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**INVESTIGATION OF THE EFFECT OF COMBINED FLAME RETARDANTS
 “PHOSPHORUS + TRIAZINE” ON COMBUSTIBILITY
 AND OPERATIONAL PROPERTIES OF EXTRUSION-TYPE POLYAMIDES**

The article describes the effect of a synergetic mixture of triazine compounds and red phosphorus on combustibility, physical, mechanical and operational properties of polymeric compositions based on polyamide-6 modified by ethylene-1-octene copolymer. Optimum on structure and final properties this polyamide composition is offered to be used in the manufacture of corrugated tubes for electric harness.

Introduction. The widespread use of polymers in modern industry is due to their inherent complex of mechanical and operational properties: light weight, high specific strength, resistance to aggressive media, dielectric properties. The presence of these properties has lead to the use of polymers in many industries: construction, aviation, shipbuilding, electrical industry, mechanical engineering, railway transport and agriculture. However in some industries (engineering, construction and electrical branches, etc.) the use of polymers is limited because of their combustibility.

The creation of non-halogen-containing polymer compositions based on polyamide-6 and possessing flame retardant properties is one of the important trends in polymer industry.

The combustion of polymers is a complex set of multistage physical and chemical transformations occurring in the condensed and gaseous phases as well as on the surface their section. The general scheme of combustion [1] consists of two related chemical processes: the thermal decomposition of polymers and the combustion of destruction products.

In the atmosphere of dry inert gas the thermal destruction of aliphatic polyamides starts at temperatures above 300°C. The basic process is the terminal linkage depolymerization by reactions of intermolecular aminolysis and acidolysis with the elimination of cyclic monomers. At high temperatures the role of radical processes increases. Cross-linking reactions and cyclization reactions are possible but they don't lead to significant coking.

When aliphatic polyamides burn the intensive dropping occurs. When you enter the filler in aliphatic polyamides (e. g. fiberglass, mineral filler) the dropping at the burning processes of polymers decreases but the time of burning of the sample increases, resulting in the need to decrease the combustibility which may be greater than in the case of other materials [2].

One of the most common non-halogen-containing flame retardants for unreinforced ali-

phatic polyamides is triazine and its compounds (melamine, melamine cyanurate, dimelamine phosphate, melamine pyrophosphate). The action mechanism [3] of triazine compounds is complex and it includes the endothermic sublimation, the decrease of oxygen concentration in the combustion zone through the provision of non-flammable vapors, the endothermic condensation in the solid phase with the release of ammonia and the solid thermostable residue on the surface of the burning polymer.

The compounds of phosphorus are more effective flame retardants of aliphatic polyamides than the halogen-containing compounds.

During the combustion process in the polyamide-6 red phosphorus is oxidized to the acid which forms esters with polyamide. The coke crust (polyphosphoric acid) is formed on the surface of the burning polymers [4]. Using red phosphorus as a flame retardant when entering 7 wt % of it the category of resistance to combustion PV-0 is achieved.

A similar mechanism of coke formation is characteristic for ammonium polyphosphate. According to the results of the thermal analysis it is revealed that the exfoliated coke crust is formed during the combustion even when entering only 10 wt % of ammonium polyphosphate. Ammonium polyphosphate helps to extract caprolactam as the main gaseous product, however the coke residue is thermally stable up to 550°C. Thus, the composition of combustible volatile products released from PA-6 in the process of combustion changes at the expense of the presence of ammonium polyphosphate.

Main part. The aim of this work is to investigate the compositions based on polyamide-6 possessing flame retardant properties and intended for extrusion processing. The AP6-1 flame retardant additive which is a synergetic blend of 1,3,5-triazine-2,4,6-triamine and red phosphorus is used as a slow-burning agent. The structural formula of this triazine compound is presented in Fig. 1.

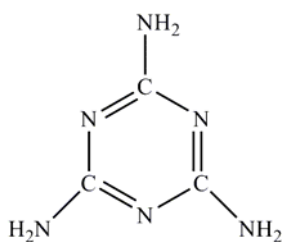


Fig. 1. Structural formula of a triazine compound

The samples of polymer compositions were prepared by the high-speed extrusion method on the twin-screw extrusion set with parallel meshing screws ($L / D = 50$), the screw diameter was 52 mm, screw speed was 450 min^{-1} , the temperature of extruder zones was $255\text{--}275^\circ\text{C}$.

Table 1 shows the mass blend composition:

Table 1
Mass blend composition, %

Component	Sample		
	N 1	N 2	N 3
Polyamide-6	66.5%	61.5%	56.5%
Flame retardant additive AP6-1	17%	17%	22%
Ethylene-1-octene copolymer	15%	20%	20%
30% concentrate of technical carbon pigment	1.5%	1.5%	1.5%

During the study the following properties of prepared compositions were investigated:

- category of resistance to burning (GOST 28157-89);
- melt flow rate (GOST 11645-73);
- Sharpy impact strength, at low temperatures including (GOST 4647-80);
- tensile strength and relative elongation at break (GOST 11262-80);
- tensile modulus of elasticity (GOST 9550-81);
- dielectric strength (GOST 6433.3-71).

These data will represent the behaviour of polymer compositions under the action of a small ignition source, the deformation and elasticity of the material as well as its operational properties:

- the ability to withstand the impact of loadings at -40 and -60°C (the frost resistance was determined on air-conditioned for 2 weeks test samples in the research laboratory);
- the dielectric strength of the material.

The values of Sharpy impact strength of polyamide-6 and extrusion compositions based on it are presented in Table 2.

Impact strength tests at room temperature ($+23^\circ\text{C}$) took place on “dry” (air-conditioned for 8 hours after injection molding) samples. The increase of the input of maleinized ethylene-1-octene copolymer increases the impact strength of compo-

sitions. For example, with the increase of the copolymer content from 15 wt % to 20 wt % (samples N 1 and 2) the impact strength on unnotched samples increases from 59 to 71 kJ/m^2 .

Table 2

Frost resistance of polymeric compositions

Impact strength, kJ/m^2 , on samples	PA-6	Sample		
		N 1	N 2	N 3
unnotched $+23^\circ\text{C}$	n.p.	59	71	40
unnotched -40°C	n.p.	83	95	55
unnotched -60°C	n.p.	73	93	53
notched $+23^\circ\text{C}$	13	12	12	9
notched -40°C	9	11	13	9

A higher content of flame retardant provides the best category of resistance to burning PV-0 but with the increase of the flame retardant content from 17 to 22 wt % (samples N 2 and 3) the polymer composition becomes fragile: the impact strength decreases from 71 to 40 kJ/m^2 .

Tests at low temperatures were carried out on samples air-conditioned for 2 weeks at the temperature of $+23^\circ\text{C}$ and humidity of 70%. During the actual operation the product made from a polymer composition absorbs some percent of moisture and becomes more malleable. It is confirmed by the values of the impact strength of air-conditioned for 2 weeks samples: the values even at low temperatures are higher than those of “dry” samples (Table 2).

During the frost resistance tests the same trend as that at room temperature is observed: the increase of the copolymer input increases the impact strength of compositions.

The anhydride groups of functionalized copolymer interact with terminal amino groups of polyamide-6 in the melt mixing process and the formed copolymer is presented in Fig. 2 [5].

A formed copolymer is at the interface between 2 polymers phases (polar and non-polar). Due to the physical and chemical interaction between the phases and the intermediate layer of polyamide-6 and ethylene-1-octene copolymer their compatibility increases considerably. It leads to a more uniform distribution of existing loads over the polymer volume.

The test results of obtained polymer compositions are given in Table 3.

From the analysis of obtained results the following is noteworthy:

1. The decrease of the impact strength of the material with the input of the same mass of flame retardant additive forestalls its increase with the input of the same amount of copolymer. The insufficient degree of powder dispersion, the agglomeration of small flame retardant particles negatively affect the elastic properties of the polyamide composition.

Table 3

Physical and mechanical properties and the category of resistance to burning of extrusion flame retardant compositions based on polyamide-6

Index	Polyamide-6		Sample N 1		Sample N 2		Sample N 3	
Category of resistance to burning	PV-2		PV-2		PV-2		PV-0	
The total burning time of five bars, s	82 s		90 s		71 s		14 s	
	1 appl.	2 appl.	1 appl.	2 appl.	1 appl.	2 appl.	1 appl.	2 appl.
– the burning time of the bar N 1, s	18-ig	0	0	2-ig	30-ig	1	0	6
– the burning time of the bar N 2, s	14-ig	0	25-ig	2	0	8	0	2
– the burning time of the bar N 3, s	13-ig	0	0	16-ig	0	12	0	2
– the burning time of the bar N 4, s	20-ig	0	0	23	0	10	0	3
– the burning time of the bar N 5, s	17-ig	0	20-ig	2	0	10	0	1
MFR, g/10 min								
275°C, 2.16 kg, 2.095 mm	21.6		26.2		14.9		25.1	
275°C, 5.00 kg, 2.095 mm	54.0		64.0		45.2		57.2	
Dielectric strength, kV/mm (plates 60×60×2 mm)	28.9		38.9		40.6		35.8	
Tensile strength, MPa	72		51		45		39	
Elongation at break, %	104		9		13		9	
Tensile Modulus, MPa	2,431		2,564		2,312		2,274	

Note. Appl. – the application of flame; ig – the sample ignited cotton.

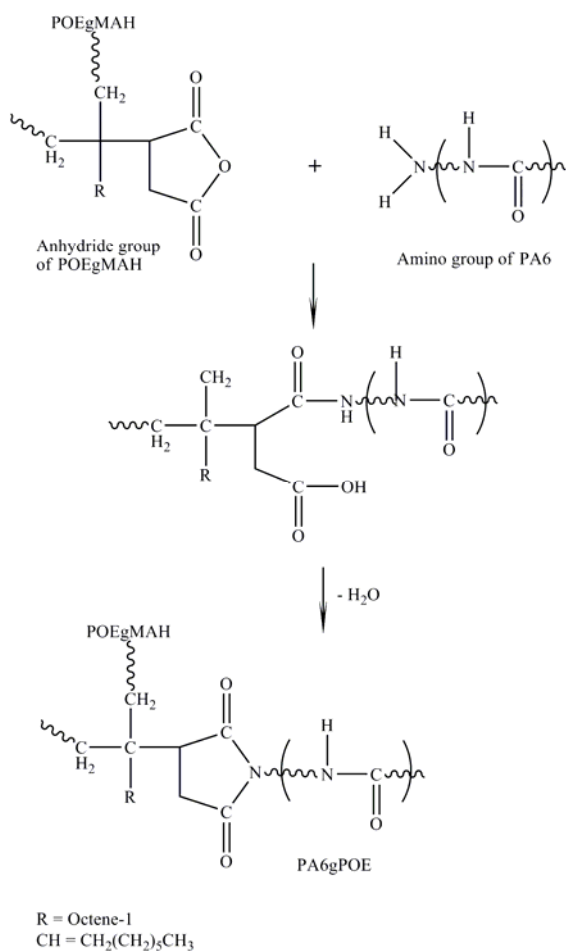


Fig. 2. Possible reaction of PA-6 and a copolymer

2. The mechanical strength of compositions based on polyamide-6 decreases with the input of both a flame retardant and a modifier elastomer,

the strength of which is about 7 MPa. The plasticity of polyamide-6, characterized by the elongation at break decreases with the input of flame retardant powder from 104 to 9%. This is explained by the fact that in the polymer matrix at compounding the agglomerates of flame retardant particles and microvoids are formed that facilitate the rapid development of microcracks under the influence of tensile loadings. The input of elastic copolymer, the elongation at break of which is more than 1000%, promotes a slight increase of the elongation of the composition. Probably the amount of copolymer in polyamide-6 in the presence of a flame retardant is not enough to change the mechanism of the formation of microcracks in the polyamide matrix.

3. The analysis of the MFR values allows to conclude that the input of amorphous ethylene-1-octene copolymer significantly decreases the flow rate of a final polyamide composition. When the copolymer content is in the amount of 20 wt % the composition which is suitable for extrusion processing into corrugated tubes can be obtained despite the effect of the flame retardant input. The increase of the flame retardant input of the AP6-1 additive with the same content of the polyolefin elastomers (from 17 wt % to 22 wt %) increases MFR of the composition in 1.5–2.0 times. This is caused by the chemical nature of triazine compositions which at temperatures of compounding (255–275°C) initiate the destruction reaction of polyamide-6 what decreases the thermal stability of the finished composition [3].

4. At the tests with sample N 2 four of five bars didn't ignite cotton and the total burning time of five bars was 71 seconds that is 11 seconds less

than in the case of original polyamide-6. In addition in the case of tests of polyamide-6 all five bars were burning and they ignited cotton at the first flame application. As you know because of the low melt viscosity polyamide-6 is characterized by dropping and decreasing of the category of resistance to burning. In the case of flame retardant compositions the mechanism of combustion changes: the samples ignite with the second flame application, the tendency to dropping decreases.

Conclusion. The input of AP6-1 flame retardant in the amount of 22 wt % ensures the highest category of resistance to burning PV-0 and the multifunctional AP6-1 additive ensures the increase of resistance to burning both in the polyamide and polyolefin phases. However the impact strength and MFR of sample N 3 don't meet the requirements: the material is too brittle and has the high flow rate (25.1 g/10 min) what is not suitable for extrusion processing.

The input of AP6-1 flame retardant additive in the amount of 17 wt % with the polyolefin elastomer content in the amount of 15 wt % and 20 wt % ensures the category of resistance to burning PV-2 which is sufficient to exploit corrugated tubes of this material for electrical harness.

The composite material developed and put out at the "Grodno Azot" Plant of PTC "Khimvo-

lokno" on sample N 2 under production conditions of UE "Vector" is remade into corrugated tubes for electrical harness. The tubes meet the requirements of consumers.

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