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СЕГРЕГИРОВАННЫЕ ЭЛЕКТРОПРОВОДЯЩИЕ НАНОКОМПОЗИТЫ НА ОСНОВЕ ТЕРМОПЛАСТИЧНЫХ ЭЛАСТОМЕРОВ И ГРАФИТА

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В работе приводятся результаты исследования электропроводящих характеристик и комплекса физико-механических свойств нанокомпозитов на основе графита, широкого набора полиолефинов – полиэтилена низкой плотности, полиэтилена высокой плотности, изотактического полипропилена, рандом сополимера полипропилена, блок-сополимера пропилена с этиленом, сополимера этилена с гексеном и сополимера этилена с бутеном-1. Для рассматриваемых нанокомпозитов на основе полиолефинов определены оптимальные концентрации графита, при которых достигаются максимальные значения электропроводности, в пределах 10^{-2}-10^{-3} $(Ом·м)^{-1}$***. Дается подробное описание механизма туннельной и электронной электропроводности в рассматриваемых нанокомпозитах. Разработаны термопластичные эластомеры (ТПЭ) на основе полиолефинов и этилен-пропилен-диенового каучука. В широком концентрационном диапазоне определены закономерности изменения электропроводности нанокомпозитов на основе термопластичных эластомеров и нанодисперсного графита. При исследовании физико-механических свойств нанокомпозитов ТПЭ были определены разрушающее напряжение, предел текучести при растяжении, относительное удлинение, прочность на изгиб, теплостойкость, показатель текучести расплава и модуль Юнга. Установлена закономерность изменения зависимости «напряжение-деформация» для ТПЭ в зависимости от содержания этилен-пропилен-диенового каучука. Методами дериватографии, рентгенфазового и SEM анализов, электронной микроскопии проведены исследования по оценке структурных особенностей нанокомпозитов термопластичных эластомеров в зависимости от соотношения используемых компонентов смеси. Для наглядной интерпретации приводится схематическое изображение процессов, протекающих в межфазной области термопластичных эластомеров. Методом ренгенфазового анализа показана закономерность изменения степени кристалличности термопластичных эластомеров в зависимости от содержа-***

ния каучука и графита. Показана принципиальная возможность получения гибких электропроводящих материалов с заранее заданными свойствами путем регулирования соотношения компонентов в составе термопластичных эластомеров.

Ключевые слова: электропроводность, разрушающее напряжение, прочность на изгиб, термопластичный эластомер, инверсия фаз, теплостойкость, показатель текучести расплава, этилен-пропилендиеновый эластомер, полиолефины, межфазная область

SEGREGATED ELECTRICALLY CONDUCTIVE NANOCOMPOSITES BASED ON THERMOPLASTIC ELASTOMERS AND GRAPHITE

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The paper presents the results of a study of the electrical conductive characteristics and a complex of physical-mechanical properties of graphite-based nanocomposites, a wide range of polyolefins - low-density polyethylene, high-density polyethylene, isotactic polypropylene, random copolymer of polypropylene, block copolymer of propylene with ethylene, ethylene/hexene copolymer and ethylene/butene-1 copolymer. For the considered nanocomposites based on polyolefins, the optimal concentrations of graphite were determined, at which the maximum values of electrical conductivity are achieved, within the range of 10^{-2}–10^{-3} $(\Omega m)^{-1}$***. A detailed description of the mechanism of tunneling and electronic electrical conductivity in the nanocomposites under consideration is given. Thermoplastic elastomers (TPE) based on polyolefins and ethylene-propylene-diene rubber have been developed. In a wide concentration range, the regularities of changes in the electrical conductivity of nanocomposites based on thermoplastic elastomers and nanodispersed graphite have been determined. When studying the physical-mechanical properties of TPE nanocomposites, the tensile strength, yield strength, elongation at break, bending strength, Vicat softening temperature, melt flow rate, and Young's modulus were determined. The regularity of the change in the dependence "stress-strain" for TPE depending on the content of ethylene-propylene-diene rubber has been established. Using the methods of derivatography, X-ray phase and SEM analyses, and electron microscopy, studies were carried out to assess the structural features of nanocomposites of thermoplastic elastomers depending on the ratio of the mixture components used. For visual interpretation, a schematic representation of the processes occurring in the interfacial region of thermoplastic elastomers is given. The method of X-ray phase analysis shows the regularity of the change in the degree of crystallinity of thermoplastic elastomers depending on the content of rubber and graphite. The principal possibility of obtaining flexible electrically conductive materials with***

predetermined properties by controlling the ratio of components in the composition of thermoplastic elastomers is shown.

Keywords: electrical conductivity, tensile strength, bending strength, thermoplastic elastomer, phase inversion, Vicat softening temperature, melt flow rate, ethylene propylene diene elastomer, polyolefins, interfacial region

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Despite numerous studies carried out in the world in the direction of obtaining and investigating electrically conductive polymer composites, there are still open problems to establish the influence of the type of polymer matrix, crystallinity degree, fineness of the filler, and compatibility of the mixed components of the mixture on the mechanism of their electrical conductivity. The lack of consistency in the study of this problem and the establishment of a relationship with the structural features of the polymer matrix and filler does not allow today to make comprehensively justified predictions for the development of electrically conductive composites with predetermined electrical characteristics. The ongoing dispute between scientists on the issue of choosing nanodispersed particles or technical carbon nanotubes has also not yet given an unambiguous answer: what is better? An analysis of the state of the problem in this area allows us to conclude that the lack of an effective industrial technology for the production of graphene and carbon nanotubes and, accordingly, their high cost today do not allow us to draw any far-reaching conclusions about the prospects for their wide practical use in the near future. At the same time, the manufacturability of the production process of graphite nanoparticles of various grades has significantly expanded research on its use as the main component in the production of electrically conductive materials.

Undoubtedly, the use of nanoparticles as a filler in a polymer matrix was the beginning of a revolutionary approach to the development of a theoretical base or scientific foundations for the process of electrical conductivity in segregated polymer composites [1, 2]. The study of the problem of segregation in electrically conductive polymer nanocomposites opens up new possibilities for a complete interpretation of the behavior of nanoparticles during the formation of electronic or tunneling conductivity. The existence of the above unsolved problems creates certain difficulties for the development of a unified integral theory on the mechanism of electrical conductivity in inhomogeneous polymer systems [3, 4].

Research on the development and study of elastic electrically conductive nanocomposites based on thermoplastic elastomers is very limited [5, 6]. Thermoplastic elastomers, unlike rubber, are distinguished by a unique combination of physical-mechanical properties, elasticity, and manufacturability of processing into various types of structural products by injection molding and extrusion [7, 8]. Therefore, it was believed that research on the development of electrically conductive thermoplastic elastomers would significantly affect the production of new types of conductors, semiconductors and antistatic agents intended for use in various areas of the electronics industry.

In this regard, taking into account the high demand of the industry for the development of new types of electrically conductive materials, the purpose of the ongoing research was to study the problem of obtaining graphite-containing nanocomposites based on a wide range of polyolefins and thermoplastic elastomers.

EXPERIMENTAL PART

Materials

In this work, various types of polyolefins were used as a polymer matrix (Table 1). High density polyethylene (HDPE) grade PETİLEN YY I668 (UV) (PETKIM, Turkey), low density polyethylene (LDPE) brand 108-14, with an average molecular weight of 125000 ("SOCAR-POLYMER", Sumgayit, Azerbaijan), isotactic polypropylene (PP) brand HP500M (firm, SOCAR-POLYMER, Sumgayit, Azerbaijan), ethylene/1-hexene copolymer (EHC) grade PE6438R and ethylene/butylene copolymer (EBC) (PJSC, Nizhnekamskneftekhim Nizhnekamsk, Russia), random polypropylene copolymer (RPP) is a thermoplastic random copolymer of ethylene with propylene grade RP2400 (ATEX, Moscow, Russia) and block copolymer of ethylene with propylene (BEP) brand HB240P (YUSİDJİ, Korea).

Synthetic ethylene-propylene-diene rubber grade СКЭПТ-40 (EPDM) (PJSC Nizhnekamskneftekhim, Nizhnekamsk, Russia) with a Mooney viscosity of 37-43. Soot-filled EPDM has a tensile strength of 18.0 MPa, elongation at break of 350%.

Table 1

Physical-mechanical properties of the original polyolefins

***Таблица 1*. Физико-механические свойства исходных полиолефинов**

Polyolefins	Tensile strength, MPa	Bending strength, MPa	Elongation at break, %	Density, kg/m^3	Vicat softening temperature, °C	Melting temperature, °C	MFR, g/10min	Crystallinity degree, %
HDPE	31.3	34.4	435	965	139	145	5.6	82
LDPE	9.6	16.2	360	923	85	101	7.8	59
PP	33.0	85.0	30	903	160	169	3.6	65
EHC	37.4	42.2	810	932	115	122	5.1	75
RPP	28.5	30.4	600	904	131	145	1.78	62
EBC	27.1	29.7	880	942	116	128	4.6	71
BEP	25.6	26.5	200	900	148	155	2.9	66

Compatibilizers – (PE-g-MA) Exxelor PE1040 maleic anhydride functionalized high density polyethylene (ExxonMobil Chemical, Houston, TX, USA, MFR=52g/10min) designed to improve the compatibility of graphite with all types of polyethylene. Maleic anhydride-functionalized polypropylene (PP-g-MA) Exxelor PO1020 (Vanderbilt Chemicals, LLC, USA, MFR = 48g/10min) designed to improve the compatibility of carbon fillers with polypropylene and random polypropylene copolymer. The degree of maleic anhydride grafting in both compatibilizers is 0.5-0.6 wt %.

Graphite (Gr) (Sverdlovsk region, Rezh, Russia) – one of the allotropic modifications of carbon, has a layered structure. The layers of the crystal lattice, being parallel to each other, form a number of structural modifications, with symmetry from hexagonal system to trigonal. The layers are slightly wavy, almost flat, and consist of hexagonal layers of carbon atoms. Graphite grade ГС-2 with a particle size of 25-45 nm was used as the object of study.

Calcium stearate (CS) (Kalpataru Organics Pvt.Ltd. India). In order to improve processability, it acts as a lubricant for composite materials and uniform dispersion of the filler in the polymer matrix. Introduced into the composition of the polymer composite in an amount of 0.5-1.0 wt %

Aluminum powder (Al) (m-tec Powder GmbH, Germany) with a particle size of 80-95 nm was used as a metal filler. The main purpose of which in filled composites of polyolefins with graphite is to improve their thermal conductivity and adhesion to a metal surface.

The curing agent – sulfur (CAS 7704-34-9, Kaspiigaz LLC, Russia) is a chemical element with atomic number 16. Elemental sulfur is a bright yellow crystalline solid at room temperature. Under normal conditions, sulfur atoms form cyclic eight-atom molecules with the chemical formula S_8. Used as a crosslinking agent for polymer blends.

Polymer mixtures based on polyolefins and graphite were obtained as follows: Polyolefins were melted on a laboratory twin-screw extruder (SJZS-10A, China) in the temperature range of 140-180 °C, with the simultaneous incorporation of 2.0 wt % of a compatibilizer and various Gr concentrations (from 3.0 to 20 wt %).

In the process of obtaining thermoplastic elastomers based on HDPE and EPDM, the rubber concentration was varied in the range from 10 to 70 wt %. The maximum Gr concentration in all samples was 30 wt %.

Tensile strength, yield strength, and elongation at break of polymer composites were determined in accordance with GOST 11262-80 (ASTM D638). The stretching speed of the samples on the tensile testing machine is 50 mm/min. The test results were processed statistically according to GOST 14359-69.

Young's modulus in tension was determined in accordance with GOST 9550-81(ASTM D638) at a strain rate of 1%/min, loading was carried out to an elongation at breal of 0.5%. This method was used to determine the effect of the elastomeric component on the nature of the change in the elastic properties of TPE.

The bending strength was evaluated according to GOST 4648-2014 (ISO 178:2010). Use samples with a thickness of 5.0 mm and a width of 10 mm. Measuring speed 30 mm/min. To determine each indicator of strength characteristics, 5 samples were tested.

Used to determine the effect of the content of EPDM on the bending strength.

The melt flow rate (MFR) of polymeric materials was determined on a capillary rheometer brand MELT FLOW TESTER, CEAST MF50 (INSTRON, Italy) at a temperature of 190 °C and a load of 5 kg. The relative error of the experiment is 5%. The use of this method of analysis made it possible to control the melt flow of TPE nanocomposites, especially after the incorporation of a filler and subsequent sulfur vulcanization.

Combined thermal analysis was carried out on a STA 6000 synchronous thermal analyzer (Perkin Elmer) in a temperature range of 20-750 °C in a nitrogen atmosphere. Samples of polymers weighing 9-12 mg were heated in a nitrogen atmosphere at a rate of 25 °C/min. This method makes it possible to determine such thermophysical characteristics as the temperature range of melting and thermal destruction.

Vicat softening temperature was determined in accordance with GOST 15088-2014 (İSO 306:2004).

The electrical conductivity of the composites was determined in accordance with GOST 20214-74. The pressing of polymer samples for testing was carried out at a temperature of 160 °C for 4-6 min until a film 150 μm thick was obtained. Measurement of volumetric electrical resistance (for further calculation of specific volumetric resistance ρ and specific volumetric electrical conductivity σ) at direct current was carried out using an E6-13A teraohmmeter (OPF METROTEKS). The thickness of the samples was measured with an ИЗВ-2 optical meter. The processing of experimental data was carried out using Microsoft Excel 2016.

The electron microscope images were taken with a Leo 912 AB Omega transmission microscope. This method of analysis makes it possible to visually trace the nature of the change in the supramolecular structure of the sample depending on the type and concentration of the filler.

The degree of crystallinity of the composites was determined from X-ray diffraction patterns obtained on a Miniflex 600 powder X-ray diffraction device (Rigaku).

The particle size of graphite was determined on a laser diffraction analyzer model Mastersizer-3000 (Malvern). The method is based on the measurement of the angular dependence of the scattered light intensity during the passage of a laser beam through a dispersed sample. The range of particle size determination is 0.01-3000 μm.

When studying the peel resistance in the adhesive-substrate system, the test was carried out in such a way that the thickness of the plate of the polymer material was in the range of 1.6-1.8 mm. Corrugated aluminum foil was used as a substrate. The test was carried out on a tensile testing machine designed for testing plastics for tensile strength. To do this, the test fixture was installed in the lower clamp of the testing machine, the free end of the foil was fixed in the upper clamp. During the movement of the movable traverse, the foil was pulled from the surface of the polymer plate at a constant speed of 100 mm/min. The load was fixed on a section of the sample with a length of at least 115 mm.

RESULTS AND ITS DISCUSSION

Interest in the study of materials using graphite was due to several specific reasons. They concluded that graphite-containing nanocomposites, due to their layered structure, are characterized by both high electrical conductivity and wear resistance while maintaining a satisfactory level of MFR of the samples [9-11].

For a comparative assessment of the properties, a wide range of polyolefin dielectrics was used as a polymer matrix: HDPE, LDPE, PP, EHC, RPP, and BEP, as well as thermoplastic elastomers based on PO and EPDM. The electrical conductivity of these polyolefins is 10^{-13} $(\Omega m)^{-1}$. The task of the study was to obtain electrically conductive materials – conductors and semiconductors based on the above dielectrics. It is quite obvious that to solve this problem it was necessary to use additional components that would increase their electrical conductivity. In this case, such a solid component with electrical conductivity is graphite. In this work, preference was given to graphite, which, as is known, in addition to high electrical conductivity, imparted wear resistance and good melt fluidity to the polymer matrix [12].

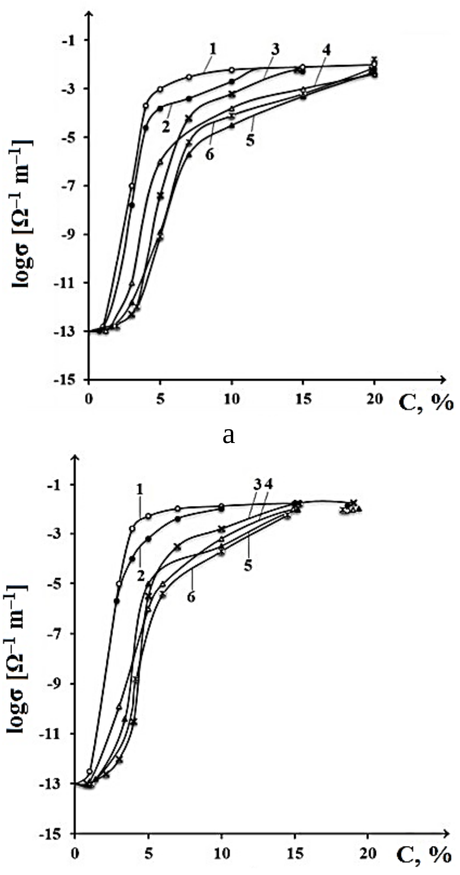
Graphite nanoparticles form aggregates of natural origin in the form of layered structures based on graphene [13]. In the process of mixing graphite in the melt mode with polyolefins, the resulting thermomechanical stresses contribute to the intercalation of macrochains of the polymer matrix into the interlayer space, followed by exfoliation, i.e., the separation of the outer layers of graphite – graphene [14]. This is explained by the fact that the layers of graphene in graphite are held together by weak van der Waals forces, which allow them to be easily separated from each other during thermomechanical action. Carbon has four free electrons. However, only three of the four electrons are involved in a covalent bond, so each carbon atom is only bonded to three carbons. The fourth electron migrates freely in the plane, making the graphite electrically conductive in a direction parallel to the plane. The electrical conductivity of graphite in the direction perpendicular to the plane of the layer, on the contrary, is hundreds of times less. The electrical conductivity of graphite is anisotropic, which depends on the direction within the graphite itself. It conducts electric current well in the direction parallel to the basal plane [15-17].

Fig. 1(a, b) shows the electrical conductivity of nanocomposites based on a number of polyolefins and graphite grade ГС-2. As can be seen from Fig. 1a, regardless of the type of polymer matrix, an increase in the electrical conductivity of all nanocomposites is observed with an increase in the graphite content. In this case, depending on the type of non-compatibilized polyolefin, the maximum value of electrical conductivity is achieved in the concentration range of 10-20 wt% and is equal to 10^{-2}-10^{-3} $(\Omega m)^{-1}$. From a comparative analysis of the curves in this figure, it can be seen that the compatibilized with PE-g-MA and PP-g-MA nanocomposites (Fig. 1b) have relatively high electrical conductivity values than non-compatibilized ones (Fig. 1a). PE-g-MA was introduced into HDPE, EHC, and LDPE in an amount of 2.0 wt. %, and PP-g-MA in an amount of 2.0 wt. % included in the PP, RPP, and BEP. For example, in non-compatibilized nanocomposites, the maximum electrical conductivity of samples based on PP, RPP, and BEP was achieved at 20 wt%, LDPE – 15 wt%, EHC – 12 wt%, HDPE – 10 wt% graphite content. In compatibilized nanocomposites, the maximum electrical conductivity of polyolefins is distributed as follows: HDPE – 5.0 wt%; EHC – 7.0 wt%; LDPE – 13 wt% and PP, RPP, BEP at 15 wt% content of graphite. It follows from the data obtained in these figures that the compatibilizer has a positive effect on the electrical conductivity of nanocomposites based on polyolefins and graphite. A situation is created when the accumulation of polar groups in the interspherulite space contributes not only to improving the compatibility of the mixed components of the mixture, but also to a significant increase in the adhesion of polar PE-g-MA macrochains on the developed specific surface area of nanoparticles [18]. According to the data in Fig. 1, HDPE nanocomposites have relatively better electrical conductivity. This fact is interpreted by the fact that during cooling and crystallization, growing crystalline formations of polyethylene displace graphite nanoparticles and PE-g-MA macrochain units containing polar groups of maleic anhydride into the interspherulitic amorphous region. According to this theory, the concentration of nanoparticles in the interspherulite space is several times higher than the average concentration over the entire volume of the polymer matrix. If the original HDPE has a degree of crystallinity equal to 82%, then this means that the bulk of the nanoparticles will be concentrated in the amorphous phase, which is only 18%. The data obtained allow us to assert that when 5.0 wt % of graphite is introduced into the polymer volume, its concentration in the amorphous (interspherolitic) region will increase by a factor of five and will be approximately 25 wt %. This is a vivid example of the segregation theory of the redistribution of nanoparticles in nanocomposites. Concentrating in the interspherolitic region, there comes a moment when graphite nanoparticles form a chain electrically conductive structure. Thus, in the supramolecular structure of the HDPE nanocomposite, double segregation occurs, consisting at the first stage in the separation into a crystalline and amorphous region, and the second stage in the redistribution and migration of nanoparticles into the interspherulitic amorphous space. In other words, the crystalline region, being a dielectric, remains free of nanoparticles, while the interspherolitic region, on the contrary, turns into a dense electrically conductive layer [19-20, 22].

It should also be taken into account that there is a distinction between tunneling and electronic conduction. Tunneling conduction predominates predominantly at low concentrations of graphite, which results in the formation of a dielectric nanolayer between nanoparticles. As the graphite content increases, this layer gradually becomes thinner, which affects the increase in the electrical conductivity of the nanocomposite. And, finally, when the interspherulite layer is saturated with graphite, the nanoparticles begin to directly contact each other, thereby promoting electronic conductivity. According to the curves shown in Fig. 1, the increase in electrical conductivity with increasing graphite content corresponds to tunneling conductivity. After reaching the maximum and constancy of the electrical conductivity in nanocomposites, there comes a moment when tunneling conductivity in the interspherolitic region changes to mixed and then to electronic conductivity. Mixed electrical conductivity corresponds to the state when, in the interspherolitic region of nanocomposites, the charge transfer process simultaneously occurs not only due to direct contact between conducting particles, but also due to electron tunneling through the dielectric interlayers of the polymer [12]. It should also be taken into account that in the process of direct contact of nanoparticles, in any case, between them there is a layer of a polymer matrix with a thickness of 1–3 nm, which leads to electronic conductivity. The proof of this is the results of the study shown in Fig. 1, according to which the electrical conductivity of the samples does not exceed 10^{-2} $(\Omega m)^{-1}$, while the value of this indicator for pure graphite is 10^{4} $(\Omega m)^{-1}$.

The effect of improving the electrically conductive properties of nanocomposites is manifested in the fact that in all samples the maximum electrical conductivity is achieved at a relatively low content of graphite nanoparticles [12, 23]. This circumstance is of fundamental importance, since the lower the concentration of the filler at which percolation occurs, the greater the probability of maintaining at a high level such fundamental properties of nanocomposites as elongation at break, strength, and MFR, which are directly related to the technological features of their processing by injection molding and extrusion. From a comparative analysis of the results obtained, it can be argued that, in general, the use of graphite as a filler makes it possible to obtain electrically conductive nanocomposites of various classes: conductors, semiconductors, and antistatics.

When studying the structure and properties of nanocomposites by derivatography, it is necessary to have sufficiently complete information regarding their melting point and thermal degradation. For example, Fig. 2 shows a DSC analysis of a HDPE* nanocomposite with 10 wt % graphite. As can be seen from this figure, the endothermic melting peak of the sample occurs at 150 °C, and the exothermic oxidation is recorded at 492 °C. Similarly, DSC analysis was carried out for all other samples of graphite-containing nanocomposites. More detailed results of derivatographic analysis are presented in Table 2.



a

b

Fig. 1 (a, b). Effect of graphite content on the electrical conductivity of non-compatibilized (a) and compatibilized polyolefins (b): 1– HDPE; 2–EHC; 3– LDPE; 4– PP; 5– RPP; 6– BEP

Рис. 1 (а, б). Влияние содержания графита на электропроводность некомпатибилизированных (а) и компатибилизированных полиолефинов (б): 1 – ПЭВП; 2 - СЭГ; 3 – ПЭНП; 4- ПП; 5- РПП; 6-БЭП

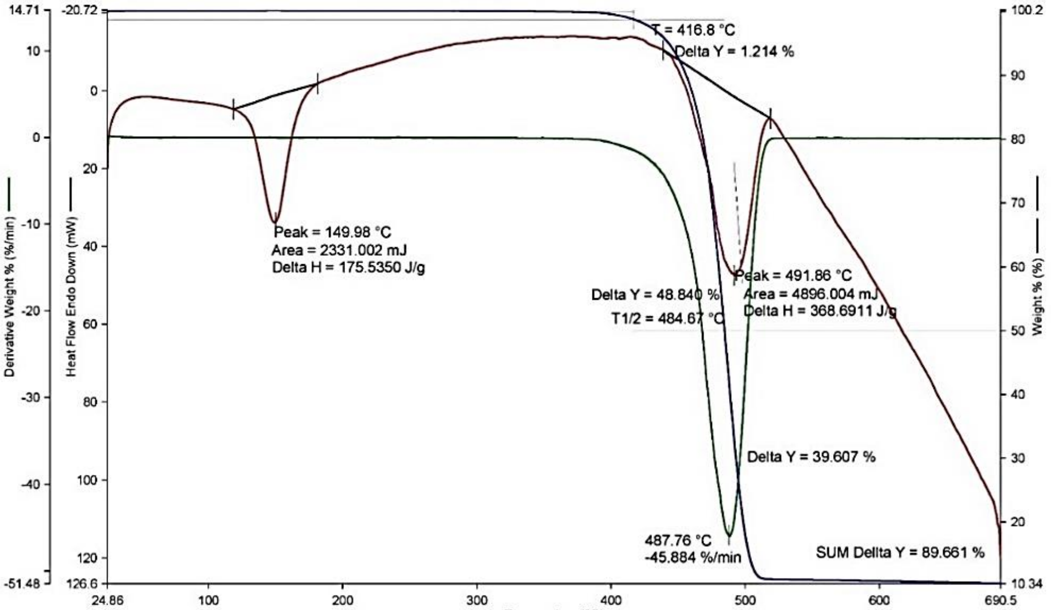


Fig. 2. Derivatographic analysis of the HDPE*+10 wt % Gr

Рис. 2. Дериватографический анализ нанокомпозита ПЭВП*+10%масс.Гр

Table 2

Results of derivatographic analysis of HDPE nanocomposites depending on graphite content

Таблица 2. **Результаты дериватографического анализа нанокомпозитов ПЭВП в зависимости от содержания графита**

Graphite content in HDPE *, wt %	$T_{m,}$ °C	$\Delta H_{m,}$ J/g	$T_{bd,}$ °C	Melting interval, °C	$\Delta H_{d,}$ J/g	T_{max} DTA °C	Δm_{700} %
HDPE*	145	177	435	66	512	494	-
5	149	189	432	59	493	491	4.69
10	150	175	417	59	369	492	10.34
15	149	175	435	60	418	491	15.43
20	143	166	427	59	394	494	18.33

Analyzing the data given in this Table, it can be established that the introduction of graphite into the composition of HDPE* in an amount of 5.0 wt% contributes to an increase in the melting point of the nanocomposite from 145 to 149 °C. A further increase in the content of graphite has practically no effect on the increase in the value of this indicator. The main differences are manifested in the HDPE* + 20 wt% graphite nanocomposite. In particular, it was shown that the melting point in this sample decreases from 149 °C to 143 °C, i.e. lower than that of the original HDPE. Such a noticeable decrease in the melting temperature in a nanocomposite with a 20 wt% graphite content indicates complex physical and physicochemical processes occurring in its supramolecular structure. It can be assumed that at such a high concentration of graphite in the melt, the high-molecular part of the polymer matrix is primarily adsorbed on the developed graphite surface, forming heterogeneous crystallization centers.

Thus, as a result of the selective selection (sorption) of high molecular weight fractions of HDPE* on the surface of nanoparticles, relatively lower molecular weight fractions remain out of contact with the solid surface. There is reason to believe that it is precisely because of this circumstance that the decrease in the melting temperature of a highly filled nanocomposite can be associated with the melting temperature of relatively low molecular weight HDPE fractions. And, finally, the second version of the decrease in the melting temperature may be due to the fact that at high concentrations of graphite nanoparticles, the mechanism of formation of crystalline formations changes significantly. And, indeed, according to the data presented by us in [24], at a 20 wt% content of graphite nanoparticles in HDPE*, the mechanism of growth of crystalline formations from a three-dimensional spherulite changes to a two-dimensional disc-shaped with the continuous formation of crystallization centers.

In the literature, the problem of obtaining electrically conductive nanocomposites based on thermoplastic elastomers has received very little attention [25-28]. This circumstance is explained by the fact that polymer mixtures based on thermoplastic polyolefins and synthetic rubbers are, as a rule, technologically incompatible, creating certain difficulties associated with ensuring their uniform mutual dispersion in the composition. But, as shown above, an effective method to improve the compatibility of a thermoplastic with an elastomer and a filler is the use of compatibilizers based on PE-g-MA and PP-g-MA in an amount of 2.0 wt. %. For this purpose, for example, we used EPDM as an elastomeric component, and HDPE as a thermoplastic and graphite as a filler. The choice of elastomer was due to the fact that polyolefins and elastomer are non-polar polymers. This fact made it possible to achieve better compatibility and mutual dispersibility of the components in the polymer mixture. However, the introduction of polar graphite into the composition of a non-polar polymer mixture again necessitates the use of a PE-g-MA compatibilizer. In this regard, it seemed interesting to study the concentration dependence of the electrical conductivity of nanocomposites of thermoplastic elastomers on the ratio of mixture components.

Fig. 3 shows the data on the effect of the HDPE/EPDM ratio and graphite content from 3.0 to 30 wt. % on the electrical conductivity of nanocomposites in polymer blends (30 wt %). The concentration of EPDM in HDPE was: 10; 30; 40; 50; 70%wt. It is quite clear that an increase in the concentration of the elastomeric component in the composition of HDPE will have a noticeable effect on a decrease in the degree of crystallinity of the polymer matrix. A similar regularity in the decrease in the degree of crystallinity of the polymer matrix will contribute to a decrease in the electrical conductivity of nanocomposites.

As can be seen from Fig. 3, as the concentration of the elastomeric component increases, a noticeable decrease in the electrical conductivity of the nanocomposites is observed. In a composition containing 10 wt% EPDM in HDPE, the electrical conductivity reaches its maximum [10^{-2} $(\Omega m)^{-1}$] at 15 wt% graphite content. With the introduction of 30 wt% of EPDM, the electrical conductivity noticeably decreases and reaches its maximum of 10^{-3} $(\Omega m)^{-1}$ at 25 wt% graphite content. In a composition with an elastomer concentration of more than 30 wt%, phase inversion occurs when the dispersed phase becomes a dispersed medium and vice versa. This is confirmed by curves 4-6, which have a slightly different pattern of change. Moreover, at a concentration of EPDM over 30 wt %, the maximum electrical conductivity at a 30 wt % graphite content becomes lower and fluctuates in the range 10^{-5}–$10^{-7}$$(\Omega m)^{-1}$. This circumstance is due to the fact that as the concentration of EPDM increases from 10 to 70 wt%, a sharp decrease in the degree of crystallinity of nanocomposites in the polymer mixture is observed. Using HDPE as an example, the effect of EPDM on the degree of crystallinity in nanocomposites occurs in the following sequence: (original HDPE) – 82%, (HDPE + + 10wt%EPDM) – 70%, (HDPE + 30wt%EPDM) – – 54%, (HDPE + 40wt%EPDM) – 43%, (HDPE + + 50wt%EPDM) – 35% and (HDPE + 70wt%EPDM) – – 18%. It becomes obvious that the lower the degree of crystallinity in the polymer mixture, the lower the probability of formation of a chain electrically conductive structure in the amorphous phase. The results of the study are in good agreement with the data shown in Fig. 3.

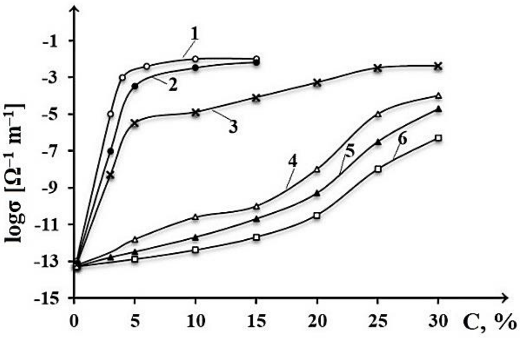


Fig. 3. The effect of graphite concentration on the electrical Fig. 3. The effect of graphite concentration on the electrical conductivity of HDPE + EPDM polymer blends compatibilized with 2.0 wt. % PE-g-MA: 1– HDPE; 2– HDPE+10 wt % EPDM; 3– HDPE+30 wt % EPDM; 4– HDPE+40 wt % EPDM; 5– HDPE+50 wt % EPDM; 6– HDPE+70 wt % EPDM

Рис. 3. Влияние концентрации графита на электропроводность компатибилизированных 2.0%масс. ПЭМА полимерных смесей ПЭВП+СКЭПТ: 1- ПЭВП; 2- ПЭВП+10%масс. СКЭПТ; 3-ПЭВП+30%масс. СКЭПТ; 4-ПЭВП+40%масс.СКЭПТ; 5- ПЭВП+50%масс. СКЭПТ; 6- ПЭВП+70%масс.СКЭПТ

Table 3 presents the results of a study of the selective effect of graphite concentration on the regularity of changes in the electrical conductivity of nanocomposites for a wide range of maleated polyolefins. In this case, for HDPE, LDPE, EHC and EHB, 2.0 wt. % PE-g-MA was used as a compatibilizer, and for PP, RPP and BEP, 2.0 wt. % PP-g-MA was used as a compatibilizer. Analyzing the data given in this table, it can be replaced that, regardless of the type of polyolefin, the introduction of graphite leads to a significant change in the electrical conductivity of nanocomposites. For a comparative assessment, the concentration of EPDM for each polyolefin was standard and amounted to a value equal to 30 wt %. The aim of the study was to study the effect of graphite concentration on the electrical conductivity of various types of thermoplastic elastomers. Table 3 discusses the regularity of changes in the electrical conductivity of nanocomposites based on polyolefins. As can be seen from this table, even the introduction of 30 wt % of graphite into the composition of a polymer mixture based on a number of polyolefins at best promotes electrical conductivity at the level of 10^{-3}-10^{-4} $(\Omega m)^{-1}$. And this is quite understandable, since with an increase in the content of the elastomeric component to 30 wt %, the degree of crystallinity of nanocomposites based on the considered polyolefins decreases. It should be noted that regardless of the type of polymer matrix, the introduction of 20-30 wt% of graphite contributes to the production of semiconductors with electrical conductivity in the range of 10^{-3}-10^{-4} $(\Omega m)^{-1}$. Samples of nanocomposites containing 10-15 wt % are also characterized by semiconductor properties, in which the electrical conductivity varies within 10^{-5}-10^{-6} $(\Omega m)^{-1}$. At 5.0 wt% content of graphite in the composition of thermoplastic elastomers, the value of electrical conductivity corresponds to antistatic agents.

For a comprehensive interpretation of the processes occurring in nanocomposites, it was considered necessary to consider in detail the main physical-mechanical properties of compatibilized thermoplastic elastomers based on polyolefins and EPDM, shown in Table 4. The concentration of EPDM in a mixture with thermoplastic polyolefins varied from 0 to 50 wt%. From a comparative analysis of the data in Table 4, it can be established that with an increase in the content of the elastomeric component, there is a general trend towards a decrease in all strength indicators and Vicat softening temperature of the polymer mixture.

At the same time, the MFR of the samples changes somewhat according to a different pattern. Initially, with an increase in the concentration of EPDM, it increases and then decreases, which, apparently, can be associated with an increase in the viscosity of the melt. A decrease in Young's modulus indicates a decrease in the elastic component of tensile strength. For a number of samples at 40 and 50 wt % EPDM content, the value of Young's modulus is not determined, which indicates the absence of Hooke's elastic deformation region. Consequently, the decrease in strength properties: tensile strength, yield strength, bending strength and Young's modulus is associated with amorphization of the supramolecular structure of semicrystalline polyolefins and a decrease in their degree of crystallinity. At the same time, attention should be paid to the nature of the change in the tensile strength and yield strength. As can be seen from this table, in all considered polyolefins at a certain content of EPDM, the values of the tensile strength and the yield strength are the same. In particular, for HDPE, EHC and EBC, the coincidence of these indicators occurs at 30 wt % content of EPDM, for LDPE – at 20 wt %, for PP, RPP and BEP – at 40 wt %. The equality of the yield strength and tensile strength is evidence of phase inversion, according to which the dispersed phase becomes a dispersed medium and vice versa. This state is characterized by the formation of thermoplastic elastomers, which exhibit the properties of rubber.

Table 3

The effect of graphite concentration on the change in the electrical conductivity of thermoplastic elastomers based on maleized LDPE*, PP*, RPP*, BEP*, EHC*, EBC* and EPDM

***Таблица 3*. Влияние концентрации графита на изменение электропроводности термопластичных эластомеров на основе малеинизированных ПЭНП*, ПП*, РПП*, БЭП*, СЭГ*, СЭБ* и СКЭПТ**

№	Nanocomposite composition, polyolefins + EPDM + graphite, wt %	Electrical conductivity, $(\Omega m)^{-1}$
1	LDPE* + 30EPDM:	
2	5.0 graphite	$1.4\cdot10^{-11}$
3	10 graphite	$3.2\cdot10^{-8}$
4	15 graphite	$2.4\cdot10^{-6}$
5	20 graphite	$5.0\cdot10^{-5}$
6	30 graphite	$4.5\cdot10^{-4}$
7	PP* + 30EPDM:	
8	5.0 graphite	$1.1\cdot10^{-10}$
9	10 graphite	$3.8\cdot10^{-6}$
10	15 graphite	$8.2\cdot10^{-5}$
11	20 graphite	$6.2\cdot10^{-4}$
12	30 graphite	$2.1\cdot10^{-3}$
13	RPP* + 30EPDM:	
14	5.0 graphite	$3.7\cdot10^{-10}$
15	10 graphite	$4.4\cdot10^{-7}$
16	15 graphite	$2.9\cdot10^{-6}$
17	20 graphite	$7.5\cdot10^{-5}$
18	30 graphite	$8.2\cdot10^{-4}$
19	BEP* + 30EPDM:	
20	5.0 graphite	$1.5\cdot10^{-9}$
21	10 graphite	$4.2\cdot10^{-7}$
22	15 graphite	$7.9\cdot10^{-6}$
23	20 graphite	$8.6\cdot10^{-5}$
24	30 graphite	$2.1\cdot10^{-3}$
25	EHC* + 30EPDM:	
26	5.0 graphite	$2.8\cdot10^{-9}$
27	10 graphite	$3.1\cdot10^{-6}$
28	15 graphite	$7.6\cdot10^{-5}$
29	20 graphite	$4.2\cdot10^{-4}$
30	30 graphite	$5.2\cdot10^{-3}$
31	EBC* + 30EPDM:	
32	5.0 graphite	$3.9\cdot10^{-9}$
33	10 graphite	$1.1\cdot10^{-6}$
34	15 graphite	$2.0\cdot10^{-5}$
35	20 graphite	$4.7\cdot10^{-4}$
36	30 graphite	$7.5\cdot10^{-3}$

Note: LDPE*, PP*, RPP*, BEP*, EHC*, EBC* – compatibilizer maleated polyolefins

Примечание: LDPE*, PP*, RPP*, BEP*, EHC*, EBC* – компатибилизатор малеинированные полиолефины

Table 4

Table 4. Physical-mechanical properties of TPE based on a mixture of polyolefins + EPDM + PE-g-MA (PP-g-MA)

***Таблица 4*. Физико-механические свойства ТПЭ на основе смеси полиолефинов+СКЭПТ+ПЭМА (ППМА)**

№	The content of EPDM-40 in the composition of polyolefins, wt %	Tensile strength, MPa	Yield strength, MPa	Elongation at break, %	Ultimate bending strength, MPa	MFR, g/10min.	Vicat softening temperature,°C	Young's modulus, MPa
1	**HDPE**	31.3	29.4	435	34.4	5.6	139	1150
2	HDPE + 10DM + 2 C_1	29.9	27.5	435	33.8	7.0	138	821
3	HDPE + 20DM + 2 C_1	23.0	22.3	450	29.4	5.6	133	436
4	**HDPE + 30DM + 2 C_1**	19.1	19.1	525	26.3	4.7	129	150
5	HDPE + 40DM + 2 C_1	14.5	14.5	430	20.8	4.0	118	85
6	HDPE + 50DM + 2 C_1	12.4	12.4	375	17.4	3.2	111	-
7	**LDPE**	9.6	9.0	360	16.2	7.8	85	209
8	LDPE + 10DM + 2 C_1	8.8	8.1	370	15.0	8.1	83	178
9	**LDPE + 20DM + 2 C_1**	6.1	6.1	360	11.9	7.2	77	94
10	LDPE + 30DM + 2 C_1	5.3	5.3	360	9.3	5.8	71	43
11	LDPE + 40DM + 2 C_1	4.2	4.2	335	7.2	3.1	67	-
12	LDPE + 50DM + 2 C_1	3.6	3.6	275	4.8	3.0	62	-
13	**PP**	33.0	34.6	30	85.0	5.4	160	1424
14	PP + 10DM + 2 C_2	31.5	32.2	45	86.8	4.3	158	1142
15	PP + 20DM + 2 C_2	27.9	28.4	60	71.5	3.5	152	655
16	PP + 30DM + 2 C_2	21.5	22.0	70	47.6	2.9	137	287
17	**PP + 40DM + 2 C_2**	17.3	17.3	65	39.3	2.3	129	108
18	PP + 50DM + 2 C_2	13.2	13.2	55	33.1	2.0	121	-
19	**EHC**	37.4	35.8	810	42.2	7.4	115	1234
20	EHC + 10CK + 2 C_1	34.0	35.9	810	40.8	6.3	113	866
21	EHC + 20DM + 2 C_1	29.4	30.6	790	37.5	5.3	109	475
22	**EHC + 30DM + 2 C_1**	23.5	23.5	790	31.1	3.5	103	185
23	EHC + 40DM + 2 C_1	18.2	18.2	570	24.9	2.7	98	99
24	EHC + 50DM + 2 C_1	15.5	15.5	465	19.7	2.2	95	-
25	**EBC**	27.1	28.4	880	38.2	6.2	113	1115
26	EBC + 10DM + 2 C_1	25.2	27.8	845	37.6	7.1	112	829
27	EBC + 20DM + 2 C_1	20.6	21.5	755	34.4	4.7	108	434
28	**EBC + 30DM + 2 C_1**	16.8	16.8	740	27.5	3.6	103	168
29	EBC + 40DM + 2 C_1	13.4	13.4	730	19.9	2.9	99	75
30	EBC + 50DM + 2 C_1	10.2	10.2	650	15.8	2.2	92	-
31	**RPP**	28.5	26.4	600	30.4	3.7	131	802
32	RPP + 10DM + 2 C_2	26.4	23.3	600	28.6	3.0	127	464
33	RPP + 20DM + 2 C_2	23.0	21.5	640	24.9	2.5	122	215
34	RPP + 30DM + 2 C_2	17.9	16.9	685	21.2	2.0	116	107
35	**RPP + 40DM + 2 C_2**	14.1	14.1	545	18.4	1.4	112	70
36	RPP + 50DM + 2 C_2	10.8	10.8	350	13.9	1.6	105	-
37	**BEP**	25.6	26.9	200	26.5	4.9	148	712
38	BEP + 10DM + 2 C_2	23.9	24.7	220	25.5	4.0	145	486
39	BEP + 20DM + 2 C_2	20.7	21.9	245	22.0	3.3	140	196
40	BEP + 30DM + 2 C_2	16.1	17.0	250	18.3	2.6	135	107
41	**BEP + 40DM + 2 C_2**	12.5	1.5	205	14.2	2.0	129	65
42	BEP + 50DM + 2 C_2	9.9	9.9	165	11.3	1.6	120	-

Note: DM- EPDM: C_1 – PE-g-MA; C_2 – PP-g-MA

Примечание: DM- EPDM: C_1 – PE-g-MA; C_2 – PP-g-MA

To confirm our arguments regarding the phase inversion in the polyolefin + EPDM polymer mixture, we carried out studies aimed at studying the deformation of thermoplastic elastomer nanocomposites from shear stress during uniaxial tension. The results of studying the deformation curves are shown in Fig. 4. As can be seen from this figure, with an increase in the content of EPDM in the composition of HDPE, the shear stress decreases. In the original HDPE and the sample with 10 wt% EPDM, one can still notice the elastic component at the minimum values of elongation. At 30 wt % content of EPDM in HDPE and above, the elastic component is replaced by an S-shaped curve characteristic of thermoplastic elastomers with rubber properties. It should be noted that as the content of the elastomeric component in the composition increases, we actually obtain compositions with different degrees of crystallinity, which, as noted above, plays a significant role in changing the electrical conductivity of nanocomposites.

Table 5 shows the results of a study of the influence of the content of synthetic rubber grade EPDM on the physical-mechanical properties of sulfur-cured electrically conductive TPE nanocomposites. In [21], we showed that Al nanoparticles have a significant effect on the increase in the peel resistance of nanocomposites to aluminum and copper foil. The latter circumstance is due to an increase in the adhesive contact between the macrochains of the modified polyolefin on the developed surface of the nanoparticles. The use of Al nanoparticles in the composition of the TPE nanocomposite significantly enhances the affinity of the polymer matrix for aluminum foil. As regards the electrical conductivity of nanocomposites, the graphite nanoparticles play the main role in increasing this index [12, 22].

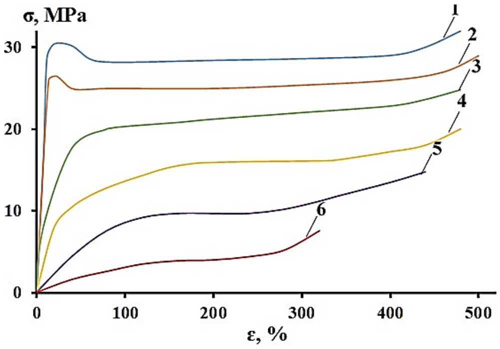


Fig. 4. The influence of EPDM content on “stress-strain” curves for compatibilized 2.0 wt. % PE-g-MA polymer mixtures based on HDPE + EPDM: 1- original HDPE; 2- 10; 3- 20; 4- 30; 5- 40; 6- 50, wt % EPDM

Рис. 4. Влияние содержания СКЭПТ на кривые зависимости «напряжение-деформация» для компатибилизированных 2.0%масс. ПЭМА полимерных смесей на основе ПЭВП+СКЭПТ: 1- исходный ПЭВП; 2- 10; 3- 20; 4- 30; 5- 40; 6- 50, %масс. СКЭПТ

Table 5

Physical-mechanical and physical-chemical properties of sulfur-cured multifunctional electrically conductive TPE nanocomposites based on maleated PO, EPDM, Gr, Al and calcium stearate

***Таблица 5*. Физико-механические и физико-химические свойства вулканизованных серой многофункциональных электропроводящих нанокомпозитов ТПЭ на основе малеинизированных ПО, СКЭПТ, Гр, Al и стеарата кальция**

Composition of nanoelastoplastics, wt %	Electrical conductivity σ, Ω^{-1} m^{-1}	Coefficient of thermal conductivity, W/m·K	Peel resistance, g/cm	Tensile strength, MPa	Bending strength, MPa	MFR g/10min.
HDPE+30EPDM+2C_1+20Gr+1Al+1CS+3S	$6.8\cdot10^{-3}$	3.5	41	25.4	31.2	3.7
LDPE+20EPDM+2C_1+20Gr+1Al+1CS+3S	$4.4\cdot10^{-3}$	3.5	40	12.4	15.1	5.3
PP+40EPDM+2C_2+20Gr+1Al+1CS+3S	$1.2\cdot10^{-3}$	3.6	42	27.0	44.6	2.9
EHC+30EPDM+2C_1+20Gr+1Al+1CS+3S	$5.7\cdot10^{-3}$	3.5	39	28.2	40.3	4.0
RPP+40EPDM+2C_2+20Gr+1Al+1CS+3S	$2.1\cdot10^{-3}$	3.4	35	24.0	30.2	3.6
BEP+40EPDM+2C_2+20Gr+1Al+1CS+3S	$1.7\cdot10^{-3}$	3.5	38	21.3	23.4	2.8

Note: Gr– graphite; C_1– PE-g-MA; C_2– PP-g-MA; Al– aluminum; CS– calcium stearate; S– sulfur

Примечание: Gr– графит; C_1– ПЭ-г-МА; C_2– ПП-г-МА; Al– алюминий; CS– стеарат кальция; S– сера

The introduction of 20 wt% graphite and higher nanoparticles promotes the formation of TPE nanocomposites and the formation of chain electronic conductivity, in which the electrical conductivity is on average 10^{-3} $(\Omega m)^{-1}$. There is reason to believe that during the cooling of samples, crystallization, and growth of spherulite formations from the melt, graphite nanoparticles are displaced into the interspherulitic amorphous region of the nanocomposite. As a result, graphite nanoparticles accumulate in the form of chains around the spherulite formations, which predetermine the high electrical conductivity of the nanocomposite. However, as the content of the amorphous component in the HDPE composition increases and, accordingly, the degree of crystallinity of the nanocomposite decreases, a relatively larger amount of graphite nanoparticles is required to fill the amorphous space and form a chain structure for tunneling or electronic conduction. At the same time, it should be borne in mind that, unlike conventional dispersed fillers, nanoparticles are 50-60 times smaller in size.

In this connection, to achieve the desired effect in changing the properties in quantitative terms of nanoparticles, much less is required. Actually, this fact is one of the important advantages of nanocomposites over conventional filled polymer systems. To confirm the above, Table 6 provides data on the content of vinyl groups in the composition of some polyolefins based on 1000 C. Therefore, the structure of TPE after sulfur vulcanization will resemble a mixture of relatively tightly cross-linked elastomers in a matrix of weakly cross-linked thermoplastic polyolefin.

And, indeed, according to the data of Table 5, with an increase in the sulfur content, the sharpest decrease in the value of MFR occurs in those samples in which the proportion of elastomer in the composition of the elastomer is 30-40 wt%. It should be noted that, ultimately, the fundamental technological characteristic of TPE is the MFR, which characterizes its ability to be processed by injection molding or extrusion. Therefore, when choosing the formulation of vulcanizates, first of all, it is necessary to take into account the technological features of their processing. So, for example, TPE vulcanizates can have high physical-mechanical properties and, at the same time, low MFR values, which make it difficult to process them on standard equipment. Difficulties are manifested in the fact that, due to the crosslinking, the TPE vulcanizate is characterized by a relatively high melt viscosity, as a result of which, simultaneously with a sharp increase in the casting pressure, the load on the screw increases significantly in the material cylinder. In this regard, in order to reduce the viscosity of the melt, it becomes necessary to increase the temperature of the melt of the cross-linked TPE in the material cylinder. Together, all these factors can lead to an unjustified increase in energy costs. Therefore, when choosing the optimal concentration of the mixture components, we generally focused on maintaining the value of the MFR of vulcanizates at a level not lower than 1.0 g/10 min.

For greater clarity, we show in Fig. 5 a schematic representation of the processes occurring in the interfacial region of TPE nanocomposites. As can be seen from this figure, with an increase in the content of the elastomeric component in TPE, the interfacial region expands, as a result of which processes are observed that contribute to the disruption of the chain structure of nanoparticles, followed by a decrease in the tunneling electrical conductivity of nanocomposites.

Table 6

Vinyl groups in HDPE and LDPE

Таблица 6. **Винильные группы в ПЭВП и ПЭНП**

Polyolefins	Terminal vinyl groups per 1000 C atoms, %	Vinylidene groups per 1000 C atoms, %	Trans-vinyl groups, per 1000 C atoms, %
HDPE	17	71	12
LDPE	43	32	25

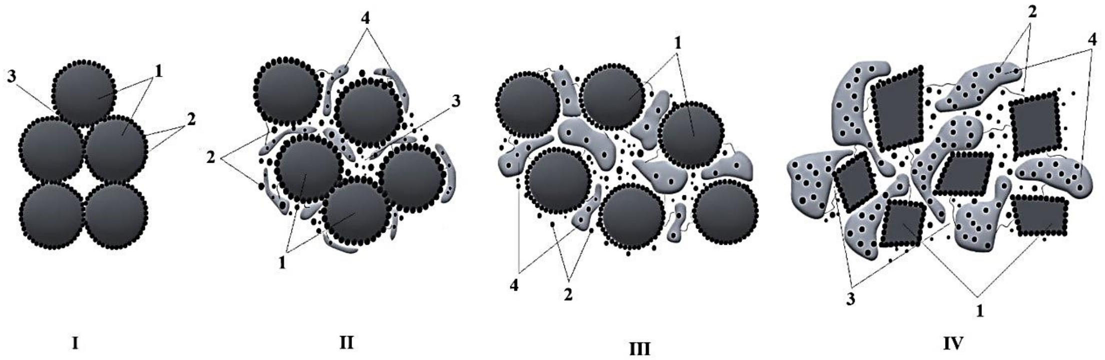


Fig. 5. Schematic representation of the redistribution of graphite nanoparticles and an elastomer component (EPDM) in the interfacial region of TPE. 1- crystalline region, 2- nanoparticles, 3- interfacial region, 4- crosslinked elastomer. The content of the elastomeric component: I- polyolefin nanocomposite without elastomer; II- TPE nanocomposite with 10-20 wt % elastomer content; III – TPE nanocomposite with 30-40 wt % elastomer content; IV- nanocomposite with 50 wt % elastomer content

Рис. 5. Схематическое изображение перераспределения наночастиц графита и эластомерного компонента (СКЭПТ) в межфазной области ТПЭ. 1- кристаллическая область, 2- наночастицы, 3- межфазная область, 4- сшитый эластомер. Содержание эластомерного компонента: I- нанокомпозит полиолефина без эластомера; II- нанокомпозит ТПЭ с 10 -20%масс. содержанием эластомера; III – нанокомпозит ТПЭ с 30-40%масс. содержание эластомера; IV- нанокомпозит с 50%масс. содержанием эластомера

As can be seen from Fig. 5, the elastomers in the TPE composition are a kind of "islands" in the interfacial region of crystalline polyolefin. We do not exclude the possibility that during the mixing of the mixture components in the elastomeric phase, some of the nanoparticles will be occluded in the composition of the vulcanizates. The other part of the nanoparticles, apparently, will be distributed in the interspherolitic region to create electrically conductive chains or clusters. Such a redistribution of nanoparticles in the composition of TPE will certainly affect the overall decrease in the electrical conductivity of TPE. Therefore, to ensure the required level of electrical conductivity in TPE, it will be necessary to introduce a significantly larger amount of nanofiller. It should also be taken into account that an increase in the elastomer content in the polyolefin composition will contribute to a gradual decrease in the role of "through chains" in the formation of the strength characteristics and plasticity of TPE nanocomposites. In this case, phase inversion will lead to a transition from plastic to highly elastic deformation, which is characteristic of rubber.

CONCLUSIONS

Thus, based on the foregoing, it can be argued that the electrical conductivity of nanocomposites based on a wide range of polyolefins and graphite has been studied. It is shown that the compatibilizer, the type of polyolefin, and the degree of crystallinity of the polymer matrix have a significant effect on the concentration dependence of the electrical conductivity of graphite-containing nanocomposites. The possibility of obtaining flexible electrically conductive graphite-containing nanocomposites of thermoplastic elastomers based on a mixture of polyolefin and EPDM has been considered for the first time. A stress – strain curve was constructed for nanocomposites based on HDPE + EPDM. An increase in the content of the elastomeric component leads to the formation of an S-shaped dependence characteristic of rubber. It is shown that with an increase in the elastomeric component, a noticeable decrease in the electrical conductivity of TPE nanocomposites is observed.

The simultaneous use of graphite, aluminum, and calcium stearate nanoparticles in the composition of vulcanized TPE made it possible to obtain multifunctional electrically conductive nanocomposites characterized by high strength characteristics, thermal conductivity, heat resistance, and adhesive strength to an aluminum substrate while maintaining the MFR values within the limits sufficient for their processing by injection molding.

Electrically conductive TPE nanocomposites of a segregated structure can be used in the electronics industry as photovoltaic generators, batteries, organic solar cells, LEDs, flexible and transparent displays, electromagnetic screens, etc.

The authors declare the absence a conflict of interest warranting disclosure in this article.

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ЛИТЕРАТУРА

1. **Sadasivuni K.K., Hegazy S.M., Moustafa Abdullah Aly A.A.A.** Chapter 11 - Polymers in electronics In: Polymer Science and Innovative Applications. Ed. by Mariam Al Ali AlMaadeed, Deepalekshmi Ponnamma, Marcelo A. Carignano. Elsevier. 2020. P. 365-392. DOI: 10.1016/B978-0-12-816808-0.00011-1.
2. **Алоев В.З., Жирикова З.М., Тарчокова М.А.** Эффективность использования нанонаполнителей разных типов в полимерных композитах. *Изв. вузов. Химия и хим. технология.* 2020. Т. 63. Вып. 4. С. 81-85. DOI: 10.6060/ivkkt.20206304.6158.
3. **Kakhramanov N.T., Allahverdiyeva Kh.V., Nurullayeva D.R.** On preparation of polymer composites with improved electrophysical and physical-mechanical properties. *Chem. Problems.* 2019. N 1. P. 26-41. DOI: 10.32737/2221-8688-2019-1-26-40.
4. **Глазырин А.Б., Абдуллин М.И., Басыров А.А., Колтаев Н.В., Кокшарова Ю.А.** Электропроводящие полимерные материалы для 3d-печати. *Вестн. Башкир. Ун-та.* 2016. Т. 21. №1. С. 81-85.
5. **Kravchenko T.P., Gorbunova I.Y., Filatov S.N., Kerber M.L., Rakov E.G., Kireev V.V.** Polypropylene-based nanostructured materials. *Int. Polym. Sci.* 2017. V. 44. N 4. P. 45-47. DOI: 10.1177/0307174X1704400409.
6. **Kakhramanov N.T., Azizov A.G., Osipchik V.S., Mamedli U.M., Arzumanova N.B.** Nanostructured composites and polymer materials. *Int. Polym. Sci.* 2017. V. 44. N 2. P. 37-47. DOI: 10.1177/0307174X1704400207.
7. **Дудочкина Е.А., Лямкин Д.И., Рудаков Г.Ф.** Модификация технологических и механических свойств высоконаполненных полиэтиленовых композиций.

REFERENCES

1. **Sadasivuni K.K., Hegazy S.M., Moustafa Abdullah Aly A.A.A.** Chapter 11 - Polymers in electronics In: Polymer Science and Innovative Applications. Ed. by Mariam Al Ali AlMaadeed, Deepalekshmi Ponnamma, Marcelo A. Carignano. Elsevier. 2020. P. 365-392. DOI: 10.1016/B978-0-12-816808-0.00011-1.
2. **Aloyev V.Z., Zhirikova Z.M., Tarchokova M.A.** Effectiveness of use of nano fillers of different types in polymeric composites. *ChemChemTech [Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol.].* 2020. V. 63. N 4. P. 81-85 (in Russian). DOI: 10.6060/ivkkt.20206304.6158.
3. **Kakhramanov N.T., Allahverdiyeva Kh.V., Nurullayeva D.R.** On preparation of polymer composites with improved electrophysical and physical-mechanical properties. *Chem. Problems.* 2019. N 1. P. 26-41. DOI: 10.32737/2221-8688-2019-1-26-40.
4. **Glazyrin A.B., Abdullin M.I., Basyrov A.A.** Conductive polymer materials for 3d printing. *Vestn. Bashkir. Uni-ta.* 2016. V. 1. N 1. P. 81-85 (in Russian).
5. **Kravchenko T.P., Gorbunova I.Y., Filatov S.N., Kerber M.L., Rakov E.G., Kireev V.V.** Polypropylene-based nanostructured materials. *Int. Polym. Sci.* 2017. V. 44. N 4. P. 45-47. DOI: 10.1177/0307174X1704400409.
6. **Kakhramanov N.T., Azizov A.G., Osipchik V.S., Mamedli U.M., Arzumanova N.B.** Nanostructured composites and polymer materials. *Int. Polym. Sci.* 2017. V. 44. N 2. P. 37-47. DOI: 10.1177/0307174X1704400207.
7. **Dudochkina E.A., Lyamkin D.I., Rudakov G.F.** Modification of technological and mechanical properties of high filled polyolefin compounds. *Plast. Massy.* 2018. N 7-8. P. 44-46 (in Russian). DOI:10.35164/0554-2901-2018-7-8-44-46.

Пласт. массы. 2018. № 7-8. С. 44-47. DOI: 10.35164/0554-2901-2018-7-8-44-46.

8. **Abreu Martins S.De, Reis J.M., Costa Mattos Da H.** Influence of graphite powder and carbon black weight percentages on the electrical properties of epoxy composite plates. *Mater. Sci. Forum*. 2016. V. 869. P. 366–370. DOI: 10.4028/www.scientific.net/MSF.869.366.
9. **Кахраманов Н.Т., Аллахвердиева Х.В., Мустафаева Ф.А., Насибов Х.Н.** Теоретические аспекты процесса литья под давлением многокомпонентных нанокомпозитов на основе полиолефинов. *Изв. вузов. Химия и хим. технология.* 2022. Т. 65. Вып. 1. С. 83-91. DOI: 10.6060/ivkkt.20226501.6451.
10. **Haghnegahdar M., Naderi G., Ghoreishy M.H.R.** Electrical and thermal properties of a thermoplastic elastomer nanocomposite based on polypropylene/ethylene propylene diene monomer/graphene. *Soft Mater.* 2017. V. 15. N 1. P. 82–94. DOI: 10.1080/1539445X.2016.1268622.
11. **Панин С.В., Корниенко Л.А., Алексенко В.О., Иванова Л.Р., Шилько С.В., Буслович Д.Г.** Сравнениеэффективности углеродных нано и микроволокон в формировании физико-механических и триботехнических характеристик полимерных композитов на основе высокомолекулярной матрицы. *Изв. вузов. Химия и хим. технология.* 2016. Т. 59. Вып. 9. С. 99-105. DOI: 10.6060/tcct.20165909.13y.
12. **Аллахвердиева Х.В., Кахраманов Н.Т., Дадашева Э.В.** Электропроводящие нанокомпозиты на основе полиэтилена высокой плотности и различных типов углеродсодержащих наполнителей. *Пласт. массы.* 2023. № 5-6. С. 53-56. DOI: 10.35164/0554-2901-2023-5-6-53-56.
13. **Janeesh G.M., Meera V., Shalom A.M., Rajan Babu D., Arunai Nambi Raj N., Sreekanth M.S., Samba Siva V., Sumangala T.P.** Enhanced electrical conductivity and structural, mechanical characterization of standalone poly(vinyl alcohol)-graphite nanoplatelets composite films. *J. Appl. Polym. Sci.* 2021. V. 138. N 10. P. 49976. DOI: 10.1002/app.49976.
14. **Jin F.L., Chu N., Yao Sh.Sh., Park S-J.** Thermal and electrical conductivity improvement in epoxy resin with expanded graphite and silver plating. *Korean J. Chem. Eng.* 2022. V. 39. P. 2182-2191. DOI: 10.1007/s11814-022-1065-8.
15. **Kakhramanov N.T., Gasimova G.Sh., Pesetsriy S.S., Kakhramanly J.N., Gurbanova R.V., Hajiyeva R.Sh., Suleymanova E.I.** Physical and mechanical properties of nanocomposites based on block copolymer propylene with ethylene and graphite. *Chem. Problems.* 2019. N 1. P. 72-80. DOI: 10.32737/2221-8688-2019-1-72-80.
16. **Zhao L., Xia W., Zhang P.** Economical conductive graphite-filled polymer composites via adjustable segregated structures: Construction, low percolation threshold, and positive temperature coefficient effect. *J. Appl. Polym. Sci.* 2021. V. 138. N 17. 50295. DOI: 10.1002/app.50295.
17. **Ye Ch.M., Shentu B.Q., Weng Z.X.** Thermal conductivity of high density polyethylene filled with graphite. *J. Appl. Polym. Sci.* 2006. V. 101. N 6. P. 3806-3810. DOI:10.1002/app.24044.
18. **Kakhramanov N., Allahverdiyeva Kh., Gahramanli Y., Mustafayeva F., Martynova G.** Physical-mechanical properties of multifunctional thermoplastic elastomers based on polyolefins and styrene-butadiene elastomer. *J. Elastomers Plast.* 2023. V. 55. N 2. P. 279-302. DOI: 10.1177/00952443221147030.
19. **Allahverdiyeva Kh.V., Kakhramanov N.T., Mustafayeva F.A.** Structure and properties of conducting composites based on polyolefins and carbon black. *Russ. J. Appl. Chem.* 2022. V. 95. N 8. P. 1146–1152. DOI: 10.1134/S1070427222080092.

8. **Abreu Martins S.De, Reis J.M., Costa Mattos Da H.** Influence of graphite powder and carbon black weight percentages on the electrical properties of epoxy composite plates. *Mater. Sci. Forum*. 2016. V. 869. P. 366–370. DOI: 10.4028/www.scientific.net/MSF.869.366.
9. **Kakhramanov N.T., Allahverdiyeva Kh.V., Mustafayeva F.A., Nasibov Kh.N.** Theoretical aspects of the injection molding process of multicomponent nanocomposites based on polyolefins. *ChemChemTech [Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol.].* 2022. V. 65. N 1. P. 83-91. DOI: 10.6060/ivkkt.20226501.6451.
10. **Haghnegahdar M., Naderi G., Ghoreishy M.H.R.** Electrical and thermal properties of a thermoplastic elastomer nanocomposite based on polypropylene/ethylene propylene diene monomer/graphene. *Soft Mater.* 2017. V. 15. N 1. P. 82–94. DOI: 10.1080/1539445X.2016.1268622.
11. **Panin S.V., Kornienko L.A., Aleksenko V.O., Ivanova L.R., Shilko S.V., Buslovich D.G.** Comparison of effectiveness of carbon nano-and microfibers for formation of physical-mechanical and tribolotechnical parameters of polymer composites based on high molecular weight matrix. *ChemChemTech [Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol.].* 2016. V. 59. N 9. P. 99-105. DOI: 10.6060/tcct.20165909.13y.
12. **Allahverdyeva K.V., Kakhramanov N.T., Dadasheva E.V.** Electrically conductive nanocomposites based on high density polyethylene and different types of carbon-containing fillers. *Plast. Massy.* 2023. N 5-6. P. 53-56 (in Russian). DOI: 10.35164/0554-2901-2023-5-6-53-56.
13. **Janeesh G.M., Meera V., Shalom A.M., Rajan Babu D., Arunai Nambi Raj N., Sreekanth M.S., Samba Siva V., Sumangala T.P.** Enhanced electrical conductivity and structural, mechanical characterization of standalone poly(vinyl alcohol)-graphite nanoplatelets composite films. *J. Appl. Polym. Sci.* 2021. V. 138. N 10. P. 49976. DOI: 10.1002/app.49976.
14. **Jin F.L., Chu N., Yao Sh.Sh., Park S-J.** Thermal and electrical conductivity improvement in epoxy resin with expanded graphite and silver plating. *Korean J. Chem. Eng.* 2022. V. 39. P. 2182-2191. DOI: 10.1007/s11814-022-1065-8.
15. **Kakhramanov N.T., Gasimova G.Sh., Pesetsriy S.S., Kakhramanly J.N., Gurbanova R.V., Hajiyeva R.Sh., Suleymanova E.I.** Physical and mechanical properties of nanocomposites based on block copolymer propylene with ethylene and graphite. *Chem. Problems.* 2019. N 1. P. 72-80. DOI: 10.32737/2221-8688-2019-1-72-80.
16. **Zhao L., Xia W., Zhang P.** Economical conductive graphite-filled polymer composites via adjustable segregated structures: Construction, low percolation threshold, and positive temperature coefficient effect. *J. Appl. Polym. Sci.* 2021. V. 138. N 17. 50295. DOI: 10.1002/app.50295.
17. **Ye Ch.M., Shentu B.Q., Weng Z.X.** Thermal conductivity of high density polyethylene filled with graphite. *J. Appl. Polym. Sci.* 2006. V. 101. N 6. P. 3806-3810. DOI:10.1002/app.24044.
18. **Kakhramanov N., Allahverdiyeva Kh., Gahramanli Y., Mustafayeva F., Martynova G.** Physical-mechanical properties of multifunctional thermoplastic elastomers based on polyolefins and styrene-butadiene elastomer. *J. Elastomers Plast.* 2023. V. 55. N 2. P. 279-302. DOI: 10.1177/00952443221147030.
19. **Allahverdiyeva Kh.V., Kakhramanov N.T., Mustafayeva F.A.** Structure and properties of conducting composites based on polyolefins and carbon black. *Russ. J. Appl. Chem.* 2022. V. 95. N 8. P. 1146–1152. DOI: 10.1134/S1070427222080092.

20. **Li C.-Q., Zha J.-W, Li Z.-J., Zhang D.-L., Wang S.-J., Dang Z.-M.** Towards balanced mechanical and electrical properties of thermoplastic vulcanizates composites via unique synergistic effects of single-walled carbon nanotubes and graphene. *Compos. Sci. Technol.* 2018. V. 157. P. 134-143. DOI: 10.1016/j.compscitech.2018.01.038.
21. **Kakhramanov N.T., Allahverdiyeva K.V., Mustafayeva F.A., Koseva N.S., Abdullin M.I.** Adhesion Properties of Metal-Filled Functionalized Polypropylene-Based Nanocomposites. *Polym. Sci. Ser. D.* 2023. V. 16. P. 98–103. DOI: 10.1134/S1995421223010124.
22. **Mokhtari M., Archer E., Bloomfield N., Harkin-Jones E., McIlhagger A.** High-performance and cost-effective melt blended poly(ether ether ketone)/expanded graphite composites for mass production of antistatic materials. *Polym. Int.* 2021. V. 70. P. 1137-1145. DOI: 10.1002/pi.6226.
23. **Paran S.M.R, Naderi G., Ghoreishy M.H.R., Heydari A.** Enhancement of mechanical, thermal and morphological properties of compatibilized graphene reinforced dynamically vulcanized thermoplastic elastomer vulcanizates based on polyethylene and reclaimed rubber. *Compos. Sci. Technol.* 2018. V. 161. P. 57-65. DOI: 10.1016/j.compscitech.2018.04.006.
24. **Allahverdiyeva K.V., Kakhramanov N.T., Martynova G.S., Mustafayeva F.A., Gahramanli Y.N., Habibova A.G., Bafadarova H.B., Ulemanova E.I., Gurbanova R.V.** Structural features and mechanism of crystallization of nanocomposites based on maleinated high density polyethylene and carbon black. *Heliyon*. 2023. V. 9. N 4. e14829. DOI: 10.1016/j.heliyon.2023.e14829.
25. **Liu M., Papageorgiou D.G., Li S., Lin K., Kinloch I.A., Young R.J.** Micromechanics of reinforcement of a graphene-based thermoplastic elastomer nanocomposite. *Compos. - A: Appl.* 2018. V. 110. P. 84-92. DOI: 10.1016/j.compositesa.2018.04.014.
26. **Qiu Y., Wang J., Wu D., Wang Z., Zhang M., Yao Y., Wei N.** Thermoplastic polyester elastomer nanocomposites filled with graphene: Mechanical and viscoelastic properties. *Compos. Sci. Technol.* 2016. V. 132. P. 108-115. DOI: 10.1016/j.compscitech.2016.07.005.
27. **Tarawneh M.A., Ahmad S., Chen R.S.** Mechanical, thermal, and electrical properties of graphene oxide–multiwalled carbon nanotubes-filled thermoplastic elastomer nanocomposite. *J. Elastomers. Plast.* 2017. V. 49. N 4. P. 345-355. DOI: 10.1177/0095244316661753.
28. **Utkarsh T.M., Syed N.A., Behravesh A.H., Pop-Iliev R., Rizvi G.** Synergistic enrichment of electrically conductive polypropylene-graphite composites for fuel cell bipolar plates. *Int. J. Energy Res*. 2022. V. 46. N 8. P. 10955-10964. DOI:10.1002/er.7898.

20. **Li C.-Q., Zha J.-W, Li Z.-J., Zhang D.-L., Wang S.-J., Dang Z.-M.** Towards balanced mechanical and electrical properties of thermoplastic vulcanizates composites via unique synergistic effects of single-walled carbon nanotubes and graphene. *Compos. Sci. Technol.* 2018. V. 157. P. 134-143. DOI: 10.1016/j.compscitech.2018.01.038.
21. **Kakhramanov N.T., Allahverdiyeva K.V., Mustafayeva F.A., Koseva N.S., Abdullin M.I.** Adhesion Properties of Metal-Filled Functionalized Polypropylene-Based Nanocomposites. *Polym. Sci. Ser. D.* 2023. V. 16. P. 98–103. DOI: 10.1134/S1995421223010124.
22. **Mokhtari M., Archer E., Bloomfield N., Harkin-Jones E., McIlhagger A.** High-performance and cost-effective melt blended poly(ether ether ketone)/expanded graphite composites for mass production of antistatic materials. *Polym. Int.* 2021. V. 70. P. 1137-1145. DOI: 10.1002/pi.6226.
23. **Paran S.M.R, Naderi G., Ghoreishy M.H.R., Heydari A.** Enhancement of mechanical, thermal and morphological properties of compatibilized graphene reinforced dynamically vulcanized thermoplastic elastomer vulcanizates based on polyethylene and reclaimed rubber. *Compos. Sci. Technol.* 2018. V. 161. P. 57-65. DOI: 10.1016/j.compscitech.2018.04.006.
24. **Allahverdiyeva K.V., Kakhramanov N.T., Martynova G.S., Mustafayeva F.A., Gahramanli Y.N., Habibova A.G., Bafadarova H.B., Ulemanova E.I., Gurbanova R.V.** Structural features and mechanism of crystallization of nanocomposites based on maleinated high density polyethylene and carbon black. *Heliyon*. 2023. V. 9. N 4. e14829. DOI: 10.1016/j.heliyon.2023.e14829.
25. **Liu M., Papageorgiou D.G., Li S., Lin K., Kinloch I.A., Young R.J.** Micromechanics of reinforcement of a graphene-based thermoplastic elastomer nanocomposite. *Compos. - A: Appl.* 2018. V. 110. P. 84-92. DOI: 10.1016/j.compositesa.2018.04.014.
26. **Qiu Y., Wang J., Wu D., Wang Z., Zhang M., Yao Y., Wei N.** Thermoplastic polyester elastomer nanocomposites filled with graphene: Mechanical and viscoelastic properties. *Compos. Sci. Technol.* 2016. V. 132. P. 108-115. DOI: 10.1016/j.compscitech.2016.07.005.
27. **Tarawneh M.A., Ahmad S., Chen R.S.** Mechanical, thermal, and electrical properties of graphene oxide–multiwalled carbon nanotubes-filled thermoplastic elastomer nanocomposite. *J. Elastomers. Plast.* 2017. V. 49. N 4. P. 345-355. DOI: 10.1177/0095244316661753.
28. **Utkarsh T.M., Syed N.A., Behravesh A.H., Pop-Iliev R., Rizvi G.** Synergistic enrichment of electrically conductive polypropylene-graphite composites for fuel cell bipolar plates. *Int. J. Energy Res*. 2022. V. 46. N 8. P. 10955-10964. DOI:10.1002/er.7898.

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