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**THE STUDY OF THE INFLUENCE OF NITROGEN-
AND PHOSPHORUS-CONTAINING FLAME RETARDANT
ON THE THERMAL-OXIDATIVE DEGRADATION AND COMBUSTION
OF GLASS FIBER REINFORCED POLYAMIDE-6**

Mechanism of flame-retardant action of the mixture of triazine compound and red phosphorus in glass fiber reinforced polyamide-6 has been studied. Derived infrared spectra of char indicate of the interaction between red phosphorus and polyamide-6, that results in polymer surface carbonization. Compact carbonized layer protects virgin polymer layers from fuels and also acts as thermal barrier. Triazine compound leads to dilution of the fuels in combustion zone.

Introduction. Polymer combustion is a complex physico-chemical process including chemical reactions of disintegration, cross-linking and carbonization of polymer in condensed phase as well as chemical reactions of conversion of gas products. True information of characteristics of high-temperature expansion of condensed substances can be achieved by method of linear pyrolysis which involves one-dimensional spread of reaction front of thermal destruction of substance under external heat source. According to work [1] kinetic parameters, received by thermal analysis of polymer degradation with lower temperatures and by linear pyrolysis agree well. Thermal gravimetric analysis of polymer compound can outline a concept of mode of action of particular flame retarder and add the results of standard experimental methodologies of combustibility evaluation.

Currently used flame retarders are introduced by a wide class of different chemical mixtures acting in gas or condensed phase. As the volume of use of halogenous flame retarders is substantially limited by a range of European directives, one of currently important recent trends in creation of flame-resistant polymeric compounds is development of non-halogenic materials.

Previously information on study of thermal breakdown and combustion of flame-resistant systems on the base of polyamide-6 (PA-6) and addition of melamine salts was reported [2]. Melamine sublimes endoenergetically which leads to weakening of combustion gases in the combustion zone. In condensed phase melamine is exposed to endoenergetic self-condensation with the release of ammonia and formation of heat-stable remanence (8 wt %) at 450°C. As can be seen from the above by appending 15 wt % of melamine to PA-6 the highest category of combustion resistance V-0 according to UL 94 standard is achieved. However, in glass fiber reinforced PA-6 application of triazine flame retarder allows to achieve only V-2 category of combustion resistance [3].

One of effective flame retarders for PA-6 including glass fiber reinforced PA-6 is red phospho-

rus. The research of composites of PA-6 with red phosphorus [4] to determine oxygen index and nitrogen oxide index, which in this case have parallel alteration tendencies, show that there is a mode of action in condensed phase. Red phosphorus upon the application of heat in inert atmosphere interreacts with polyamide with formation of phosphorus ethers, which catalyzes dehydration processes of pyrolyzed polymer substrate and makes it carbonize.

In the work [5] it is reported of combined mode of action of nitrogen-phosphorus-containing organic flame retarder in glass fiber reinforced PA-6. The flame retarder acts in gas as well as in condensed phases, which allows receiving material with V-0 UL 94 category of combustion resistance.

Main part. The aim of this work is research of influence of chosen flame retarder on the process of thermal oxidative breakdown of PA-6, and also of its flame resistant mode of action. The analyzed polymer compounds were received on the base of PA-6, produced by engineering and manufacturing complex "Khimvolokno" of JSC "Grodno Azot" according to technical specifications of the Republic of Belarus 500048054.009-2001. Reinforcing component is E-type fiberglass with filament diameter of 13 μm and linear density 2400 tex. Sample No. 1 is glass fiber reinforced PA-6 without flame retarder. In samples No. 2–5 additive "AP6-1" is used as fire retardant, which is a mixture of 1,3,5-triazine-2,4,6-triamine (melamine) and red phosphorus. Table 1 illustrates mass composition of the analyzed polymer compounds.

Table 1

Composition (wt %)

Sample number	PA-6	Glass fiber	"AP6-1"	Carbon black
1	69.5	30.0	–	0.5
2	55.5	30.0	14.0	0.5
3	52.5	30.0	17.0	0.5
4	49.5	30.0	20.0	0.5
5	46.5	30.0	23.0	0.5

Samples of polymer compounds were received by extrusion compression molding in a double-screw extruder with uniaxial intermeshed screws ($L/D = 50$), screw diameter 52 mm, screw rotation rate $7,25 \text{ s}^{-1}$, temperature in extrusion device zones: 215; 245; 250; 250; 240; 250; 240; 240; 255; 265; 270°C.

Resistance to ignition sources was estimated under combustion resistance descriptor according to GOST 28157-89 (method B) on test slats with length of 125 mm and thickness of 4.0 and 1.6 mm.

The process of thermal breakdown was studied by thermal gravitational analysis on TGA/DSC1 device of Mettler Toledo Company under the following conditions: atmosphere – air, rate of heating $10^\circ\text{C}/\text{min}$, heating within 30–500°C. By infrared spectroscopy we researched composition of original sample No. 5 and fixed residue sampled composition at the stage of 50 and 75 wt % loss of the original sample during thermal analysis. The tests were made with Fourier transform infrared spectrometer Nexus by Thermo Nicolet within the rate of $400\text{--}4000 \text{ cm}^{-1}$.

The surface of the samples after tests for combustion resistance under GOST 28157-89 was researched by scanning electron microscope investigation by microscope JEOL JSM-5610 LV.

Without flame retarder in PA-6 reinforced with fiberglass pieces, intensive combustion and polymer dropping can be observed (Table 2). High combustibility of sample No. 1 is determined by the fact that fiberglass in polymer volume results in capillary feed of destroyed polymer to the combustion zone and in intensification of combustion. With input of antiretardant additive “AP6-1” the burning behavior changes: polymer extinguishes faster after removal of flame source; emerging on the surface carbonized layer prevents dropping.

Table 2

PA composition resistance to burning

Index	Sample number				
	1	2	3	4	5
Test of bars with a thickness of 4.0 mm					
Category	N. C.	N. C.	N. C.	ΠB-0	ΠB-0
$t_{tot}, \text{ s}$	569	367	128	5	5
n	5	1	0	0	0
Test of bars with a thickness of 1.6 mm					
Category	N. C.	N. C.	V-2	V-1	V-0
$t_{tot}, \text{ s}$	256	142	95	62	6
n	5	3	1	0	0

Note: t_{tot} stands for total time of burning of a series of five bars, n stands for the number of bars that set fire to the cotton indicator, N. C. does not correspond to resistance to burning.

At thermogram of samples No. 2–5 two stages of weight loss can be observed (Figure 1).

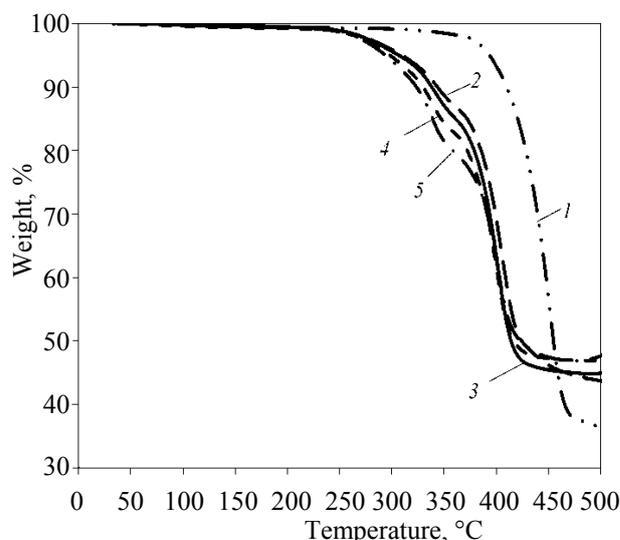


Fig. 1. Thermogravimetric curves:

1 – sample No. 1; 2 – sample No. 2; 3 – sample No. 3; 4 – sample No. 4; 5 – sample No. 5

In Figure 2 surface texture of samples No. 2–5 after exposure to flame is shown. At content of flame retarder of 20–23 wt % carbonized layer becomes more dense and effectively prevents diffusing combusting gases to unaffected polymer and also fulfills a role of temperature barrier. Samples No. 2 and 3 shows the worst barrier conditions for the reason of pore structure of carbonized layer.

Apparently in the samples with less content of flame retarder mechanism of melamine influence in gas phase by sublimation prevails, and red phosphorus is not enough to prevent dropping and to promote effective carbonization of the surface.

The original sample No. 5 showed characteristic melamine absorption bands $3469, 3418, 3130, 1437, 1020$ and 814 cm^{-1} (Figure 3). Apart from absorption bands 2933 and 2859 cm^{-1} , determined by C–H stretching vibrations in aliphatic compound of PA-6, the rest characteristic bands 3323 cm^{-1} (N–H stretching vibrations), 1651 cm^{-1} (amide I) and 1551 cm^{-1} (amide II) are overlaid with intense melamine absorption bands. Infra-red spectrums of fixed residues of sample No. 5 are similar to spectrum of net PA-6, which gives evidence of melamine sublimation. Part of melamine stays in fixed residue (absorption band 814 cm^{-1}), which is determined by presence of 1, 3, 5-triazine ring. Apparently, the rest melamine in polymer compound is exposed to self condensation reaction. In fixed residue nitrile end groups (2245 cm^{-1}) were found, which formed during dehydration of primary PA-6 amide groups.

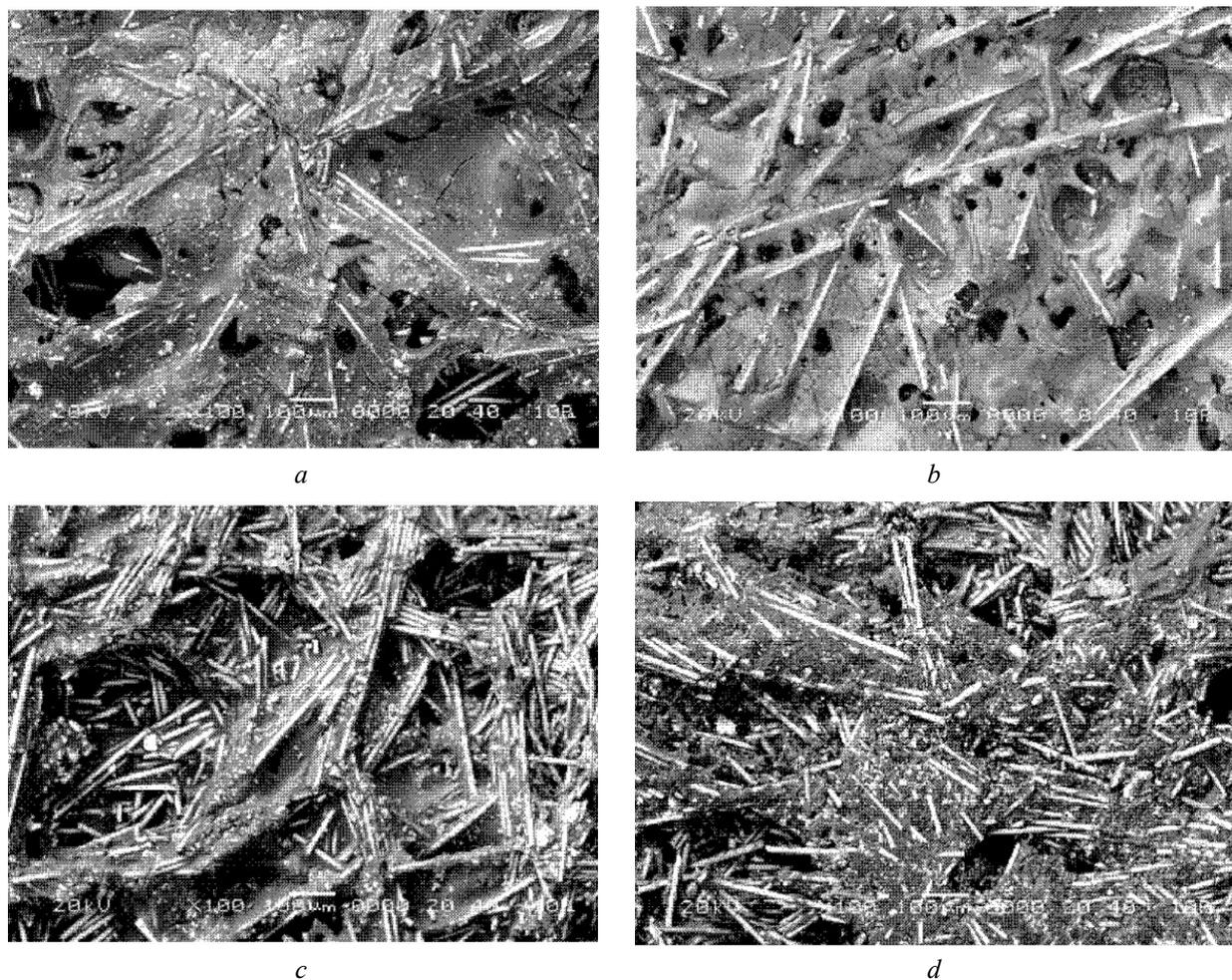


Fig. 2. The surface structure of the sample surface after exposure to flames:
a – sample No. 2; *b* – sample No. 3; *c* – sample No. 4; *d* – sample No. 5

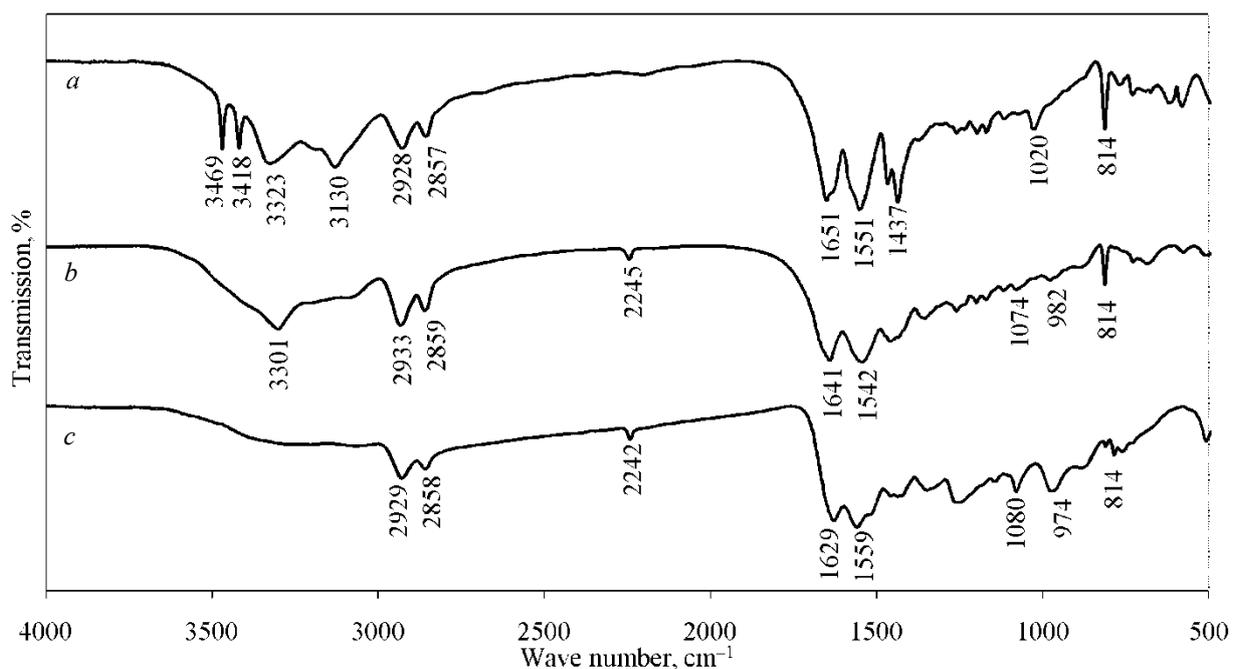


Fig. 3. IR spectra:
a – not-treated sample No. 5; *b* – 50% weight loss of the sample No. 5;
c – 75% of the mass loss of the sample No. 5

New absorption bands emerged, which are characteristic of phosphate esters: 982 cm^{-1} (P–O–C stretching vibration) and 1074 cm^{-1} (P–O–C stretching vibration). Apparently, residuals, which are formed during brake of red phosphorus polymer chains, react selectively with PA-6 oxygen atoms with formation of phosphate esters which leads to formation of carbonized noncombustible layer at the polymer surface.

Conclusion. Flame retarder “AP6-1” content of 20–23 wt % allows decreasing general combustion time to 5 s compared to net glass-filled PA-6, for which combustion during 569 s is characteristic. Formation of unflammable carbonized layer on the surface of combusting polymer prevents dropping. Sample No. 1 which is net glass-filled PA-6, all five slats set cotton tracer material on fire. There is no dropping in sample No. 5, which makes it non-combustible as during combustion no flinging of burning drops of polymer occurs.

During polymer heating in an air atmosphere below 500°C in the temperature interval from 240 to 380°C sublimation of melamine can be observed. Apparently, during combustion of polymer compound melamine sublimates and decreases combustible gases concentration.

The presence of absorbing bands 982 and 1074 cm^{-1} , characteristic for P–O and P–O–C chains confirms effect of red phosphorus in condensed phase by formation of phosphate esters and further carbonization of polymer surface.

So, the combined flame retarder “AP6-1” acts simultaneously in gas and condensed phases and is an effective flame-retardant system for glass-filled PA-6.

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