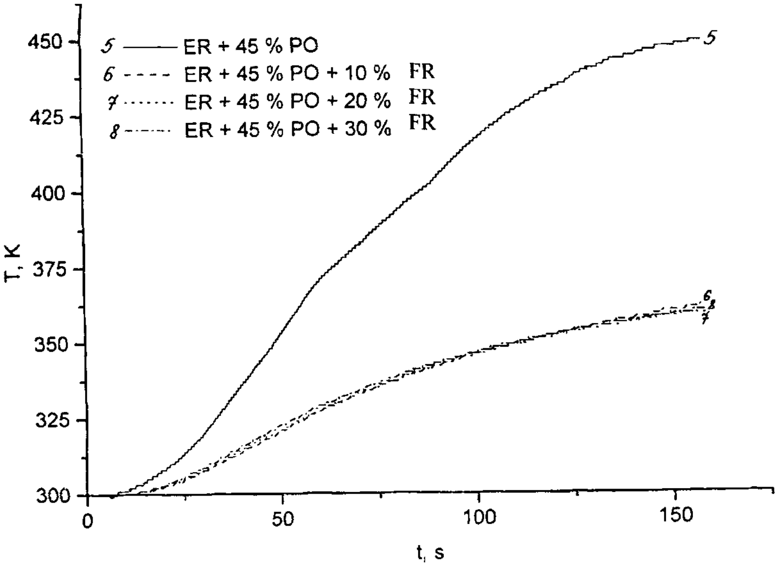

FIGURE 10 Variations of back side sample temperature on time.

For the epoxy resin based composition, hardened by 35 m. u. of PO-300 and containing 10, 20, 30 m. u. of FR (plots 2, 3, 4, respectively), it is typical to find higher rates of formation and growing of coke in comparison with the composition without FR (Fig. 9, plot 1). TPP of the produced cokes is essentially higher and the effect of the influence grows with increasing of FR content.

The established influence of FR on the processes of high and low temperature pyrolysis is confirmed by indicators of the material flammability (see Tab. I).

With increasing of FR content from 10 m. u. to 30 m. u., mass losses in air combustion decrease from 42% down to 0.3% (for compositions hardened by 35 m. u. of PO-300) and from 70% down to 4,4% (for composition hardened by 45 m. u. of PO-300) (see Fig. 10).

References

[1] Kodolov, V. I., Knyazeva, L. F. *et al.* (1985). *Plastic Masses*, No. 11, pp. 56–57 (in Russian).

[2] Khramaya, G. S., Sadakova, G. P. *et al.* (1984). *Plastic Massess*, No. 4, pp. 58–59 (in Russian).

[3] Kodolov, V. I., Povstugar, V. I. *et al.* (1979). *Journal of Physical Chemistry*, **53**(4), 944–947 (in Russian).

[4] Ota, E. and Otani, S. (1975). *Chem. Letters*, No. 3, pp. 241–242.

[5] Kovacic, P. and Kyriakis, A. (1962). *Tetrahedron Letters*, p. 467.