УДК 678.2:614.841.41

M. A. Kostsyuchenko, PhD student (BSTU);
M. M. Revyako, D. Sc. (Engineering), professor (BSTU)

DEVELOPMENT OF FLAME-RETARDED POLYAMIDE COMPOSITION WITH IMPROVED PROCESSABILITY

The article describes influence of reduction of complex flame-retardant (triazine and red phosphorus) and grafted olefin copolymer on performance characteristics of polymeric compositions based on polyamide-6, and also on their extrusion processability. Optimum on structure and final properties polyamide composition is offered for use in manufacture of corrugated tubes for electric harness.

Introduction. Engineering plastics and special-purpose compositions based on them are widely used among the polymers in modern industry due to their inherent complex mechanical and performance properties: lightness, high specific strength, resistance to aggressive environments, dielectric and other properties. For use in certain industries (engineering, construction and electrical industry, etc.), where the use of polymers is limited because of their flammability, developed a whole range of flame-retarded compositions.

For example, for the production of corrugated tubes with nominal diameter 7.5–17 mm UE "Vector" (Shchuchin) used flame-retarded polyamide compositions. Tubes are used for laying electrical harnesses in vehicles. During the extended production test previously developed and proven extrusion material [1] identified the need to improve processor manufacturability polyamide composition by reducing the amount deposited on the surface of the molding extrusion plant components of flame retardant. Tube made from an improved composition should have flame-retarded properties and flexibility.

Tendency to self-extinguishing after the removal of a small ignition source (match, cigarette butt, a lighter) depends on the nature of the flame propagation on the surface of the polymer. General scheme of the flame propagation is represented in Fig. 1 [2].

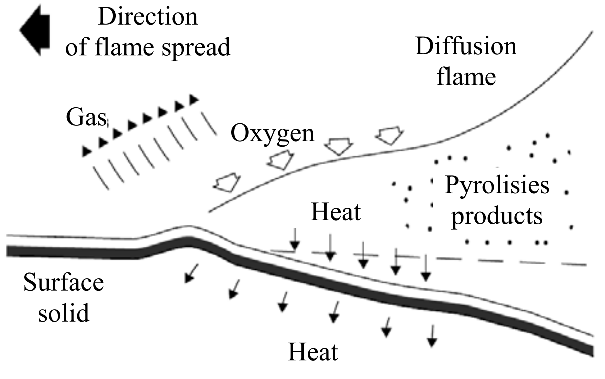

Fig. 1. Scheme of flame propagation

Diffusion flame moves across the surface of the polymer degrades. The surface temperature of the polymer (500°C) is lower than the diffusion flame, and the flame temperature at the boundary where reaction occurs with oxygen (1,200°C).

On the surface of the flame propagation also affects the heat released during thecombustion of the polymer. Increasing the amount of heat generated by combustion of a polymer leads to an increase in the amount of heat generated in the flame region, thus maintaining combustion cycle. Along with fast gas-phase reactions occur more slowly smoke, soot and coke.

The main polymer additives to reduce the flammability are halogen-, phosphorus-, nitrogen-containing flame retardants, as well as a number of inorganic salts, oxides and hydroxides. Their main feature is the inhibition efficiency of gas-phase or solid-phase combustion processes coke, leading to the formation of the protective char layer, which is an excellent thermal diffusion barrier.

One of the most common nonhalogen flame retardants for unreinforced aliphatic polyamides is melamine and its derivatives (melamine cyanurate, dimelamine phosphate, melamine pyrophosphate). Mechanism of action [3] melamine and its salts is complexan include comprising an endothermic sublimation, reduction of oxygen concentration in the combustion zone through the provision of combustible vapors, endothermic condensation in the solid phase with the liberation of ammonia and the thermally stable solid residue on the surface of a burning polymer.

Melamine and its salts induce gap H-CC(O) bonds in the polyamide-6, whereby the role of crosslinking the polymer and carbonization. Some part of the melamine remains a condensed phase, gradually turning in melem and melon derivatives by heating.

Pretty unusual mechanism gap CH_2-C(O) bonds in the macromolecule polyamide was proposed for compositions containing melamine [4] (Fig. 2). The resulting gap in the primary circuit isocyanurate terminal fragments may be subjected to the dimerization or trimerization of the carbodiimide formation, leading to N-alkilizotsianuratu. As a result of these processes increases the heat resistance of the secondary solid coke.

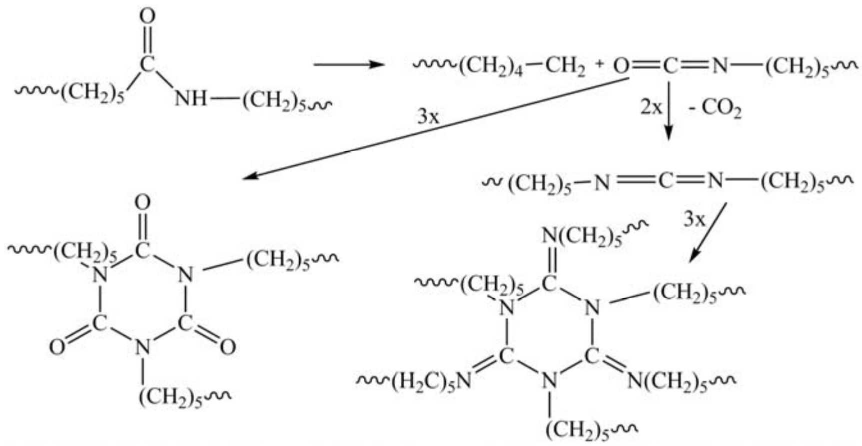

Fig. 2. Mechanism of thermal destruction of polyamide-6 and melamine composition

Phosphorus-containing compounds are known to be used as additives intumesented and red phosphorus, which is an effective fire retardant for polyamides. Red phosphorus by heating in an inert atmosphere, is reacted with the polyamide to form a phosphate ester. At the same time, found that during the thermal decomposition of the polyamide in the composition is formed with the red phosphor greater quantity of free radicals than pure polyamide. Furthermore, the lifetime of these radicals is considerably larger than in a pure PA-6, indicating their different reactivity and chemical nature. As a result, suggested two possible ways of interaction with the polyamide red phosphorus: radical mechanism of interaction according to which the radicals formed upon rupture of the polymer chains of red phosphorus react with amide groups of the polyamide to give phosphoric esters, and the second – by reaction with phosphorus adsorbed and released polyamide during thermolysis of water, giving phosphine and phosphorous acid, which in turn react with the polyamide.

Main part. The aim of this work is to improve the proccessability of previously proven UP "Vector" polyamide composition. Liberated as a white powder during processing component of the flame retardant is melamine solids. During thermogravimetric studies triazine compounds [3] found that weight loss (sublimation) melamine starts at temperatures 240–250°C. In the process of production of corrugated tubes used a single screw extruder without degassing zone with elongated mandrel unheated. Set temperature in the zones of the extruder: 220; 230; 240; 235°C. In addition, the polymer melt affects the shearing stress produced in the gap between the screw material and barrel, leading to local heating of the melt and filling. This causes sublimation of melamine and its subsequent deposition as white powder on the tooling extrusion plant (mandrel tracks).

A possible way to decrease the amount of powder emitted is the reduction of the content of the flame retardant and the elastifying modifier (maleated ethylene-1-octene) in the composition.

Additive "AP6-1" is used as a flame retardant, which is a mixture of 1,3,5-triazine-2,4,6-triamine (76 wt %) and red phosphorus (24 wt %).

Using a combination of flame retardants such as melamine and red phosphorus, allows modification of the mechanism of flame propagation (Fig. 1) due to:

–reducing the concentration of combustible gas in the combustion phase;

–formation of the thermal diffusion barrier on the surface of the burning polymer.

To produce the polymer compositions was used a polyamide-6 having the characteristics presented in Table 1.

Table 1

Characteristics of base PA-6

Property	Value
MFR (230°C; 2.16 kg load), g/10min	5.5
Charpy impact strength, kJ/m^2	no break
Tensile strength, MPa	79
Elongation at break, %	101

Samples of polymer compositions were prepared by high speed twin-screw extruder at an extrusion installation with unidirectional intermeshing screws (L / D = 50) screw diameter – 52 mm, a screw rotation speed – 400 min^{-1}, the temperature of the extruder zones – 255–275°C.

Table 2

Compositions (wt %)

Component	Previously proven composition	Sample	
		No. 1	No. 2
Polyamide-6	61.5	88.0	78.0
Flame-retardant "AP6-1"	20.0	2.0	10.0
Polyethylene-co-1-octene	17.0	8.0	10.0
Black masterbatch	1.5	2.0	2.0

Table 2 shows the composition by weight of the compositions. Flammability and performance of polyamide compositions were determined according to standard procedures:

– category of resistance to combustion;

– melt flow rate;

– Charpy impact strength, including at low temperatures;

– tensile strength and tensile modulus, elongation at break.

Determination of the melt flow rate (MFR) will determine the rheological properties of and compare processing ability of new compositions and previously proven (MFR = 14.9 g/10 min at 275°C and 2.16 kg).

Determination results of MFR extrusion compositions (samples number 1 and 2) and the base polyamide-6 are shown in Fig. 3.

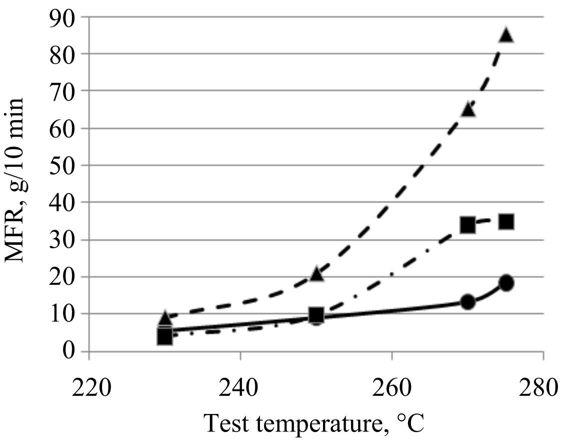

Fig. 3. MFR vs. test temperature:
● – PA-6; ▲ – sample No. 1; ■ – sample No. 2

Triazine compounds initiate degradation reaction of polyamide-6, resulting in a reduction of molecular weight and increase strength. Reduction of functionalized olefin copolymer and flame retardant on to a ratio of 1 to 4 does not allow to neutralize the negative impact of the flame retardant on the rheological properties of polyamide-6. Decreasing the amount of copolymer of from 10 to 2 wt % of the composition increases MFR 2.5. Based on these data it can be assumed that the sample No. 1 is not suitable for processing corrugated tube. Sample No. 2 characterized MFR less extreme dependence on temperature, the higher the thermal melt stability.

The results of the physical-mechanical tests of the obtained polyamide compositions are shown in Table 3.

Anhydride groups of the copolymer react with the functionalized amine-terminated polyamide-6 in the melt mixing and formed copolymer. Due to physical and chemical interaction with the phases of the intermediate layer of polyamide-6 and a copolymer of compatibility, and hence the elasticity of the entire composition is significantly increased. The content of the olefin copolymer in an amount of 10 wt% and a flame retardant in an amount of 10 wt% To reduce the negative impact on the agglomeration of particles retardant polyamide composition toughness.

Degree of stiffness of the sample No. 2 is comparable to the previously-tested recipe, which is confirmed by the values of toughness and modulus of elasticity of 66 and 71 kJ/m^2, and in 2,551 and 2,312 MPa, respectively. The total burning time was 158 s, which is two times higher than in the tests previously proven composition. Sample No. 2 has a category of resistance to burning PV-2, i.e. characterized by spontaneous decay after removal of the ignition source.

Conclusion. With a decrease in the amount of fuel than the polyamide-6, an olefin copolymer, it is possible to reduce the amount of flame retardant, and that leads to:

– to reduce the negative impact of melamine on the plasticity of the final polyamide composition (flexible tubes);

– to reduce the vapor emissions during processing melamine (processability of the composition).

Table 3

Physical-mechanical propertiesand flammability of polyamide composition

Properties	Previously proven composition	Sample No. 1	Sample No. 2
Charpy impact strength, kJ/m^2			
– at +23°C	71	48	66
– at –40°C*	95	23	74
– at –60°C*	93	13	73
Tensile strength, MPa	45	75	56
Elongation at break, %	13	5	7
Tensile modulus, MPa	2,312	3,850	2,551
Flammability	PV-2	PV-2	PV-2
Total afterflame time, s	71	114	158

Note. Testing at low temperatures was carried on the specimens conditioned at temperature +23°C and humidity 70% during 2 weeks.

In UE "Vector" made initial production testing polyamide composition (sample No. 2), the company released the PTC "Khimvolokno" (Grodno). During processing decreased amount deposited retardant. According to test results finished tube meets the requirements in terms of flexibility and appearance, but not all of the samples tested decay after removal of the flame source. Use of polymer modifiers that reduces the content of combustible polyolefin fraction while retaining the flexibility of the tube, is a promising direction. UE "Vector" is interested in continuing to develop joint cooperation polyamide extrusion composition.

References

1. Костюченко, М. А. Исследование влияния комбинированных антипиренов «фосфор + триазин» на горючесть и эксплуатационные свойства экструзионных полиамидов / М. А. Костюченко, М. М. Ревяко // Труды БГТУ. – 2012. – № 4: Химия, технология орган. в-в и биотехнология. – С. 40–43.

2. Horrocks, A. R. Fire Retardant Materials / A. R. Horrocks, D. Price. – Abington: Woodhead Publishing Ltd, 2001. – 429 p.

3. Levchik, S. V. Effect of melamine and its salts on combustion and thermal decomposition of polyamide 6 / S. V. Levchik, A. I. Balabanovich, L. Costa // Fire and Materials. – 1997. – Vol. 21. – P. 75–83.

4. Levchik, S. V. Effect of the fire-retardant, ammonium polyphosphate, on the thermal decomposition of aliphatic polyamides: Part II –polyamide 6 / S. V. Levchik, L. Costa, G. Camino // Polymer Degradation and Stability. – 1992. – Vol. 36. – P. 229–237.

Received 01.03.2013