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ESTIMATING THE INFLUENCE OF POLYORGANOSILOXANES ON THE PROPERTIES OF FIRE-RETARDANT HALOGEN-FREE POLYMER COMPOSITIONS FOR CABLE ARTICLES

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The object of this study is the processes of supramolecular structure formation and the thermophysical, rheological, physical-mechanical, and electrophysical properties of halogen-free fire-resistant polymer compositions. Aluminum oxide trihydrate is used as a flame retardant. The effect of the flame-retardant filler becomes noticeable only with a significant filling (60%), when the rheological and operational properties of polymer compositions deteriorate. The use of polyorganosiloxanes makes it possible to reduce the negative impact of the filler on the thermophysical, rheological, physical-mechanical, and electrophysical properties. Therefore, the effective use of polyorganosiloxanes to regulate the properties of fire-resistant polymer compositions is an urgent task under consideration.

Fire-retardant halogen-free polymer compositions were studied. The content of the flame-retardant filler is 60%. The samples under study additionally contain polyorganosiloxanes, which were used as modifiers for the directed regulation of properties of fire-retardant compositions. The effect of polyorganosiloxanes on the formation of the supramolecular structure of filled polymer compositions for cable articles has been established. Due to this, the phase transition temperatures increase by 2–4°C, the temperature of the beginning of decomposition by 12–17°C and the end of decomposition by 5–6°C. The effect of the influence of polyorganosiloxanes with a viscosity of 50–500 Pa•s on a decrease in the melt viscosity of fire-retardant polymer compositions from 5.342 to 4.330 Pa•s with an increase in the shear rate from 20 to 60 s^{-1} has been shown.

The results make it possible to use polyorganosiloxanes for targeted regulation of rheological and operational characteristics of fire-resistant polymer compositions for the manufacture of insulation and sheath of power cables.

Keywords: cable articles, fire-resistant polymer compositions, polyorganosiloxanes, rheological properties, thermophysical properties

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1. Introduction

In modern cable production, polymer composite materials are widely used. Currently, the requirements for fire safety indicators of cable articles for power plants, especially nuclear power plants, subways, airports, municipal facilities, oil and gas and other industries have increased significantly [1]. In these industries, the requirements for fire safety of cable materials are much higher than for general-purpose cables. The most serious requirements are imposed on the indicators of non-spreading of combustion and smoke emission. These requirements are met by cable articles manufactured using halogen-free polymer compositions with reduced flammability [2, 3]. Metal hydroxides are used as flame retardants. However, the effectiveness of metal hydroxides becomes noticeable only under conditions of significant filling, about 50–60%, when the technological and operational properties of polyolefins deteriorate.

Therefore, manufacturers of polymer composite materials are constantly faced with the issue of choosing modifiers to regulate the properties of halogen-free polymer compositions. It is also important to study their influence on the properties of polymer compositions during processing and operation. Therefore, research in the field of new structurally modified fire-resistant polymer compositions is relevant.

Given the growing need to restore destroyed infrastructure (electric power industry), devising new methods for improving the technological and operational characteristics of halogen-free polymer compositions is an important task of modern science. This could not only increase the durability of cable articles but also reduce risks to human health and the environment.

2. Literature review and problem statement

Our review of the literature demonstrates that low-pressure polyethylene and ethylene-vinyl acetate copolymer are mostly used for the production of polyolefin compositions [4, 5]. Polyolefins are one of the most flammable materials with a high heat of combustion, a low oxygen index value, and high heat release, which leave little or no coke residue [6]. Metal hydroxides are used as flame retardants [7, 8]. Low cost and significantly lower smoke generation during combustion of materials containing them are the main advantages of these flame retardants compared to materials containing organic flame retardants. However, the effectiveness of metal hydroxides is much lower than that of halogen- and phosphorus-containing compounds, as a result of which the effect of metal hydroxides becomes noticeable only under conditions of significant filling of about 50–60% (wt.) [9], when the physical and mechanical properties of polyolefins deteriorate. The negative impact of a large amount of filler on the rheological and operational properties of polymers can be reduced by using various types of surface modifiers of inorganic fillers [10–12]. In [10], the possibility of modifying polyethylene with polydimethylsiloxane with terminal aminopropyl groups and grafted maleic anhydride was shown. It was shown that the melt viscosity of the mixtures increased. In [11], a chemical modification was proposed to optimize the rheological and mechanical properties of composite materials based on polyethylene to increase the degree of filling. In [12], a relationship between rheological characteristics and processability of polyethylene of different molecular structures was established. Those studies can be used as a basis for designing complex polymer systems containing a mixture of polyolefins and a high content of fillers.

For the modification of inorganic flame retardants with hydroxyl groups on the surface, organosilanes are known to be used [13–15]. These are compounds with easily hydrolyzed groups, the interaction of which with hydroxyl groups on the surface of flame retardants provides chemical bonding with the flame retardant, and organic radicals that give the surface organophilicity, and, therefore, improve compatibility with polymers. In [13], the effectiveness of using silicon additives for polymer compositions based on EVA, natural magnesium hydroxide and natural hydrated mineral – calcium borate is shown. Studies on fire resistance have been conducted but the influence of silicon additives and calcium borate on rheological, thermophysical, and physical-mechanical characteristics has not been shown. In [14], the chemical interaction of alkoxysilanes and ethylene-vinyl acetate copolymer and maleic anhydride was studied by IR spectroscopy. In [15] it is shown that the rheological properties of highly filled polymer systems are influenced by the filler content and the nature of the components that are included in the composition. This indirectly ensures the final properties and processability of the materials. The disadvantage of organosilanes is their high fire hazard. The flash point is not higher than 80°C. These disadvantages can be avoided by using polyorganosiloxanes. The use of polyorganosiloxanes for the modification of fire-resistant polymer compositions has not been studied. The most popular and most widely used inorganic flame retardant is aluminum oxide trihydrate. Aluminum oxide trihydrate as a flame retardant differs in particle size, specific surface area, and impurities.

To determine the influence of modifiers on the processing technology of halogen-free compositions, rheological measurements of polymer melts are widely used [16–18], and therefore for quality control and process optimization. In [16], the effect of a modifier (organoclay) on the rheological properties of polyethylene was investigated. The results indicate a decrease in viscosity due to the presence of a small amount of organoclay. In [17], rheological studies of PE/EVA blends were conducted. In [18], the effect of two different modifiers of polyethylene grafted with maleic anhydride and oxidized polyethylene on the rheological properties of polyethylene/clay nanocomponents with different clay contents was investigated. Another interesting area of rheology is obtaining information about the molecular parameters of polymers and the structure of heterogeneous polymer systems. The effect of polyorganosiloxanes on the rheological properties of fire-resistant polymer compositions is not known. In [19], an overview of the effect of molecular weight, molecular weight distribution, and degree of branching on various rheological characteristics is given. Rheological measurements can be used as a simple method for qualitatively investigating interactions between different phases and changes in geometric structures created by inhomogeneities [20]. However, the effect of polyorganosiloxanes on the change of molecular to supramolecular structure of fire-resistant polymer compositions has not been investigated. For melting, mixing, and forming of polymer compositions during the production of cable articles, extrusion is used as the main method [21, 22], which requires the determination of their thermorheological behavior.

In addition to rheological properties, thermophysical, mechanical, and electrical characteristics are also important in the processing and operation of halogen-free polymer compositions and in the aging process [23–25]. In [23], the importance of studying the physical-mechanical and thermophysical properties of polyethylene compositions, including mixtures with other polymers, fillers and nanofillers in the field of additive manufacturing, especially material extrusion, is shown. Experimental studies on the dielectric constant on short sections of used XLPE cable are reported in [24]. In [25], it is stated that one of the potential diagnostic tools for the assessment of electrical cables during operation is the measurement of the dielectric loss tangent. Both parameters describe the processes of energy loss in the dielectric and can be related to the specific volume electrical resistance of the insulation. When studying samples of fire-resistant polymer compositions, it is advisable to examine the dependence of specific volume electrical resistance on the composition of polymer products.

The cited studies show that the properties of polymer compositions vary depending on their composition. However, many questions related to improving the properties of polymer compositions that do not support combustion are still insufficiently studied. A special issue is the influence of various types of modifying additives on the supramolecular structure of polymer compositions. The main factors in this may be difficulties associated with the rheological properties of additives.

3. The aim and objectives of the study

The purpose of our study is to determine the influence of the characteristics of polyorganosiloxanes on the rheological, thermophysical, mechanical, and electrophysical properties of halogen-free fire-retardant polymer compositions for power cables with voltages up to 1 kV. This will make it possible to reasonably approach the determination of the characteristics of polyorganosiloxanes for the directional regulation of properties of polymer compositions. This could also allow for the rapid adjustment of the polymer composition formulation depending on the desired technological and operational properties of the final product.

To achieve the goal, it is necessary to solve the following tasks:

– to investigate dependence of the thermophysical properties of fire-retardant polymer compositions on the characteristics of polyorganosiloxanes;

– to establish the patterns of change in the rheological properties (shear rate, shear stress, viscosity) of fire-retardant polymer compositions with the addition of polyorganosiloxanes;

– to investigate dependence of the physical-mechanical and electrophysical properties on the characteristics of polyorganosiloxanes.

4. The study materials and methods

The object of our study is the processes of supramolecular structure formation and thermophysical, rheological, physical-mechanical, and electrophysical properties of modified fire-resistant halogen-free polymer compositions.

The hypothesis of the study assumes that the formation of an ordered supramolecular structure and the improvement of thermophysical, rheological, physical-mechanical, and electrophysical properties of fire-resistant polymer compositions is possible through the introduction of modifiers – polyorganosiloxanes.

The assumptions accepted imply that the ability of polyorganosiloxanes to influence the formation of the supramolecular structure of polymer compositions can improve their rheological and operational properties.

The simplifications adopted imply that the introduction of modifiers improves intermolecular interaction and ensures a uniform distribution of components in the structure of the polymer composition.

Fire-retardant halogen-free polymer compositions were investigated: samples 1, 2, 3, 4. The polymer composition (sample 4) for polymer compositions is a mixture of polyolefins (linear low-density polyethylene; polyolefin elastomer and linear low-density polyethylene modified with maleic anhydride). The flame-retardant filler is aluminum oxide trihydrate. The content of the flame-retardant filler in polymer compositions is 60%. Polymer materials are defined as fire-retardant if their oxygen index under the condition of cessation of fire exceeds 27%. This is ensured by the content of the flame-retardant filler. Polymer compositions in samples 1, 2, 3 additionally contain polyorganosiloxanes, which were used as modifiers for the directional regulation of the properties of fire-retardant compositions. The main structural component of polyorganosiloxanes is a group containing a Silicon-Oxygen-Silicon chain, in which at least one organic group is located next to the Silicon atom [26]. Technical characteristics of polyorganosiloxanes are given in Table 1.

Table 1

Properties of polyorganosiloxanes

Indicator	Value		
	Sample 1	Sample 2	Sample 3
Viscosity (25°C), Pa·s	50	500	1500
Flash temperature,°C	285	236	236
Density (25°C), g/cm^3	0,960	0,950	0,99

Polymer compositions were manufactured at laboratory equipment by Brabender (Germany), consisting of a laboratory station Plasticorder, a measuring mixer 350 E, a measuring extruder (19 × 24), a cooling system, and granulation.

A series of experiments to study phase and structural transformations, processes of thermo-oxidative destruction were carried out using a thermogravimetric analysis (TGA) and the differential scanning calorimetry (DSC) TGA/DSC 1/1100 SF device from METTLER TOLEDO (Switzerland). Heating rate was 10 degrees/min. Operating temperature range – from room to 1100°C; heating rate – from 0.01 to 100 degrees/min. Microbalance – maximum weight during weighing is 1 g. Resolution of the TGA device – 1 μg in the entire weighing range. DSC measurement range: 1 – ± 350 mW; resolution – 0.04 μW. Determination of temperatures of phase and structural transformations was conducted by characteristic points of description of physical phenomena on DSC diagrams. The onset of the glass transition effect was determined as the point of intersection of the baseline with the diagram before the phase transition. The end of the effects was determined as the point of intersection of the baseline with the diagram after the phase transition and the tangent curve, which was drawn to the inflection point.

The decomposition temperatures of polymer compositions were determined using the DSC diagram, which was acquired using the TGA/DSC 1/1100 SF device (temperature rise rate – 10 degrees/min). The temperatures of the beginning and end of decomposition were determined as the intersection points of the baseline with the diagram before and after the decomposition of polymer compositions and the tangent to the diagram, which was drawn to the inflection point. The mass loss was determined as the distance on the ordinate axis between the tangent to the TGA diagram and parallel to the abscissa axis at the end point of the process.

The study of the rheological properties of polymer materials was carried out on a measuring extruder (19 × 24) using a rheometric capillary die. The technical characteristics of the capillaries according to the Instruction manual: Rheometric slotted capillary die. Ident. No. 6 28 272.xxx. Iss. 0719 Brabender GmbH & Co. KG, Duisburg Germany, are given in Table 2.

Table 2

Technical characteristics of capillaries

	Capillary dimensions (diameter and length), mm	Shear speed range
Measurement range	3 × 18	3×10^1–8×10^2 s^{-1}
	3 × 24	3×10^1–8×10^2 s^{-1}
	3 × 30	3×10^1–8×10^2 s^{-1}

Polymer melts, due to their macromolecular structure, exhibit a structurally viscous flow behavior. This means that as the shear rate increases, the shear stress τ decreases subproportionally with respect to the viscosity η. The shear stress as a function of the shear rate is referred to as the rheological curve, and the viscosity as a function of the shear rate is referred to as the viscosity curve. The viscosity η is an independent parameter for Newtonian materials, while for non-Newtonian materials it depends on the shear rate. The shear rate, shear stress, and viscosity calculated from the Newtonian flow behavior are also called imaginary values. Measurements obtained with capillary rheometers with circular capillaries require correction due to inlet/outlet effects. These effects negatively affect the pressure drop across the capillary (Begley correction), and an additional correction related to the nature of the material under study (Weissenberg-Rabinovich correction), which is due to viscosity [27]. Correction of the apparent values obtained by measuring rheological parameters taking into account the nature of the deviation of the polymer melt flow from a Newtonian fluid on a rheometric capillary die is performed using the device software.

The melt flow index was determined according to EN 60811–511:2012/A1:2017 Electric and optical fiber cables – Test methods for non-metallic materials – Part 511:

Mechanical tests – Measurement of the melt flow index of polyethylene and polypropylene compounds. The activation energies of viscous flow of polymer compositions were determined according to [28]. Plots of the dependence of shear stress on shear rate and viscosity on shear rate were constructed.

The mechanical properties of polymer compositions were investigated according to HD 605 S2:2008; AC:2010 Electric cables – Additional test methods and EN 60811-511:2012/A1:2017 Electric and optical fiber cables – Test methods for non-metallic materials – Part 511: Mechanical tests – Measurement of the melt flow index of polyethylene and polypropylene compounds.

The oxygen index was investigated according to ISO 4589-2:2017. Plastics – Determination of burning behavior by oxygen index – Part 2: Ambient-temperature test.

Electrophysical tests according to [29]. Experiments to determine the electrical strength were carried out using an AII-70 type apparatus, the electrical resistivity – a KISI-1 type device.

Statistical analysis was performed by the analysis of variance (ANOVA) method using the asymptotic regression model according to the Levenberg-Marquardt integral algorithm with a significance level of α 0.05.

5. Results of studies on the influence of polyorganosiloxanes on

5. 1. Dependence of thermophysical properties of fire-resistant polymer compositions on the characteristics of polyorganosiloxanes

Thermophysical characteristics, such as temperatures of phase and structural transformations, temperatures of the onset of decomposition, are of great importance for determining the parameters of the extrusion process of polymer materials, as well as the operation of cable articles at elevated temperatures and short-circuit temperatures (170°C – duration not more than 5 s).

Fig. 1 shows DSC diagrams of polymer compositions, the composition of which is given in Table 3.

Table 3

Composition of halogen-free polymer compositions

Components	Content,% wt.			
	1	2	3	4
Basic polymer composition	99,5	99,5	99,5	100
Polyorganosiloxane, sample 1	0,5	–	–	–
Polyorganosiloxane, sample 2	–	0,5	–	–
Polyorganosiloxane, sample 3	–	–	0,5	–

Analysis of Fig. 1 reveals that the basic polymer composition (sample 4) is in the lower range of phase transition and decomposition temperatures compared to the polymer compositions (samples 1, 2, 3) containing polyorganosiloxanes.

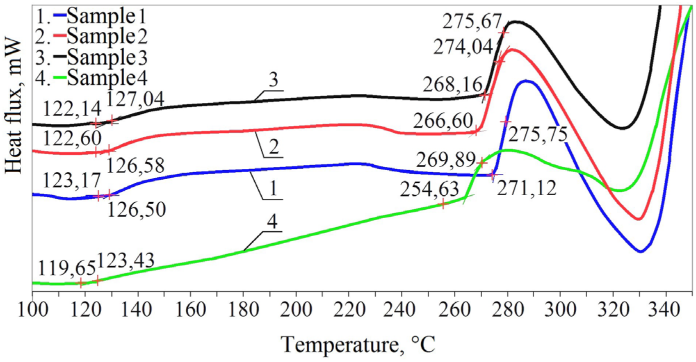

Fig. 1. Differential scanning calorimetry diagram of phase transitions and the beginning and end of decomposition of polymer compositions

Table 4 gives the phase transition and decomposition temperatures of polymer compositions.

Table 4

Phase transition and decomposition temperatures of polymer compositions

Indicator name	Results			
	Sample 1	Sample 2	Sample 3	Sample 4
1. Glass transition temperature of the beginning of the effect,°C	123,17	122,60	122,14	119,65
end of effect,°C	126,50	126,58	127,04	123,43
2. Temperature of the start of the decomposition,°C	271,12	266,60	268,16	254,63
end of decomposition,°C	275,75	274,04	275,67	269,89

Fig. 2 shows TGA diagrams of polymer compositions, Table 5 gives the mass loss data determined from the TGA diagram (Fig. 2).

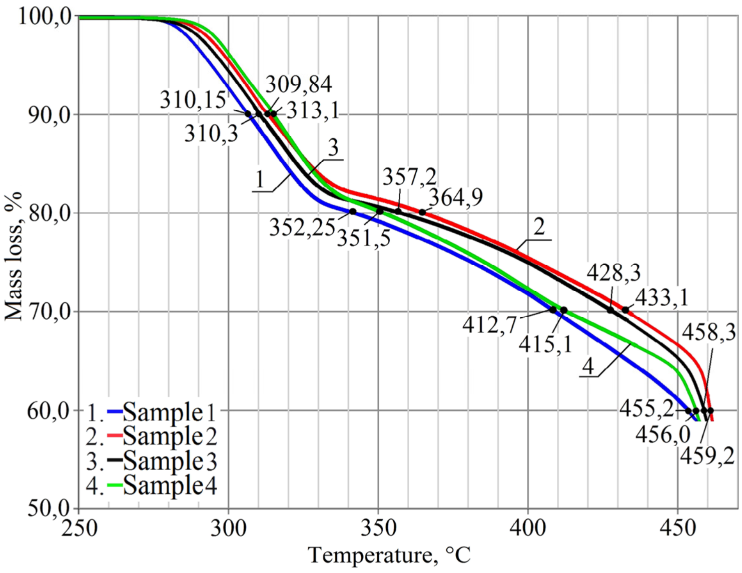

Fig. 2. Thermogravimetric diagram of polymer compositions

The description of the physical data and decomposition of polymer compositions in the DSC and TGA diagrams shows the effects of the beginning and end of the decomposition of polymer compositions and mass loss.

Table 5

Mass loss

Mass loss,%	Temperature,°C			
	Sample 1	Sample 2	Sample 3	Sample 4
10	310,15	313,1	310,3	309,84
20	352,25	364,9	357,2	351,5
30	415,1	433,1	428,3	412,7
40	455,2	459,2	458,3	456,0

5. 2. Regularities of change in the rheological properties of fire-resistant polymer compositions with the addition of polyorganosiloxanes

Fig. 3, 4 show the dependences of viscosity on the shear rate of polymer compositions. For the correct construction of experimentally obtained flow curves, the input pressure losses that appear during the flow of the melt of polymer compositions at the entrance to the capillaries, as well as their nature, are taken into account.

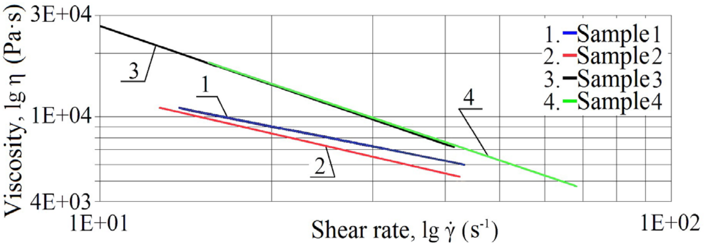

Fig. 3. Dependence of viscosity on the shear rate of polymer compositions taking into account the Begley correction

The curves in Fig. 3 are described by the regression equations:

– for sample 1:

$y=10794-101\cdot x$, $R^2=0{,}9905$;

– for sample 2:

$y=10784-112{,}85\cdot x$, $R^2=0{,}9941$;

– for sample 3:

$y=18066-225{,}99\cdot x$, $R^2=0{,}9887$;

– for sample 4:

$y=18197-226{,}96\cdot x$, $R^2=0{,}9919$.

The curves in Fig. 4 are described by the regression equations:

– for sample 1:

$y=9591-89{,}742\cdot x$, $R^2=0{,}9925$;

– for sample 2:

$y=9436-98{,}743\cdot x$, $R^2=0{,}9941$;

– for sample 3:

$y=16024-195{,}13\cdot x$, $R^2=0{,}9914$;

– for sample 4:

$y=16147-200{,}03\cdot x$, $R^2=0{,}9895$;

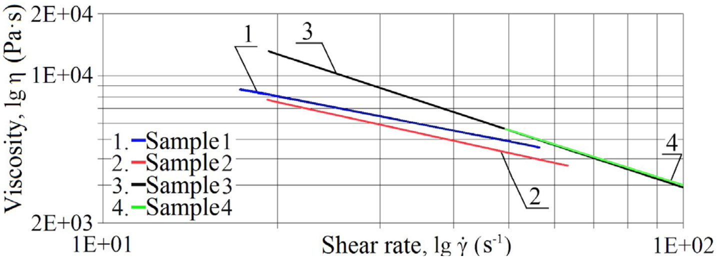

Fig. 4. Dependence of viscosity on the shear rate of polymer compositions taking into account the Weissenberg-Rabinovich correction

In Fig. 3, 4 it is observed that the viscosity of polymer compositions containing polyorganosiloxanes moves to the region of lower values compared to the base polymer composition (sample 4).

In Fig. 5, 6, the dependences of shear stress on the shear rate of polymer compositions are represented taking into account the Begley and Weisenberg-Rabinovich corrections.

The curves in Fig. 5 are described by the regression equations:

– for sample 1:

$y=124017+2980{,}7\cdot x$, $R^2=0{,}9933$;

– for sample 2:

$y=137783+2073{,}6\cdot x$, $R^2=0{,}9903$;

– for sample 3:

$y=272385+710{,}71\cdot x$, $R^2=0{,}9791$;

– for sample 4:

$y=272099+803{,}18\cdot x$, $R^2=0{,}9993$;

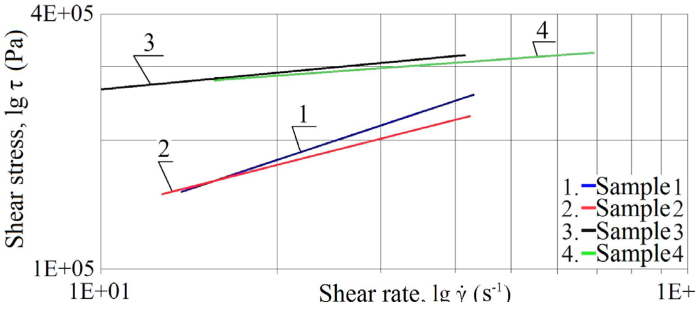

Fig. 5. Shear stress dependence on the shear rate of polymer compositions taking into account the Begley correction

The curves in Fig. 6 are described by regression equations:

– for sample 1:

$y=110196+2648{,}5\cdot x$, $R^2=0{,}9936$;

– for sample 2:

$y=120560+1814{,}4\cdot x$, $R^2=0{,}9913$;

– for sample 3:

$y=235702+1026\cdot x$, $R^2=0{,}9831$;

– for sample 4:

$y=241256+781{,}5\cdot x$, $R^2=0{,}9819$.

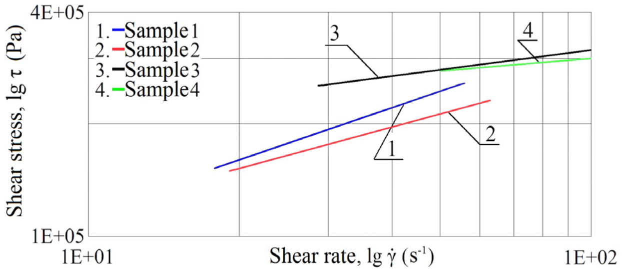

Fig. 6. Shear stress dependence on the shear rate of polymer compositions taking into account the Weissenberg-Rabinovich correction

In Fig. 5, 6, it is observed that the shear stress of polymer compositions containing polyorganosiloxanes moves to the region of lower values compared to the base polymer composition (sample 4).

The change in rheological characteristics at fixed values of shear rate (20 s^{-1}, 40 s^{-1}, 60 s^{-1}) is demonstrated in Tables 6, 7.

Table 6

Viscosity of polymer composition melts as a function of shear rate

Shear rate, s^{-1}	Viscosity, Pa·s			
	Sample 1	Sample 2	Sample 3	Sample 4
20	9040,51*	8844,50*	14270,00*	14420,60*
40	6222,11*	5636,42*	7580,30*	7593,20*
60	5000,63*	4330,56*	5230,47*	5342,32*
20	8033,02**	7738,95**	12733,54**	12783,11**
40	5528,71**	4931,88**	6996,15**	6874,08**
60	4443,35**	3789,25**	4928,52**	4782,04**

*Note: * – viscosity with Begley correction; ** – viscosity with Weissenberg-Rabinovich correction*

Table 7

Shear stress of polymer composition melts depending on shear rate

Shear rate, s^{-1}	Shear stress, Pa·s			
	Sample 1	Sample 2	Sample 3	Sample 4
20	180810,11*	176889,95*	285400,00*	288412,00*
40	248884,32*	225456,96*	303212,00*	303728,00*
60	300037,55*	259833,77*	313828,20*	320539,20*
20	160660,41**	154779,06**	254670,76**	255662,12**
40	221148,35**	197275,30**	279846,04**	274963,18**
60	266601,00**	227355,07**	295711,07**	286922,18**

*Note: * – shear stress with Begley correction; ** – shear stress with Weissenberg-Rabinovich correction*

The study of rheological characteristics was carried out at temperatures in the measuring extruder in the zones: 155°C, 160°C, 165°C, 170°C; on the rheometric head: 175°C; the melt temperature of polymer compositions was 185°C.

5. 3. Dependence of physical-mechanical and electrophysical properties on the characteristics of polyorganosiloxanes

The physical-mechanical, technological characteristics, and oxygen index of polymer compositions were determined. The results of our studies are given in Table 8.

Table 8

Physical-mechanical properties of polymer compositions

Indicator	Value			
	Sample 1	Sample 2	Sample 3	Sample 4
Density, g/cm^3	1,43	1,44	1,43	1,455
Melt flow index 150°C, 21.6 kg, g/600 s	5,25	4,94	4,81	4,85
Activation energy, kJ/mol	44,467	36,435	41,021	40,965
Tensile strength, N/mm^2	16,7	16,3	17,2	18,5
Elongation at break, %	242	242	250	220
Modulus of elasticity at break, MPa	14,357	11,217	9,647	8,489
Tensile strength, after holding for 7 × 24 hours at a temperature of (100 ± 2)°C, N/mm^2	17,55	17,67	17,74	17,76
Change in tensile strength after 7 × 24 h at (100 ± 2)°C,%	4,86	7,75	3,04	–4,16
Elongation at break after 7 × 24 h at (100 ± 2)°C,%	215	222	210	180
Change in elongation at break after 7 × 24 h at (100 ± 2)°C,%	–12,60	–9,00	–19,00	–22,2
Shore hardness *D*	56,6	55,0	57,7	58
Oxygen index,%	35	34	34	33,5

The electrophysical properties of polymer compositions were investigated. The specific electrical resistance is determined by the presence of free charges (electrons and ions) and their mobility. The electrical strength is the electric field strength at which a breakdown occurs.

The results of our study are given in Table 9.

Table 9

Electrophysical parameters of polymer compositions

Indicator	Sample 1	Sample 2	Sample 3	Sample 4
Specific volume electrical resistance, Ohm·cm	$1{,}15\cdot 10^{16}$	$1{,}32\cdot 10^{16}$	$1{,}1\cdot 10^{16}$	$1\cdot 10^{16}$
Electrical strength, kV/mm	47,0	48,5	45,5	45,0

The electrophysical properties of fire-resistant polymer composite materials are significantly influenced by the characteristics of polyorganosiloxanes. The formation of the supramolecular structure of the resulting compositions has an important impact on the electrophysical properties of fire-resistant polymer compositions. This is evidenced by the results of investigating electrical strength and specific volume electrical resistance.

6. Discussion of results based on the influence of polyorganosiloxanes on the characteristics of fire-resistant polymer compositions

Thermophysical, rheological, physical-mechanical, and electrophysical characteristics of fire-resistant polymer compositions have been studied and systematized. The change of these characteristics depending on the physicochemical properties of modifiers – polyorganosiloxanes – has been established. A method of directional regulation of the properties of highly filled (60 wt.%) fire-resistant polymer compositions has been devised. It has been shown that the advantages of this study are the improvement of rheological and increase of thermophysical, physical-mechanical, and electrophysical properties of fire-resistant polymer composite materials. The analysis was performed using high-precision instruments.

The data on DSC diagrams and Table 4 show that the phase transition temperatures increase for polymer compositions that additionally contain polyorganosiloxanes (samples 1, 2, 3) compared to the polymer composition (sample 4), the temperatures of the onset of the glass transition effect increase by 2–3°C, the end of the effect by 3–4°C. The temperatures of the onset of decomposition for polymer compositions 1, 2, 3 significantly increase by 12–17°C, and the end of decomposition by 5–6°C compared to the polymer composition sample 4.

The results of TGA studies indicate an increase in the thermal stability of polymer compositions containing polyorganosiloxanes. The temperatures of loss of 10%, 20%, 30%, 40% of the mass (Table 5) increase for polymer compositions containing polyorganosiloxanes. A significant increase in temperature is observed for the polymer composition (sample 2) by 4–13°C, containing polyorganosiloxane, with a viscosity of 500 Pa·s. Our results are attributed to the different physicochemical, thermophysical properties of polyorganosiloxanes. The formation of the supramolecular structure of the obtained compositions containing polyorganosiloxanes has an important influence on the thermophysical properties of polymer compositions (this is evidenced by the results of phase transformation studies).

A significant decrease in viscosity is observed with an increasing shear rate (Fig. 3, 4). At the same time, a more significant decrease in viscosity is observed for polymer composition 2, containing polyorganosiloxane with a viscosity of 500 Pa·s. According to the influence of polyorganosiloxanes on the change in viscosity, the polymer compositions are arranged in the following order: 2 – viscosity of polyorganosiloxane 500 Pa·s; 1 – viscosity of polyorganosiloxane 50Pa·s; 3 – viscosity of polyorganosiloxane 1500 Pa·s. The effect of reducing shear stress is observed to achieve higher shear rates of polymer compositions sample 1 and sample 2 compared to polymer composition sample 4. The shear stress of polymer composition sample 3 is practically at the level of polymer composition sample 4, which does not contain polyorganosiloxanes.

By using the results of rheological studies, high productivity of cable articles manufacturing on extrusion lines for polymer compositions sample 1 and sample 2 (polyorganosiloxane viscosity 50–500 Pa·s) is achieved. The use of polyorganosiloxane with a viscosity of more than 500 Pa·s as a modifier does not give the desired result.

Analysis of the data in Table 6 reveals that the lowest viscosity value in the case of increasing shear rate is observed for composition sample 2, containing polyorganosiloxane with a viscosity of 500 Pa·s in comparison with polymer composition sample 4 (does not contain polyorganosiloxane). The viscosity for polymer composition sample 1 (containing polyorganosiloxane with a viscosity of 50 Pa·s) differs slightly in the direction of increase. The viscosity index for the polymer composition sample 3 (containing polyorganosiloxane with a viscosity of 1500 Pa·s) is practically the same as for the polymer composition that does not contain polyorganosiloxane.

The nature of the dependences indicates that achieving higher shear rate values during the flow of polymer compositions requires higher shear stresses. For polymer compositions, the shear stress increases towards higher values in the same direction as the increase in viscosity.

The results of studies on physical and mechanical properties indicate an increase in the melt flow index for polymer compositions sample 1 and sample 2, the activation energy of viscous flow is significantly reduced for polymer composition sample 2. The elongation at break increases. A significant result is also an increase in tensile strength and elongation at break after exposure for 7 × 24 hours at a temperature of 100°C compared to the polymer composition sample 4, which does not contain polyorganosiloxane.

These results, together with the results from thermophysical and rheological studies, indicate a change in the molecular and supramolecular structure towards a more ordered one and the provision of a thermostabilizing effect to polymer compositions due to the introduction of polyorganosiloxanes.

From the data in Table 9, it can be seen that with the introduction of polyorganosiloxanes, the specific volume electrical resistance increases from $1.1 \cdot 10^{16}$ to $1.32 \cdot 10^{16}$ Ohm·cm, the electrical strength increases from 45 to 48.5 kV/mm. The highest values of the specific volume electrical resistance and electrical strength were obtained for the polymer composition sample 2 (containing polyorganosiloxane, with a viscosity of 500 Pa·s).

Our research results could be used in the manufacture of fire-resistant halogen-free polymer compositions and cable articles based on them with improved technological and operational properties.

The results of our study have limitations and are adequate provided that high-precision dosing, mixing, and extrusion equipment is used for uniform distribution of polyorganosiloxanes.

In the future, the study may be advanced by making polymer concentrates of polyorganosiloxanes and introducing them into the polymer composition.

7. Conclusions

1. As a result of our study on the influence of polyorganosiloxanes on the formation of supramolecular structure of filled fire-resistant polymer compositions for cable articles, it was found that the phase transition temperatures increase by 2–4°C, the decomposition onset temperature by 12–17°C, and the decomposition end temperature by 5–6°C.

2. As a result of our study on the influence of polyorganosiloxanes with a viscosity of 50–500 Pa·s, a decrease in the melt viscosity of fire-resistant polymer compositions from 5.342 to 4.330 Pa·s with an increase in the shear rate from 20 to 60 s^{-1} was found.

3. As a result of our study on the influence of polyorganosiloxanes on the physical, mechanical, and electrophysical properties of fire-resistant halogen-free polymer compositions, it was found that:

– the elongation at break increases;

– the tensile strength and elongation at break increase after exposure for 7 × 24 hours at a temperature of 100°C compared to the polymer composition that does not contain polyorganosiloxane;

– the electrical resistance increases from $1.1{\cdot}10^{16}$ to $1.32{\cdot}10^{16}$ Ohm·cm, and the electrical strength increases from 45 to 48.5 kV/mm.

Conflicts of interest

The authors declare that they have no conflicts of interest in relation to the current study, including financial, personal, authorship, or any other, that could affect the study, as well as the results reported in this paper.

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Data availability

The data cannot be provided for the reasons stated in the data availability statement.

Use of artificial intelligence

The authors confirm that they did not use artificial intelligence technologies when creating the current work.

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