Досліджено вплив на процеси в'язкого плину композиційних матеріалів кополімеру етилену з вінілацетатом, які не підтримують горіння та наповнювачів-антипіренів. В якості наповнювачів-антипіренів досліджували тригідрати оксиду алюмінію, дигідрати оксиду магнію, гідромагнезити. Встановлено вплив типу, а також дисперсності наповнювачів-антипіренів на реологічні властивості полімерних композицій: показник плинності розплаву (ППР), напруження зсуву, швидкість зсуву, ефективну в'язкість, енергію активації

Ключові слова: композиційні матеріали, вогнестійкість, кополімер етилену з вінілацетатом, наповнювачі-антипірени, реологічні властивості

Исследовано влияние на процессы вязкого течения не поддерживающих горение полимерных композиций на основе сополимеров этилена с винилацетатом и наполнителей-антипиренов. В качестве наполнителей-антипиренов исследовались тригидраты оксида алюминия, дигидраты оксида магния, гидромагнезиты. Установлено влияние, как природы, так и дисперсности наполнителей-антипиренов, на реологические свойства полимерных композиций: показатель текучести расплава (ПТР), напряжение сдвига, скорость сдвига, эффективную вязкость, энергию активации

Ключевые слова: композиционные материалы, огнестойкость, сополимер этилена с винилацетатом, наполнители-антипирены, реологические свойства

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EFFECT OF FLAME RETARDANT FILLERS ON THE RHEOLOGICAL PROPERTIES OF COMPOSITE MATERIALS OF ETHYLENE-VINYL ACETATE COPOLYMER

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1. Introduction

One of the most large-capacity consumers of insulating polymers is cable industry. In recent years, technical requirements for cable products have increased, and, as a result, the need to develop new advanced materials, including polymeric composite materials that do not sustain combustion. The prospect of composite polyolefine materials that do not sustain combustion is a consequence of their increasing usage and more strict requirements for fire safety of wires and cables in power industry, nuclear power engineering, railway transport, construction, etc. In other words, insulating and covering materials should meet European standards: EN 50363-7:2005 Insulating, sheathing and covering materials for low voltage energy cables. Part 7: Halogen-free, thermoplastic insulating compounds, EN 50363-5:2005 Insulating, sheathing and covering materials for low voltage energy cables. Part 5: Halogen-free, cross-linked insulating compounds, EN 50363-6:2005 Insulating, sheathing and covering materials for low voltage energy cables. Part 6: Halogen-free, cross-linked sheathing compounds. Processing of polymeric composite materials that do not sustain combustion causes great difficulties, which is predetermined by the high content of flame retardant fillers [1]. Therefore, the study of rheological properties, their dependence on chemical composition and the amount of fillers, as well as dispersion, is a relevant problem.

2. Literature review and problem statement

An analysis of scientific literature demonstrates that one of the means of decreasing flammability of the polymeric materials polyolefins is the introduction of flame retardant fillers to a polymer composition [2]. For this purpose, inorganic flame retardant fillers are used. Under condition of a real fire, PVC plasticates that are elements of cables, which have a KI value to 40 units, are a source of release of corrosion-active HCl gases and significant smoke. That is why, in order to address the problems, associated with the release of HCl and smoke blanketing, the cable materials were created that do not emit corrosion-active gases and have a much lower level of smoke release [3]. These materials not only increase fire resistance by absorbing more heat, but also neutralize acidic gases, which results in lower smoke formation. Polyolefins are typically used as a polymer base of these materials, while magnesium oxide trihydrates, aluminum oxide dihydrates and magnesites are used as flame retardants. A significant number of studies are carried out in this direction. Mechanical and fire-resistant properties of EVA composite materials and aluminum oxide trihydrate with various diameters of particles were explored, and a change in these properties depending on the dispersion of a filler was determined [4]. Effectiveness of calcium hydroxide for improvement of fire resistance of polyethylene of medium density was shown [5]. With the help of TGA/DSC methods, the study of polymeric compositions with magnesium dioxin, used as fire retardant, was conducted. Thermal capacity of these materials was determined [6]. Synergic effects of aluminum oxide hydrate and magnesium oxide dehydrate, used as flame retardants of EVA, were studied. Efficiency of these fillers was proved using the methods of X-ray structural and calorimetric analysis, as well as by determining an oxygen index [7]. It was found that in order to provide composite materials with the properties that do not sustain combustion, for insulation and cable covering and better safety of electrical equipment and devices, a degree of filling of a polymer matrix with hydrates of metals must be very high, which can lead to the loss of flexibility and low mechanical properties with simultaneous problems during processing [8]. That is why a study of the influence of the formulation of polymer compositions that do not sustain combustion on the rheological properties is a relevant issue. However, many problems, connected with the creation and processing of these materials, are still insufficiently studied.

3. The goal and objectives of the study

The goal of present research is to study specific features of rheological properties of composite materials of ethylene-vinyl acetate copolymer that do not sustain combustion, depending on the composition of flame retardant fillers, and their fractional composition.

To accomplish the set goal, the following objectives were assigned:

– to study dependence of melt flow index of polymeric compositions on their formulations and properties of ingredients;

– to establish the patterns of change in the shear rate depending on shear stress, effective viscosity, depending on the shear stress of polymeric compositions with different flame retardants;

– to establish the patterns of change in the activation energy of viscous flow of polymeric compositions on the amount of flame retardant fillers.

4. Examined materials and equipment used in the study of rheological characteristics of polymeric compositions

We studied ethylene-vinyl acetate (EVA) copolymers whose characteristics are given in Table 1, as well as aluminum oxide trihydrates, magnesium oxide dihydrates, mixture of magnesite and hydromagnesite as flame retardant fillers. Characteristics of flame retardant fillers are listed in Table 2.

The data given in Table 1, 2 were derived from the certificates of the supplier and are the results of entrance control of the raw materials.

Experimental samples of EVA polymeric compositions with different percentage of flame retardant filler, contained in each composition, were fabricated by the author of present article with using the method of rolling at a temperature of (443±5) K for (7–10) min. The rollers have a friction of 1.5.

EVA and flame retardant fillers were weighed on the balance with an accuracy of up to 0.001 g and then sequentially loaded on the rollers. Temperature of the working roller was (443±5) K. Temperature of the cold roller was (438±5) K. The samples were rolled for 3 minutes at a gap of 0.4–0.5 mm. Next, the gap was adjusted to 2 mm. In the process of rolling, they were periodically undercut not less than 2 times per minute. Within the last minute, they were rolled without undercuts.

The samples were conditioned at a temperature of (293±2) K for not less than 24 hours.

The formulation of polymeric compositions is given in Table 3.

Table 1

Characteristics of EVA

Indicator	EVA 1	EVA 2
Density, kg/m^3	939	951
Melt flow index, 2.16 kg, g/10 min	2.5	5
Content of vinyl acetate, %	18	28

Table 2

Characteristics of flame retardant fillers

Indicator	$Al(OH)_3$		$Mg(OH)_2$		$Mg_5(CO_3)_4(OH)_2{\cdot}4H_2O$; $Mg_3Ca(CO_3)_4$
	Sample No. 1	Sample No. 2	Sample No. 3	Sample No. 4	Sample No. 5
Mass fraction, %:					
– $Mg(OH)_2$	–	–	>93	>93.2	98.96
– $Al(OH)_3$	>99.2	>99.5	–	–	–
– SiO_2	<0.05	<0.1	<0.05	2.2±0.2	0.67
– Fe_2O_3	<0.035	<0.03	<0.3	0.12±0.02	0.04
– Na_2O	<0.6	<0.4	<0.05	–	<0.05
– CaO	–	–	–	2.2±0.2	–
Mean diameter of particles, μm:					
– medium(D_{50})	1.5	3	3	3.7	1.4
– max. (D_{98})	3.6	18	20	12.5	8.35
– min. (D_{10})	0.5	1	1	1.1	1.02

Table 3

Formulation of polymer composition

Polymer composition	Components, %						
	EVA 1	EVA 2	$Al(OH)_3$	$Al(OH)_3$	$Mg(OH)_2$	$Mg(OH)_2$	$Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$; $Mg_3Ca(CO_3)_4$
			Sample No. 1	Sample No. 2	Sample No. 3	Sample No. 4	Sample No. 5
1a	60	–	40	–	–	–	–
2a	–	60	40	–	–	–	–
3a	60	–	–	40	–	–	–
4a	–	60	–	40	–	–	–
5a	60	–	–	–	40	–	–
6a	–	60	–	–	40	–	–
7a	60	–	–	–	–	40	–
8a	–	60	–	–	–	40	–
9a	60	–	–	–	–	–	40
10a	–	60	–	–	–	–	40
1b	50	–	50	–	–	–	–
2b	–	50	50	–	–	–	–
3b	50	–	–	50	–	–	–
4b	–	50	–	50	–	–	–
5b	50	–	–	–	50	–	–
6b	–	50	–	–	50	–	–
7b	50	–	–	–	–	50	–
8b	–	50	–	–	–	50	–
9b	50	–	–	–	–	–	50
10b	–	50	–	–	–	–	50
1c	40	–	60	–	–	–	–
2c	–	40	60	–	–	–	–
3c	40	–	–	60	–	–	–
4c	–	40	–	60	–	–	–
5c	40	–	–	–	60	–	–
6c	–	40	–	–	60	–	–
7c	40	–	–	–	–	60	–
8c	–	40	–	–	–	60	–
9c	40	–	–	–	–	–	60
10c	–	40	–	–	–	–	60

The study of rheological properties of polymeric materials was carried out using the method of capillary viscosimetry in the device IIRT-AM. Results were processed and graphs were plotted using the software Microsoft Office Excel 2007.

Adequacy of regression equation was verified by checking statistical significance of determination coefficient R^2 by the F-criterion, defined by formula [9]:

$$F_p = \frac{R^2}{1-R^2} \times \frac{n-m-1}{m},$$

where n is the number of observations; m is the number of factors in regression equation.

5. Results of rheological studies of polymeric compositions

Rheological properties of the filled EVA were assessed, first of all, melt flow index (MFI) according to EN 60811-511:2012 Electric and optical fibre cables – Test methods for non-metallic materials – Part 511: Mechanical tests – Measurement of the melt flow index of polyethylene compounds (IEC 60811-511:2012). Viscosity (η) and activation energy (E_{ac}) were estimated as well. Melt viscosity, as well as flow temperature (T_f) of polymers, are known to depend significantly on the concentration of filler, its composition and dimensions of particles [10, 11].

The composition of a flame retardant filler in polymeric compositions was varied from 40 % by weight to 60 % by weight. We determined the way in which MFI depends on the amount of a flame retardant filler at a temperature of 423 K. Successive segments of the material of polymeric compositions, pressured out from the cylinder of capillary viscometer, were weighed on the balance Mettler Toledo with an accuracy of up to 0.0001 g, and their average mass was determined. The difference between the maximum and minimum values does not exceed 5 % of the average weight. Results are shown in Fig. 1, 2.

According to calculation results, $F_r > F^{cr}_{pr,\alpha}$ ($F^{cr}_{pr,\alpha}$ is the tabular value), with a reliability rate of 95 %, regression equation by the Fisher F-criterion is adequate.

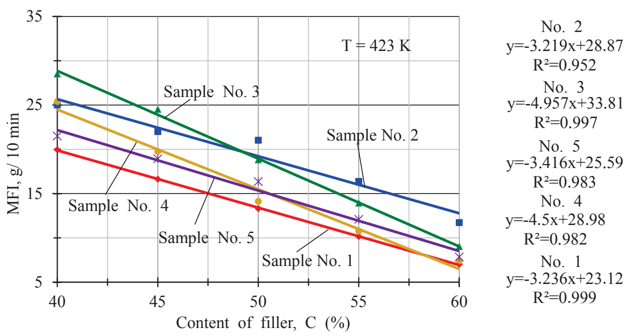

Fig. 1. Dependence of MFI of EVA polymeric compositions 1 on the amount of flame retardants (samples No. 1–5)

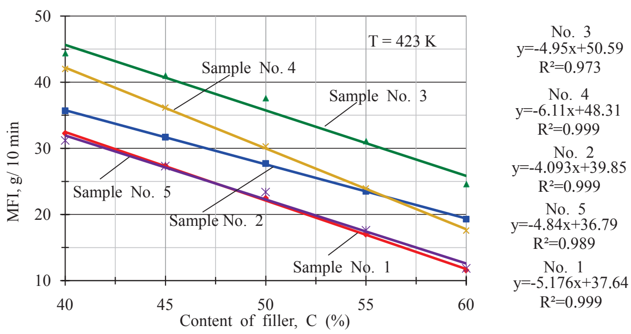

Fig. 2. Dependence of MFI of EVA polymeric compositions 2 on the amount of flame retardants (samples No. 1–5)

Reological behavior of polymeric compositions is determined not only by temperature and MFI, but also by shear stress, shear rate at which melt flow occurs.

Rheological properties of polymeric compositions were studied at a temperature of 403–423 K and at a load of 21.6 N, 38 N, 50 N, 100 N, 125 N, and 216 N.

By using the data obtained, we calculated the shear stress, shear rate and effective viscosity [12].

Shear stress was determined by formula:

$$\tau=\left(P-P_{ol}\right)\frac{r}{2\cdot L\cdot \pi\cdot R^{2}},$$

where τ is the shear stress, Pa; P is the pressure, required to provide losses through a capillary, dyn; P_{ol} is the output losses, dyn; R is the radius of the cylinder, cm; r is the radius of the capillary, cm; L is the length of the capillary, cm.

Shear rate was determined by formula:

$$\dot{\gamma}=\frac{4\cdot Q}{\pi\cdot r^{3}},$$

where γ is the shear rate, s^{-1}; Q is the consumption of material, cm^3/s ($Q=\pi\cdot R\cdot 2\cdot h$, where h is the stationary velocity of piston immersion, cm/s; R is the radius of the cylinder, cm); r is the radius of the capillary, cm.

Effective viscosity was determined by formula:

$$\eta_{ef}=\frac{\tau}{\dot{\gamma}},$$

where η_{ef} is the effective viscosity, Pa·s.

The graphs were plotted of logarithmic dependence of shear stress on the shear rate and of dependence of effective viscosity on the shear rate.

Results are shown in Fig. 3–5.

Fig. 3–5 show graphs of dependence of shear rate on shear stress (that is, flow curves) for EVA 2 with various flame retardants (samples No. 1–5) at different concentrations of the filler.

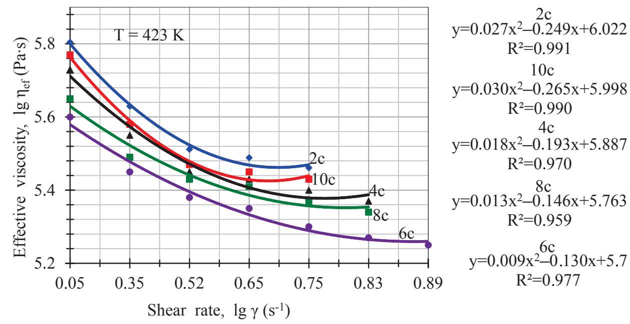

Fig. 3. Dependence of shear rate on shear stress of EVA polymeric compositions 2 with different flame retardants at a temperature of 423 K

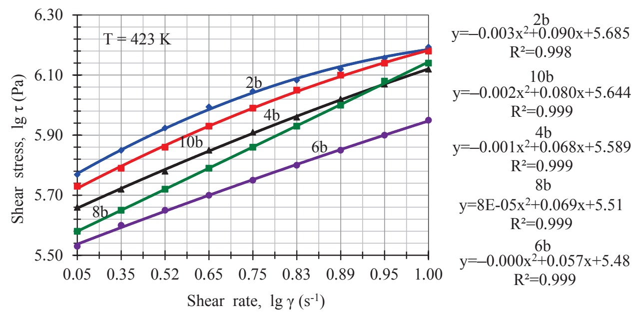

Fig. 4. Dependence of shear rate on shear stress of EVA polymeric compositions 2 with different flame retardants at a temperature of 423 K

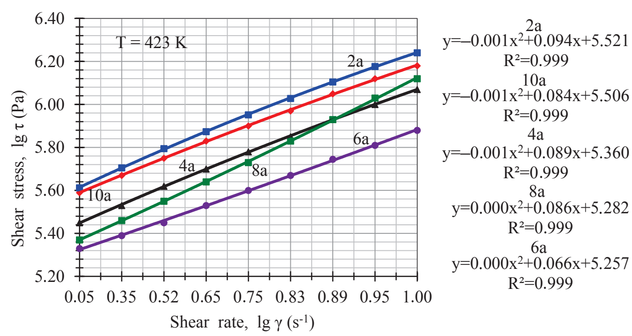

Fig. 5. Dependence of shear rate on shear stress of EVA polymeric compositions 2 with different flame retardants at a temperature of 423 K

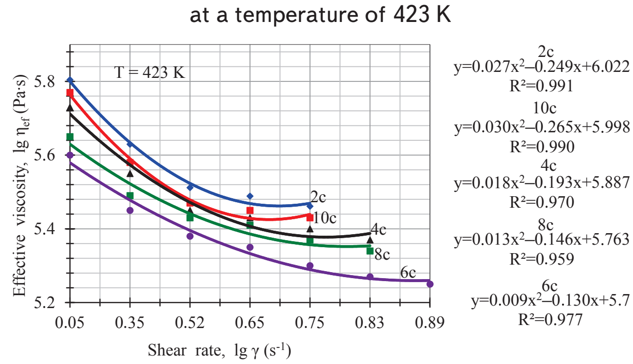

Fig. 6. Dependence of effective viscosity on shear rate of EVA polymeric compositions 2 with different flame retardants at a temperature of 423 K

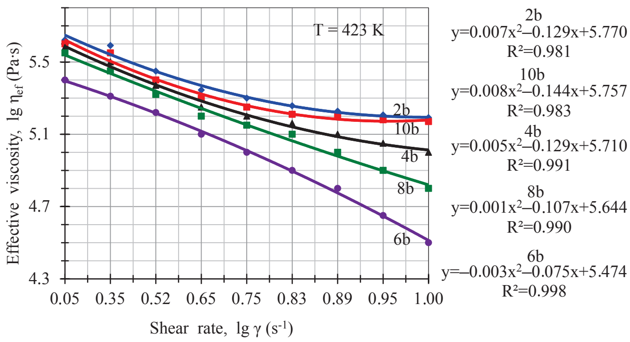

Fig. 7. Dependence of effective viscosity on shear rate of EVA polymeric compositions with different flame retardants at a temperature of 423 K

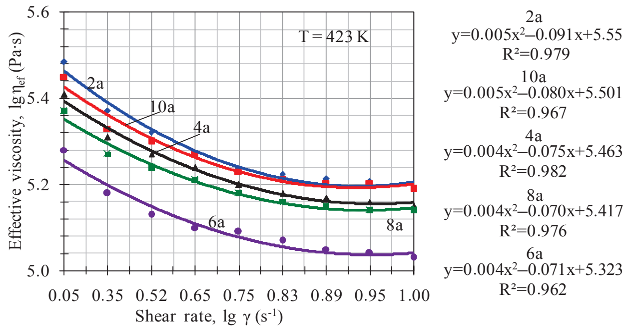

Fig. 8. Dependence of effective viscosity of shear rate of EVA polymeric compositions 2 with different flame retardants at a temperature of 423 K

For the purpose of evaluation of energy that is required for the transition of the system into the so-called transitional state, that is, when destruction and creation of bonds are balanced, it is necessary to calculate the activation energy.

Activation energy of the viscous flow was determined by formula [13]:

$$E_{ac} = \frac{R \cdot T_1 \cdot T_2 \ln\left(MFI_2 / MFI_1\right)}{T_2 - T_1},$$

where T is the temperature of measurement, K; MFI_1 and MFI_2 are the melt flow indices at T_1 and T_2, g/10 min; R is the universal gas constant, $R = 8.314$ J/mol.

Results are given in Table 4 and Fig. 9.

Results of the studies (Table 4, Fig. 9) define the energy barriers that are eliminated in the elementary flow act depending on the type and amount of flame retardant fillers.

Table 4

Activation energy of viscous flow of EVA polymeric compositions 2

Indicator	Polymeric composition														
	2a	2b	2c	10a	10b	10c	4a	4b	4c	8a	8b	8c	6a	6b	6c
Activation energy, E_{ac}, kJ/mol	47.2	48.9	50.4	46.8	47.7	49.4	39.7	41.5	43.7	30.5	32.1	34.2	28.8	30.7	32.0

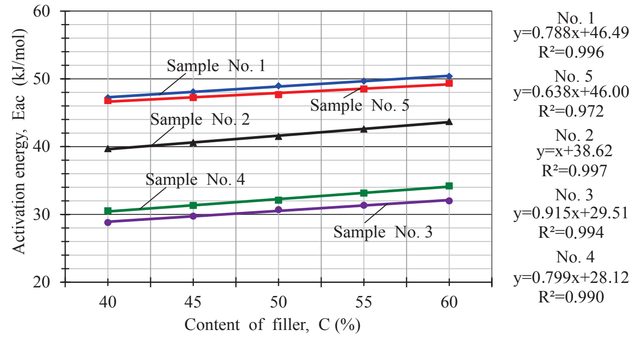

Fig. 9. Dependence of activation energy of content of filler of EVA polymeric compositions 2

6. Discussion of results of research into rheological properties of polymeric compositions that do not sustain combustion

The graphs (Fig. 1, 2) show that the indicators of MFI in the case of using EVA 2 are higher than those in the case of applying EVA 1 with a lower content of vinyl acetate. A noticeable decrease in MFI occurs when using EVA 1, filled with any flame-retardant filler.

An analysis of the results obtained also reveals a significant decrease in MFI when using aluminum oxide trihydrates with a smaller diameter of particles. The same dependence is observed in the case of using magnesium oxide dihydrates. Magnesite occupies a middle position between sample No. 1 and No. 2 of aluminium oxide trihydrate.

Fig. 3–5 show that with an increase in the concentration of fillers, the flow curves move up. Greater stresses are required to achieve the assigned shear rate. Shear stress increases with an increase in the concentration of filler.

Let us consider results of rheological studies (Fig. 3–5) at the same values of shear rate. The highest shear stress is characteristic of the compositions 2a, 2b, 2c, which contain EVA 2 and oxide aluminium trihydrate (sample No. 1) with a less dispersion and the mean diameter of particles of 1.5 µm. Lower shear stresses are characteristic of the polymeric compositions 6a, 6b, 6c, which contain EVA 2 and magnesium oxide dihydrate (sample No. 4).

On the graphs of dependence of effective viscosity on the shear rate (Fig. 6–8), we can observe an increase in effective viscosity as the concentration of filler increases. For polymeric compositions with the use of aluminum oxide trihydrates and magnesites (compositions 2a, 2b, 2c, 10a, 10b, 10c), effective viscosity is considerably higher than that in polymeric compositions 6a, 8a, 6b, 8b, 6c, 8c, in which magnesium oxide dihydrates were used.

The lowest effective viscosity was observed in polymeric compositions with the lowest dispersion of fillers.

According to Table 3 and Fig. 9, the lowest values of activation energy were observed in polymeric compositions, containing magnesium oxide dihydrates, higher values were observed in the cases when aluminum oxide dihydrates and magnesite were used. In this case, the values of activation energy slightly change for polymeric compositions with a dufferent degree of filling. This indicates an insignificant dependence of activation energy of viscous flow of polymer compositions on the concentration of fillers.

Thus, rheological properties of polymeric compositions that do not sustain combustion depend on melt flow index of the polymer matrix, chemical composition of the dispersion of metal oxides hydrates and hydromagnesites.

7. Conclusions

1. Melt flow index of ethylene-vinyl and acetate copolymer, composition and dispersion of aluminum oxide trihydrates, magnesium oxide dihydrate, and of hydromagnesites affect melt flow index of polymer compositions. Ethylene-vinyl acetate copolymer, which has a higher melt flow index, provides a higher melt flow index of the filled polymer composition for all flame retardant fillers. Aluminum oxide trihydrate and magnesium oxide dihydrate with smaller average dimensions of particles decrease melt flow index of polymeric compositions.

2. The use of flame retardant fillers of different composition and dispersion affects a change in shear stress and effective viscosity for achieving the assigned shear rate. Shear stress and effective viscosity increase for polymeric compositions, which include flame retardant fillers with smaller average dimensions of particles.

3. It was established that the concentration of filler practically does not change the value of activation energy of polymeric compositions, while the nature and dispersion of a flame retardant filler has a significant influence on a change in the activation energy. Activation energy increases for polymeric compositions with aluminum oxide trihydrate, magnesium oxide dihydrate with a smaller average diameter of particles. Depending on the composition of flame retardant fillers, activation energy increases in the following order of samples: 3, 4, 2, 5, and 1.

Thus, the study has demonstrated the possibility of directed regulation of formulation of polymeric compositions by such means as the use of various polymeric matrices, quantitative, qualitative and fractional composition of flame retardant fillers.

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