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Article

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DEPENDENCE OF CURRENT CONDUCTIVITY OF POLYETHYLENE-GRAPHITE COMPOSITIONS ON THE METHOD OF THEIR MANUFACTURE

The paper presents the results of the study of the dependence of the properties of polymer composites of the linear high-pressure polyethylene (LHPPET) system – graphite fillers of various types: natural GAK-2, thermally expanded (TEG) and with ultrasonic treatment. The test samples contained a filler in a wide concentration range (5–35 wt. %). Samples were manufactured using rolling, pressing and powder technology methods. Electrical resistance was measured by the four-probe potentiometric method at constant current. It is shown that the electrical resistance decreases sharply in a narrow concentration interval of 5–15 wt. % from $6.77 \cdot 10^{10}$ to $4.9 \cdot 10^{2}$ Ω·m (for compositions obtained by rolling), from $2.96 \cdot 10^{10}$ to 1.2 Ω·m (for pressed samples), from $2.87 \cdot 10^{9}$ to 0.14 Ω·m (for compositions obtained by powder technology). For samples of the LHPPET – GAK-2 system, a rapid decrease in electrical resistance is observed at filler concentrations of 5–30 wt. % from $1.36 \cdot 10^{12}$ Ω·m to $2.79 \cdot 10^{2}$ Ω·m. Using thermally expanded graphite with and without ultrasonic treatment (and to a lesser extent GAK-2) it is possible to obtain polymer composite materials (PCM) with volume resistivity ranging from 6.77 to $1.9 \cdot 10^{-3}$ Ω·m. It has been experimentally confirmed that electrical conductivity largely depends on the PCM manufacturing technology. The established dependences of the current conductivity of composites, depending on the manufacturing method, are associated with the corresponding structural differences. These structural differences are manifested in an increase in the number and area of contacts of filler particles – graphite and in a change in the thickness of the layers of the polymer matrix. Dry powder technology is the most effective method of obtaining LHPPET – graphite compositions. The optimal composition of the composition is 25 wt. % TEG and 75 wt. % LHPPET. Directions of practical use of the obtained results can be effectively used in industry and housing and communal economy.

Keywords: *thermally expanded graphite, high-pressure linear polyethylene, powder technology, electrical resistance, flow threshold.*

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1. Introduction

The term polymer composite materials (PCM) refers to heterophase systems obtained by combining two or more components (component parts), where one component is a matrix, in which the filler components, separated from the matrix by a distribution boundary, are distributed in a certain way. Such materials are distinguished by properties that none of the components taken separately can possess [1].

Until recently, PCMs were developed in most cases to improve such mechanical characteristics as stiffness, viscosity, and heat resistance. At the same time, in the future, a significant improvement in magnetic, electrical, and dielectric properties is confidently expected in this way [2–5].

Thus, the authors of [6–9] developed the scientific basis for the formation of the macrostructure and properties of thermoplastic polymer composite systems (polymer-carbon black or graphite) within a wide range of component concentrations. They developed the basics of the technology for obtaining effective composite materials with different content of components in the polymer-thermo-expanded graphite (TEG) system: promising methods of formation, schemes for manufacturing composite mixtures, materials and products. The regularities of the formation of PCM properties were determined depending on the macrostructure of clusters of components of their content, the nature of the distribution of components, the chemical nature of polymers, and adhesive interaction at the boundary of phase separation.

In works [10–13], the regularities of the phase formation of dispersed fillers in the polymer matrix were established for the first time. A physical model is proposed that takes into account the influence of interphase interactions on the percolation effect of the conductivity of the filling phase. The study of electrical and thermal conductivity in systems filled with metals made it possible to establish the peculiarities of these processes. The electrical and adhesive properties of electrically conductive polymer compositions were also analyzed.

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Works [14–16] are devoted to the properties of electrically conductive polymer composites based on carbon, in particular carbon nanotubes and nanoplates. Special attention is paid to the phenomenon of percolation, as well as factors that affect the percolation threshold. The mechanism of electrical conductivity and factors affecting electrical conductivity are considered.

In order to widely introduce into the production of the linear high-pressure polyethylene (LHPPET) – graphite system (brands GAK-2 and TEG based on it), it is necessary to develop methods of their production. To obtain homogeneous mixtures, it is considered promising to use such methods of obtaining as: rolling, pressing, powder technologies, as they are available and well researched by scientists. Reduction of compositional heterogeneity is achieved by preliminary mixing of the initial components, which ensures the stability of electrical resistance throughout the entire volume (plane) of the sample and uniform heat transfer of the product.

The purpose of this article is to assess the influence of the method of obtaining polymer compositions of the LHPPET – graphite system on their electrical conductivity and to determine the optimal composition of components. For this, a study of the physical and chemical properties of natural and thermally expanded graphite was carried out; optimal technological regimes for the production of PCM for each of the selected methods are determined; obtained samples of these compositions in a wide concentration range of graphite fillers of various types by methods of rolling, pressing and powder technology (with preliminary joint dispersion of components in a ball mill).

2. Materials and Methods

2.1. The object of research. Graphites of various types, in particular GAK-2, TEG based on it and TEG that has previously undergone ultrasonic (US) grinding, were selected as *research objects*. The studied properties of graphite are listed in Table 1.

Table 1

Physico-chemical properties of graphite fillers

Parameters	GAK-2	TEG	TEG with US grinding
Bulk density, g/cm^3	0.646	0.006	0.061
True density, g/cm^3	3.251	0.550	1.243
Total porosity, %	56.70	94.35	44.26
Specific effective surface, m^2/g after wetting with water by wetting with benzene	 1.7 1.5	 43.1 13.7	 71.2 27.6

LLDPE M3802R WP is a linear high-pressure polyethylene with a narrow molecular weight distribution and a large number of side branches. LHPPET is similar in structure to HPPET, but has the following main advantages:

– better operational properties at low and high temperatures;
– higher chemical resistance;
– 2–3 times greater resistance to tearing and puncture;
– high strength and relative elongation at break;
– surface gloss and resistance to cracking. LHPPET is the most commonly used polymer on the world market.

The properties of the LLDPE M3802RWP linear HPPET are shown in Table 2.

Table 2

Properties of LLDPE M3802RWP, Thailand

Indicator	LLDPE M3802RWP
Density, g/cm^3	0.924
PCR (230 °C, 2.16 kg), g/10 min	7
Tensile modulus, 1 mm/min, MPa	315
Tensile yield strength, 50 mm/min, MPa	12
Tensile strength, MPa	8.5
Relative elongation during stretching, %	More than 50
Impact strength according to Izod with notch, J/m	640
Wick softening temperature (50 °C/h, 10 N), °C	94

2.2. Preparatory stage of preparation of powder composition (LPEVT – graphite). The basis of obtaining composite materials is the process of mixing components, i. e. reducing compositional heterogeneity. Taking into account the different degree of dispersion of the starting materials (graphite and LHPPET) and their physical and chemical properties, a ball mill was used.

The technological process is carried out in a closed space and is not accompanied by environmental pollution. All uploaded materials are components of the composition, so this technology is zero-waste. The dispersion time, determined experimentally, is 24 hours for each filler concentration, which varied in the range of 5–30 wt. % in steps of 5 wt. %. The volume of the chamber is 0.5 l, the rotation speed of the rolls is 40–45 rpm.

Experimental samples were obtained from the resulting powdery composition.

2.3. Obtaining samples by rolling. Samples in the form of sheet blanks were obtained by the rolling method. A TRM 150 laboratory rolling machine manufactured by Neoplast Engineering Pvt Ltd., India (roll width – 350 mm, diameter – 115 mm) was used.

The main indicators of the technological mode of rolling of the LHPPET – graphite composition are given in Table 3.

Table 3

Technological mode of rolling the composition

Parameter	Value
Temperature of roll No. 1, °C	110
Temperature of roll No. 2, °C	130
PCM mass, g	100
Mixing time, min	20
Faction	1:1.2

2.4. Obtaining samples by the pressing method. To preserve the initial worm-like shape of TEG particles, the pressing method was used without prior co-dispersion of the composition.

Compression pressing on a hydraulic press with a static (non-impact) mechanism of action was used.

The main indicators of the technological mode of pressing the LHPPET – TEG composition are given in Table 4.

Table 4

Technological mode of pressing the composition

Parameter	Value
Temperature of the upper plate, °C	150±1
Temperature of the lower plate, °C	150±4
Pressing pressure, kg/cm^2	153
Pressing time, min	6

2.5. Powder technology. The essence of this technology consists in pre-mixing the initial components and applying the powdery mixture in an even layer on the plate. To prepare the filler, its preliminary ultrasonic treatment was carried out in an ultrasonic bath VK-9050 (China) with a frequency of 40 kHz for 24 hours.

To form the coating, the composition was sintered in a thermal cabinet.

The main indicators of the technological mode of powder formation of the LHPPET – TEG composition are given in Table 5.

Table 5

Technological mode of powder molding

Parameter	Value
Sintering temperature, °C	190±2
Sintering time, min	30
Thickness of the applied layer, mm	0.40–1.0

2.6. Electrophysical characteristics of composite materials of the LHPPET – graphite system. Electrical resistance was measured by the four-probe potentiometric method at constant current. Electrical contacts to the surface of the samples were attached with silver paste. The selected current that passed through the samples (0.01 mA) made it impossible to heat the samples. The voltage from the potentiometric contacts of the sample was applied to the input of the P363 potentiometer (Estonia) and was measured with an accuracy of 0.005 %. The current in the circuit was determined from the voltage drop across the Ω reference resistance. To exclude the influence of parasitic EMFs, each resistance measurement was carried out in two opposite current directions. The current direction of the sample circuit was changed by the current switch built into P363. The resistance between the potentiometric contacts was found by the formula:

$$R_x = \frac{1}{2}\left(\frac{U_1}{U_{e1}} + \frac{U_2}{U_{e2}}\right),$$

where U_1, U_2, U_{e1}, U_{e2} – the measured voltage drops on the sample and on the reference resistance of 1 Ω in two current directions, respectively.

The value of ρ of high-resistivity samples of composite materials with a low content of graphite filler was determined using the theraometer E6-13A (Estonia). The electrophysical characteristics of PCM were evaluated from the change in electrical resistance at room temperature for different methods of obtaining samples. The parameters of the experimental samples for the study of electrical conductivity obtained by rolling, pressing and powder technology were on average 0.7×0.7 cm; height 0.12, 0.2 and 0.07 cm, respectively.

3. Results and Discussion

Dependencies of electrical resistance on the concentration of GAK-2 and TEG for samples obtained by different technologies are presented in Fig. 1.

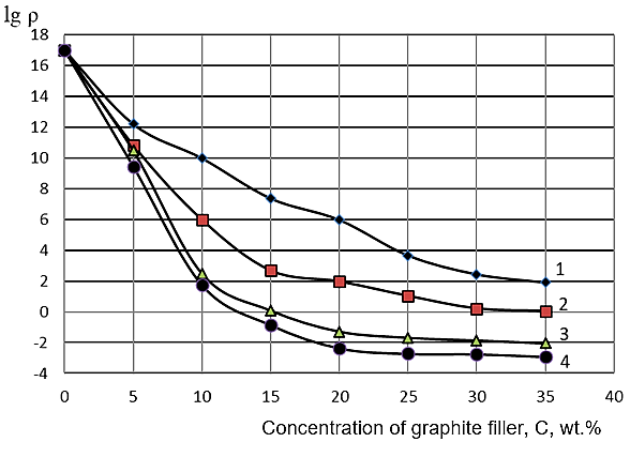

Fig. 1. Dependence of specific electrical resistance of PCM samples on graphite concentration: 1 – LHPPET – GAK-2 samples composition obtained by pressing; 2 – LHPPET – TEG samples obtained by rolling; 3 – LHPPET – TEG samples obtained by pressing; 4 – LHPPET – TRG samples with ultrasonic grinding, obtained by powder technology

The dependence of the logarithm of the specific electrical resistance of PCM samples on the concentration of graphite has the same power-law form. It is shown that the electrical resistance decreases sharply in a narrow concentration interval of 5–15 wt. % from $6.77 \cdot 10^{10}$ to $4.9 \cdot 10^2$ Ω·m (for compositions obtained by rolling). From $2.96 \cdot 10^{10}$ to 1.2 Ω·m (for pressed samples), from $2.87 \cdot 10^9$ to 0.14 Ω·m (for compositions obtained by powder technology). For samples of the LHPPET – GAK-2 system, a rapid decrease in electrical resistance is observed at filler concentrations of 5–30 wt. % from $1.36 \cdot 10^{12}$ Ω·m to $2.79 \cdot 10^2$ Ω·m. A further increase in the concentration of TEG and GAK-2 in PCM is accompanied by a continued decrease in electrical resistance, which is for pressed material with a concentration of 25 wt. % TEG $2.05 \cdot 10^{-2}$ Ω·m, for the composition obtained by sintering (TEG content, after ultrasonic grinding, 25 wt. %) – $1.9 \cdot 10^{-3}$ Ω·m, for a rolled sample with a TEG concentration of 30 wt. % – 1.67 Ω·m. For the pressed sample of the LHPPET– GAK-2 system (filler concentration 35 wt. %), the specific electrical resistance was 80.8 Ω·m. Since the obtained dependences have a power-law form, the expression of the theory of flow (percolation) should be used to describe them. According to this theory, the components of the PCM structure are considered using clusters.

On the basis of the obtained data of electrical studies, as well as the optical method (with the help of a JSM 6060 raster microscope, Japan), it was established that in the non-conductive region (for samples obtained by pressing and sintering, the filler content is 5–15 wt. %), the formation of separated from each other occurs clusters of TEG particles in the polymer matrix. When the

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content of TEG in PCM increases, the aggregation of isolated clusters of the filler takes place, and at a critical concentration equal to 20 wt. % (leakage threshold), PCM samples become conductors. But with such a content of TEG, continuous clusters with a portion of LHPPET do not disappear and the system consists of two interpenetrating meshes of polymer particles and filler. With a further increase in the concentration of the filler, the continuous cluster of polyethylene particles disappears and the system consists of an electrically conductive network of TEG particles and polymer regions isolated from each other, the sizes of which decrease with an increase in the concentration of TEG in PCM.

The resulting developments can be effectively used in industry and housing and communal services. At the same time, a limited number of types of graphite fillers were used in the presented work, therefore the use of other types of fillers and the expansion of directions of practical use require detailing the composition of composites in accordance with the conditions of operational purpose, which may be the subject of further research.

4. Conclusions

As a result of the work carried out, samples of compositions in a wide concentration range of graphite fillers of various types (5–35 wt. % in steps of 5 wt. %) were obtained by methods of rolling, pressing, and powder technology. Using TEG with and without ultrasonic treatment (and to a lesser extent GAK-2) it is possible to obtain PCM with a volume resistivity ranging from 6.77 to $1.9 \cdot 10^{-3}$ Ω·m. It has been experimentally confirmed that electrical conductivity largely depends on the PCM manufacturing technology. Dry powder technology is the most effective method of obtaining LHPPET – graphite compositions. The optimal composition of the composition is 25 wt. % TEG and 75 wt. % LHPPET. On an industrial scale, it is also advisable to produce such compositions by pressing (25 wt. % TEG).

Conflict of interest

The authors declare that they have no conflict of interest in relation to this research, whether financial, personal, authorship or otherwise, that could affect the research and its results presented in this paper.

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Data availability

The manuscript has no associated data.

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