ON PREPARATION OF POLYMER COMPOSITES WITH IMPROVED ELECTRO-PHYSICAL AND PHYSICAL-MECHANICAL PROPERTIES

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The work deals with the results of analytical review of the development and research of polymer composite materials with improved electro-physical and physical-mechanical properties. It found that the selection of special fillers, their variation by quantity and particle sizes in the polymer matrix can essentially affect the electro-conductivity of material and thereby regulate their electret properties on the whole. It revealed that the use of traditional fillers of carbon-black, graphite, minerals, metals, etc. in the composition of thermoplastics, reactoplastics and rubber makes it possible to prepare antistatic products, electromagnetic protective coatings, resistors, various types of current-conducting materials. The use of various light-weight fillers allows preparing low-density composites with higher physical-mechanical and electret properties. The spheroplastics based on siloxane elastomer began gaining a larger popularity. There is the data on carbon-black-filled composite materials based on polyolefins which, at definite ratios, allow preparing the electroconductive products. A certain place in the review is given to the use of highly dispersed metal powders for the improvement of the electret characteristics of composites. Much attention is paid to the investigation of nanofilled composites with the use of large set of the dispersed minerals. The use of hybide polymer nanocomposites opens up new perspectives for their wider use in the production of current-conductive materials. The possibility of chemical binding of mineral filler particles with polymer matrix using the binders with conjugated double bonds provides innovative approaches to the creation of high-strength and heat-resistant electroconductive composites. It becomes obvious that the most perspective direction of preparation of materials with high electret properties must be based on mechanical-chemical synthesis of composite materials.

Keywords: polyethylene, electroconductive polymer compositions, specific volume resistance, nanofibers, graphite, electret, technical carbon, carbon fibers, electroconductivity

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INTRODUCTION

In modern science, there are problems arising from low-temperature heating, screening of sensors and constructions of radio-electronic equipment, measurement of statistical pressure, etc. The optimal solution of the problems cited above is the use of electroconductive polymer composition materials (PCM) where the polymer is used as a matrix in PCM, and filler as a current-conductive powder [1-4]. Note that the addition of disperse fillers into initial polymer matrix makes it possible to regulate various mechanical and electrical-physical properties of polymers. The creation of composite polymers with improved electrical-physical and physical-mechanical properties is one of the most perspective directions from practical point of view in the field [2-4]. The primary focus is on the analysis of the results of preparation of electroconductive polymers with various fillers published in the literature. The works of various authors explored the subject, and the results in this direction were presented. Materials obtained can serve as a basis for purposeful selection of technologies to form the polymer composites with the required level of electroconductivity.

Also explored were materials on preparation of nanocomposites on the basis of polyolefins and mineral fillers. This is
explained as being due to the fact that as distinct from usual disperse fillers, the introduction of nanoparticles contributes to the essential improvement of strength and electret properties.

**Influence of the nature and quantity of fillers on electrophysical properties of polymer composites**

The traditional electroconductive polymer materials (EPM) are compositions based on various polymers (thermo- and reactoplasts, rubbers) and electroconductive fillers (carbon-black, graphite, carbon, metallic, etc) which are used in antistatic products, electromagnetic protective coatings, high-value resistors, electrical non-metallic heaters, in current-conductive varnishes and adhesives. A basic electrical characteristic of EPM is the electroconductivity. The electroconductive materials on GOST 20214-74 are the materials with conductivity less than $10^6$ ohm$^{-1}$·cm$^{-1}$, $\gamma<10^5$ ohm$^{-1}$·cm$^{-1}$ – conductors, $\gamma=10^3$–$10^{-10}$ ohm$^{-1}$·cm$^{-1}$ – semiconductors, $\gamma>10^{-10}$ ohm$^{-1}$·cm$^{-1}$ – dielectrics. For explanation of the electroconductivity of polymers, a theory of jumps, band conduction theory, presentations of solitons (charged ion centers with zero spin) are used. For stimulation of the electroconductivity in polymers, there is used the so-called doping effect, a special case of modification with the use of the polymer reaction with donor or electron acceptors [5].

Note that inadequate attention is paid to the electrophysical properties of the polymer films with solid dispersed fillers while mechanisms of processes occurring in the composite polymer films and responsible for relaxation of the electret state in them are not studied properly and no clear understanding of the mechanisms of conductivity of these materials is provided. In this case the electrets on the basis of filled polymer films are sufficiently produced and used in completely different branches of industry beginning with packaging materials for food products and ending with elements of electroacoustic and electromechanical transformers [2-4].

The syntactic foams (spheroplastics with hollow spherical filler) were used in industry since mid-past century. The general application of these materials provides for heat-isolation with high physical-mechanical characteristics [6], heat protection of high-speed aircrafts [7] and sealing compositions [8].

Today, widely applied is the spheroplastics on the basis of thermosetting polymer binders filled with glass microspheres. The organosilicon polymers (polyorganosiloxanes) find wide application due to their long service life [9, 10].

However, all above-mentioned materials are characterized by low electroconductive characteristics. In a number of cases the spheroplastics should have definite electroconductive properties. In particular, it refers to materials used in terms of explosive components where it is necessary to exclude the formation of charges of statistical electricity. Also, the electroconductive properties are needed when using the composition as an absorber of electromagnetic energy, electric heating element, etc. The use of hollow carbon microspheres as a filler [CMS] is of particular interest. The hollow carbon microspheres are prepared by means of pyrolysis of hollow microspheres from polymers with high coke number [11].

An introduction of carbon fillers allows creating light weight electroconductive products with higher physical-mechanical properties, including inertness of the carbon fillers which facilitates their exploitation and recycling [12].

In the work [13], the electrical properties of spheroplastics based on polydimethylsiloxane elastomer and filled with hollow carbon microspheres were explored. The low-molecular oligodimethylsiloxane with hydroxyl groups SKTN-1 was used as a binder and the catalyst K-18 (tin diethylidicaprylate and tetraethoxysilane) as a hardener. The carbon microspheres were prepared by means of pyrolysis of phenyl formaldehyde hollow microspheres in terms of argon at temperature 1473 K for 4 h. The prepared microspheres had particle sizes from 20 to 80 mcm. For measurement of the electroconductive
properties of spheroplastics, there was used a measuring cell consisting of two stainless steel electrodes (one movable and one immovable) and a clamping device providing given clamping force of the electrodes to the sample. Before the measurement, the ends of the sample contacting with electrodes were treated by electroconductive paste. As a result of the investigation, a conclusion was made that the use of hollow carbon microspheres allows preparing electroconductive syntactic foams. The experimental transition point to the electroconductive state corresponds to 26% (rev.) filler content in spheroplast. It revealed that the temperature dependence of electrical resistance has a reversible character and decreases with growth of semiconductor in the spheroplastics.

In the work [14] the polymer compositions based on polyvinyl acetate containing various carbon fillers allowing their use in technology of 3D printing. This technology allows preparing polymer products of any form and complexity in terms of considerably falling labor-intensity and rising production rates [15].

For estimation of electroconductivity of the polymer compositions, there were used cylindrical bundles of length 20±0,05 mcm and diameter 4±0,04 mcm. The determination of electroconductivity of compounds was produced by contact method according to GOST 223-72. Various-branded carbon fiber of mark UVIS AK-P and technical carbon of mark P 805-E, Printex XE-2B were used. A choice of filler was due to high electric characteristics provided by the manufacturer. The carbon fillers were introduced in the polymer in quantity 0-70%. It established that for polyvinyl acetate filled by technical carbon is characteristic an abrupt increase of electroconductivity together with the growth of filler content. Three characteristic sites can be distinguished on the curve of dependence \( \lg \sigma \) of the carbon-filled polymer compositions in the content of technical carbon (Fig.1):

A – initial section characterized by low values of electroconductivity of the composite \( (\lg \sigma \cdot 6 (\text{Om}\cdot\text{cm})^{-1}) \).

B – section characterized by sharp increase in conductivity \( (\lg \sigma \cdot 6 \text{ to } -1 (\text{Om}\cdot\text{cm})^{-1}) \).

C – gentle section in line with insignificant changes of conductivity.

Fig.1. Dependence of electroconductivity of filled polymer compositions on the nature of filler and its content: 1. PE2287-TY Printex XE-2B; 1. PP 01030-TU Printex XE-2B; 2. SBS LG Printex XE-2B; 3. PP 01030-UVIS AK-P; 4. PE 2287-TU P805E.

So in case of polyvinyl acetate containing technical carbon of mark Printex XE-2B from 0 to 20% mass %, a section B corresponds to the filler content 10-15 mass %, whereas if filled with technical carbon of mark P-805E a figure stands at 50-70 mass %. The electroconductive properties in the filler content make up more than 50 mass %.
difference was due to the fact that a technical carbon of mark Printex XE-2B is characterized by high degree of structuredness and much smaller size of particles in comparison with P-805E. When using the carbon fiber of mark UVIS AK-P as an electroconductive one, a growth of electroconductivity is observed in more than 5 mass % of filler content and changes of \( \lg \sigma \) in the concentration of carbon filler were not sudden and remained monotonous.

The authors [16] as well as the authors [16] used the carbon fillers of mark P805E with average particle sizes 8.7 mc, Printex XE-2B with average number 18.2 nm and the carbon fibers of mark UVIS AK-P with fiber diameter 5-8 mc and by length 50-300 mc as a filler in preparing electroconductive polymer materials for technology of 3D-printing. As a matrix there were selected the following industrial thermoplasts: syndiotactic 1,2-polybutadiene (SPB), polyvinyl acetate (PVA), high density polyethylene (HDPE) and polypropylene (PP). The polymer current-conductive compositions were made by mixing a pre-crushed polymer (with particle size to 1-2 mm) and a carbon filler in the cylindrical mixer with mixing rates at 400 min\(^{-1}\) for 5 min. The prepared powdered compositions were granulated on a laboratory single-screw extruder at a temperature of 190-220 °C. The extruder used had the following characteristics: L=300 mm, L/D =15, screw rotation rate 0.9 rev./min. The electroconductivity was determined by the same method as was in the work [14].

In this case the filler content in the composition of polymer composites varied from 3 to 30 mass %. According to [17], the composites with electroconductivity more than \( 10^{-2} \) (Ohm-m\(^{-1}\) can be referred to the electroconductive materials. Taken as initial polymers were the typical dielectrics (specific volumetric electrical resistance \( 10^{-14}-10^{-15} \) (Ohm-m\(^{-1}\)), and as carbon-containing compositions were conductors characterized by comparatively high electroconductivity (to \( 1.7 \times 10^{3} \) (Ohm-m\(^{-1}\)).

As follows from experimental data of the works [14] and [16], the use of dispersed carbon fillers allows preparing composites with higher electroconductivity. A maximum value of electroconductivity of compounds prepared on the basis SPB \([1.38 \times 10^{-7} \text{ (Ohm-m)}^{-1}]\) is slightly lower than those based on polyolefins and PVA \([1.66 \times 10^{-7} \text{ (Ohm-m)}^{-1}]\). This was due to the influence of nature of the polymer matrix: decrease of parameter \( \sigma \) can be stipulated by availability of strong adhesion interaction at the border of carbon filler-polydiene [18].

Using carbon nanotubes (CNT) one can add antistatic and electroconductive properties to polymers. Every year there appear a lot of works on the study into electroconductivity of polymers filled with CNT both thermoplasts [19], and reactoplasts [20].

Leys Z.G. and et al. [21] have studied the electroconductivity of CNT of series “Taunit” in the polymer matrix. A polyether sulfone Ultraslon 6020 of firm «Basf» in a form of the film with thickness of 20-40 mc was used as a polymer matrix in the analysis of electroconductivity. A volume resistance of this dielectric is \( >1.0 \times 10^{6} \) Om [22].

At the same time the polyethersulfone filled with electroconductive fillers (for ex., graphite, carbon) to 50 weight % is widely used as electroconductive materials, for ex., in heating elements [23]. The film resistance was measured on Teraommeter E6-13A apparatus. The data obtained say that the introduction of CNT of “Taunit” series in the polymer matrix of polyethersulfone makes its resistance decreased. A growth of conductivity correlates with concentration of CNT: with growth of concentration the conductivity rises.

The authors [24] have showed that the use of pressing process makes it possible to increase the electroconductivity of the carbon-containing composition and keep a high positive temperature coefficient of resistance providing self-regulation effect. It is assumed that the loss of conductivity in the composition materials during heating is explained as being due to the increase of distance between contacting particles of the filler involved in the thermal expansion of the binder. An increase of the distance, in its turn, leads to a decrease of a number of contacts up to their disappearance, i.e. to a sharp increase of
contact resistance. To show the self-regulation effect, two conditions must be fulfilled:

– the filler should well react to thermal expansion of the binder, at least, from physical contact standpoint.

In the work [25], the electroconductivity of the polymer composites on the basis of polypropylene with various fillers content α-\(\text{Al}_2\text{O}_3\) and α-\(\text{Fe}_2\text{O}_3\) was explored. The filler content in the composite ranged around 1-10% of the volume. The measurements of the resistance of samples were also carried out on Teraommeter E6-13A apparatus as shown in the work [21]. The used fillers α-\(\text{Al}_2\text{O}_3\) and α-\(\text{Fe}_2\text{O}_3\) had a specific resistance \(10^{11}\) and \(10^7\) Ohm-cm, the particles size are 10 and 25 mcm, respectively. It revealed from experimental results that at room temperature the composite consisting of 96% PP and filled with 1% α-\(\text{Al}_2\text{O}_3\) and 3% α-\(\text{Fe}_2\text{O}_3\) has the largest value of specific resistance and the composite consisting of 93 % PP and filled with 2% α-\(\text{Al}_2\text{O}_3\) and 5% α-\(\text{Fe}_2\text{O}_3\) – the lower value of specific resistance. Presumably this was due to the fact that in such quantity (1% α-\(\text{Al}_2\text{O}_3\)/3% α-\(\text{Fe}_2\text{O}_3\)) of filling a rigidity of the polymer links increases which leads to a decrease of electroconductivity of the composite. According to the data on IR- spectroscopy, as the percentage quantity of the fillers of aluminum and iron (III) oxide rises the optical density of the absorption bands in the composites rises as well.

The authors [26] have investigated the electroconductivity of nanocomposites on the basis of low density polyethylene with nanoparticles of \(\text{Cu}_2\text{S}\). The temperature dependences of the electroconductivity of LDPE and \(\text{Cu}_2\text{S}\) were explored. The authors revealed that the temperature dependence of the electroconductivity beginning with a definite temperature was described with equation \(\sigma = \sigma_0 \exp(-E/RT)\) to comply with the Arrhenius view on several sites depending on \(\ln\sigma = f(10^3/T)\) with various activation energy values. The electroconductivity of nanocomposites of LDPE/\(\text{Cu}_2\text{S}\) was determined by the mobility value of macromolecules of the polymer matrix in the composite, electric properties of the filler and – the material should have a nonlinear thermal expansion coefficient, by the interaction of polymer with the filler in the interphase border.

In the paper [27], the influence of electroconductivity in forming a solution and relative air moisture on stationary jet at capillary-free electro-formation of polyurethane fibers and on morphology of the material was investigated. The work used an aliphatic thermoplastic polyurethane Elastollan (BASF) of 2 marks: 1180A (on Shore hardness 80-A), 1195A (on Shore hardness A-96, on Shore hardness D-48), with high resistance to hydrolysis and frost, and the stability of microorganisms activity. The electroconductivity of solutions was regulated by addition of tetrabutyl ammonium iodide (TBAI) and measured by means of conductometer WTW inoLab Cond 720 (Germany). Results of the investigation showed that the obtained results were well correlated with ideas on the influence of the electroconductivity on formation process: at the first stage of electroforming the surface of forming solution deformed. In this case, the more intensive is the electroconductivity the greater is the deformation of its surface. Thus, following the exploration of electroforming of fiber from polyurethane Elastollan (BASF) in the various conditions, the influence on stationary jet and morphology of prepared material of the electroconductivity of solution and relative air moisture revealed. It found that an increase of the electroconductivity of the solution to 26 mcCm/cm and relative moisture to 36-48% provides for the stable electroforming of polyurethane fibers.

On the basis of polysulfone copolymer with polysulfide sulfone in the work [28], the solid polymer electrolyte with high electrical conductivity and adhesion to the materials of the electrodes of lithium current source was developed. One of the methods of achieving a necessary level of the electroconductivity of the polymer electrolyte was its plasticization by introduction of some quantity of plasticizer-liquid solution of lithium salt in an aprotic solvent in its structure [29]. However, the authors suppose that the plasticized electrolyte can hardly be used in the structure of...
composite electrodes; in addition, it is impossible to exclude the interaction of plasticizer with metallic lithium and components of composite electrodes with all the ensuing consequences arising from such an interaction. For solution of this problem the authors developed the solid polymer electrolytes (SPE). The electroconductivity of the solid polymer electrolyte was determined by means of a bridge between alternating currents P5021. As expected, the maximum electroconductivity of the films of the solid polymer electrolyte was achieved within a range of their elastic homogeneous states. Changes in the kinetics of electrolyte films drying makes it possible to increase their electroconductivity by a factor of ten while the characteristic of electroconductivity-concentration is of an extreme nature with maximum manifestation.

Electret properties polymer compositions

The authors [30] have studied the corona electrets on the basis of polystyrene composition with electroconductive filler – graphite. During preparation of electrets in the corona discharge the accumulation of homocharge in the surface layer of dielectric due to deposition and bearer injection by charge was realized [31]. The polystyrene (PS) of mark PSM-115 (GOST 20282-86) and graphite of mark GS-1 were chosen as the objects of investigation. The mixing of polymer with filler was carried out on microrollers at 140°C for 5 min. The electriﬁcation of the polymer films was carried out in a negative corona discharge using an electrode containing 196 pointed needles equally located on an area of 49 cm² as a square. A distance between a sample and an electrode was 20 mm, polarization voltage $U_{pol}$=30 kV, polarization time $\tau_{pol}$=30 s. Before electriﬁcation the samples were sustained for 10 min. at 90°C. The investigations showed that a level and temporal stability of composition was largely accounted for by the graphite content in a volume of polymer. It revealed that an introduction of filler to 8 rev. % in composition of polymer increases a level, temporal and thermal stability of its electret properties.

In the work [32], the results of influence of the aluminum powder on electret properties of polypropylene were presented. The filler content in the polymer matrix was 2 and 4 % on volume. Thickness of the samples was about 200 mcm. The investigations were carried out by means of thermo-stimulated and isothermal relaxation of surface potential. Experimental data revealed that an addition of aluminum powder to the initial polymer leads to an improvement of the stability of electret state. It noted that the polypropylene with 2% volume content of aluminum powder had the best electret properties.

The authors [33] have developed the physical models of electret state of the polymer. For realization of this purpose, there was used a complex methodology where the same samples were studied by two methods – thermostimulated potential relaxation (TSPR) and optical methods. The high pressure polyethylene (HPPE), pure and composite with nanodispersed silica was chosen as a matrix. The composite films contained the particles of aerosil and white carbon black in a quantity of 2% ($\gamma$=0.02) and 4% ($\gamma$=0.04). When a filler was introduced in the polymer, the electroconductivity of composition slightly decreased due to the decrease of “catalyst” content of electroconductivity: molecules of $\text{H}_2\text{O}$ (in the films containing diatomite) which were adsorbed by filler particles. It was established by optical methods that an introduction of SiO₂ to PE leads to an increase of its density and degree of crystallinity in the composition of composite and, as a consequence, to a decrease of its moisture permeability, which leads to a decrease, consequently, to an increase of stability of electret state of the composite films.

In the work [34], the influence of zeolite on electret properties of low pressure polyethylene of mark PE2NT 11-285 were investigated. A diameter of filler particles is less 50 mcm. The electriﬁcation of the polymer films was carried out in corona discharge by means of electrode consisting of
196 pointed needles equally located on an area of 49 cm² as a square. It was established that the zeolite positively influenced electret properties of polyethylene: in its introduction with the quantity of 6% an increase of electret difference of potentials of polyethylene of low pressure in 3 times was observed.

The electret properties of polystyrene with TiO₂ were investigated in the work [35]. The authors have chosen the polystyrene (PS) of mark PSM (GOST 20282-86) (density – 1,06 g/cm³), medium viscous molecular weight – 3·10⁶ and specific electrical volume resistance –2·10¹⁴ Ohm·m) and TiO₂ of mark P-02 with density 4,10 g/cm³, diameter of particles 0,3 mcm and specific surface S₀=1,25 m²/g. The authors came to the conclusion that the content of polystyrene by 2-10% of TiO₂ leads to a growth of its electret characteristics. An increase of electret difference of potentials and effective surface density of charge of polystyrene in filling was stipulated by appearance and increase of fraction of macromolecules of the polymer with lower mobility, appearance of interphase polarization and formation of high-energetic traps located at the border of phase division “polymer-filler”. Also in filling of polystyrene with titanium dioxide the thermal stability of its electret properties considerably increased. In endurance at 170⁰C for 60 min., the values of electret difference of potentials and effective surface of corona electrets decreased by 40-45% while in polystyrenes it fell to zero.

The author [36] has also studied the mechanism of charge relaxation and influence of titanium dioxide on stability of electret state of polyethylene plates charged in the field of corona charge. The electrification of the polymer plates was carried out in the work as well [34]. It found that an introduction of titanium dioxide in polyethylene raises the stability of electret state due to the increase of capture energy of the injected charge carriers. It also revealed that the charge relaxation runs not due to its own surface, but due to the release of charge carriers from traps.

The electret properties and conductivity of the polyethylene films with micro- and nanodispersed fillers was investigated by authors [37]. The high density polyethylene (HDPE) of mark PE2NT11-285D was chosen as the objects of investigation. The nanoporous fillers had the following characteristics: diatomite density – 1,9 g/cm³, zeolite density – 2,4 g/cm³, particles size of diatomite and zeolite didn’t exceed 50 mcm. The stability of electret state of HDPE with concentration of zeolite 6 rev.% is higher than that of stability of HDPE with the same concentration of diatomite. The optical control of the samples showed that passing of laser radiation with wave length 0,63 mcm through polyethylene film with porous nano-additions as diatomite and zeolite depends on filler concentration.

In the work [38], the electret characteristics of material on the basis of high pressure polyethylene and chitosan were studied. For investigation there was chosen HPPE 11503-070 (TU 6-05-1636-91) and chitosan (TU №9289-046-04689375-96) as scales with sizes 0,2-0,5 mm. The mixing of polymer with filler was carried out on microrollers at 140⁰C for 5 min. The films by thickness 0,8 mm were made by a method of pressing at 170⁰C. The electrification was carried out as well as in the work [34]. The different authors in their works [39,40] have showed that an introduction of dispersed fillers in polyethylene essentially changes its electret properties. The electret state is inherent to the chitosan itself [41]. Thus, it revealed that the filling of high-pressure polyethylene by chitosan reduces its electrical characteristics, although their level is sufficient for practical application of the developed materials as packaging ones. When storing the electret state of polyethylene compositions with chitosan in the soil relaxes by the 20th day, i.e. after burial, the electret field of materials does not interfere with their assimilation by various microorganisms. Over a year of storage of polyethylene compositions with chitosan in the soil, the weight loss as a result of their biodegradation reached 23%.

In the work [42], the electret properties of polyethylene composition with nanoporous diatomite were investigated. In the course of the work it became clear that an introduction of diatomite raised the electret properties of low density polyethylene which was explained by availability of traps on the surface of
dielectrics, which can serve as nanopores of diatomite and where a homocharge forming in the preparation process of electrets was kept. It revealed that when introducing the diatomite and electrification the content of oxygen-containing groups on surface of polyethylene films considerably increased.

In the work [43], the films of impact-resistant polystyrene (IRP) and polypropylene (PP) with percentage content of rutile and aerosil were investigated, respectively. A rutile content (TiO$_2$) in impact-resistant polystyrene was 0.2, 4 and 6%, and in the film from polypropylene an aerosil content (SiO$_2$) was 0, 2, 3, 4 and 6%. The relaxation time of electret state of PP film calculated on experimental data showed that the composite films on the basis of PP with 2% aerosil content possess the best electret stability. With increase of volume concentration of the filler to 4% a stability of electret state in the sample IRP grows. The further increase of volume concentration of rutile in the sample to 6% leads to a decrease of temperature stability. An increase of stability of electret state in the composite polymers in this case the authors explain by the fact that the filler modifies the polymer conductivity. Owing to water adsorption on nanosized inclusions of the filler a volume conductivity of the polymer decreased following which a stability of electret state increased.

**Physico-mechanical properties of composite materials based on polyolefins**

In recent years, the investigations directed to the preparation of nanocomposites on the basis of polyolefins and mineral fillers were considerably expanded at the Institute of Polymer Materials of ANAS under the leadership of Professor Gahramanov N.T. in the laboratory of “Mechano-chemical modification and processing of polymers”. This is explained as being due to the fact that unlike usual dispersed fillers, an introduction of nanoparticles favors an essential improvement not only strength, but also electret properties. To clarify processes connected with the improvement of the electret properties of the polymer materials, it is necessary, first of all, to have sufficiently convincing data on the structure and properties of the filled composite materials. In particular, in the work [44,45] the general state of the problem of preparation and investigation of the composite materials on the basis of polyolefins and mineral fillers is considered. The main perspective directions of preparation, processing and application of the composite materials were shown.

In the works [46-50], the results of investigation of influence of the standard mineral fillers on basic physical-mechanical and physical-chemical properties of nanocomposites on the basis of comparatively new types of thermoplastic polyolefins – statistic copolymer of ethylene with propylene (REP) and block copolymer of propylene with ethylene (BEP) were presented. It revealed that an introduction of multifunctional structure-forming agents – alizarin and zinc stearate within the ranges of 1.0% mass in the composition of above-mentioned polyolefins improves essentially the strength and rheological characteristics of the composite materials on their basis. The most probable formation mechanism of heterogeneous nucleation centers with formation of a small-spherulite permolecular structure with the participation of structure-forming agent and nanofiller particles is proposed. By the methods of IR-spectral and X-ray phase analysis of nanocomposites the detailed analysis of structure of nanocomposites was carried out. In particular, in the analysis process of structure of the samples the displacement of the characteristic absorption bands and reflexes of the filler confirming possibility of behavior of the orientation processes of macrorhains on its surface was established. The formation mechanisms of interphase field in nanocomposites during the interaction with strength properties was considered, the basic regularities of change of the physical-mechanical properties of the polymer nanocomposites on the basis of REP, BEP and such natural minerals of Azerbaijan,
as vesuvianite and CLT were revealed. It found that the natural minerals by their strength characteristics do not yield to the standard mineral fillers. The main advantage of natural mineral fillers is that they not only improve the exploitation properties of nanocomposites but also retain the rheological peculiarities of melt on a satisfactory level. The latter circumstance makes it possible to prepare the highly filled polymer composites with concentration of 30-40% mass, which can be recommended for preparation of qualitative construction products by methods of casting under pressure and extrusion.

The authors [50-53] have established that the availability of nanoclay in the composition of natural mineral fillers (vesuvianite and CLT) leads to essential improvement of rheological properties (shift rate) of the polymer composites on the basis of BEP and REP in 2.8 times. The flow curves and melt viscosity of the initial REP and its filled composite were investigated. It found that the structural branch on flow curves is characterized by availability of areas close to the highest and lowest Newtonian viscosity. In Arrhenius coordinates it was established the dependence of viscosity on temperature, according to which the "apparent" activation energy of the viscous flow for polyolefins and their nanocomposites with vesuvianite and CLT varied within a sufficiently wide ranges of 23.5-58.4 kJ/m. The temperature-invariant dependence of the viscosity of nanocomposites allowing its extrapolation to the field of high shift rates, close to the real conditions of plastics processing by methods of casting under pressure and extrusion was constructed. The influence of structure of composites on the basis of REP and BEP, type of filler (vesuvianite and CLT), number of revolutions of the screw, pressure in the material cylinder and temperature regime of extrusion on productivity of the extruder was investigated. It showed that the highest productivity of the extruder (22.6 and 22.3 kg/h) is reached at concentration of vesuvianite and CLT within the ranges of 10% mass in composition of REP. The maximum productivity of the extruder (32.6 and 33.8 kg/h) was achieved in the composites on the basis of BEP also with 10% mass with content of vesuvianite and CLT.

The influence of temperature regime on pressured strength properties and volumetric shrinkage of polymer nanocomposites on the basis of REP and BEP and mineral fillers – vesuvianite and CLT was analyzed. It revealed that comparatively high values of strength properties of nanocomposites on the basis of BEP +5% mass vesuvianite and BEP+10% mass of CLTs was fixed at a temperature regime of material cylinder 160-180-195-210°C, holding time under pressure 20 sec., and a mold temperature 50°C [51].

Another perspective direction in the modification of polymers is the preparation of hybride composites on the basis of polyolefins and mineral fillers [54-55]. For this purpose there was developed a method of synthesis of silicon-containing epoxide compounds on the basis of hydrosilylation reaction of glycidyl ethers of allyl series with methyldiethyl silane in the presence of platinohydrochloric acid. It found that the latter underwent the reaction on oxirane ring with various reagents and the corresponding silicon-containing derivatives were formed. The synthesized 12 organosilicone compounds were used as appretes of quartz nanoparticles. It revealed that the synthesized organosilicone compounds possess good finishing properties favoring the improvement of compatibility of the mineral filler with polymer matrix. The quartz of nanosized level (to 100 nm) was used as mineral filler. The quartz nanoparticles were prepared on analytical mill A-11 at rotorate – 28000 rev./min. The size of nanoparticles was determined on apparatus of model STA PT1600 Linseiz (Germany) to make up 20-100 nm. To analyze the physical-mechanical properties of the polymer nanocomposites they were subjected to pressing at a temperature 190-200°C. The samples were cut from pressed plates to determine the breaking stress, specific elongation, bending strength of the filled composites. The results of investigation of influence of type and concentration of appretes and filler on basic physical-mechanical properties of nanocomposites were presented. The finishing of nanoparticles was...
carried out in 0.5-2.0% aqueous solution of acid to \( \text{pH} = 3.5 \), at a temperature 55°C for 60 min. Optimal concentrations of appretes and filler providing maximum values of the physical-mechanical characteristics of composites were established. The main reasons favoring improvement of strength characteristics of finished nanocomposites were revealed. The comparative analysis of the obtained experimental data showed that nanocomposites with 2-methyl-5-(methyldiethylsilyl-2-(methylenoxy-1,3-dioxolano)-pentane was used as an apprete and characterized by relatively high physical-mechanical properties [56].

In the work [57], the influence of kaolin, apprete–aminoethyl-aminopropyl-trimethoxy-silane and zinc stearate concentration on basic physical-mechanical properties of nanocomposites based on polypropylene was considered. An introduction of mineral filler more than 10% mass leads to the deterioration of breaking stress and specific elongation of considered samples. This is explained as being due to the fact that the introduction of excess quantity of nanosized filler in the composition of the polymer matrix is accompanied by accumulation of nanoparticles in the amorphous regions rigidly reinforced by passing chains in the inter-spherulite space. A schematic image of the proposed mechanism of interaction of the filler with apprete, as well as a summary table of experimental investigations on the study of selective and joint influence of ingredients in the composition of composite on basic physical and mechanical properties was presented. The data on finishing mechanism of nanoparticles were presented. It showed that the joint use of the zinc stearate and apprete makes it possible to improve the breaking stress, bending strength, specific elongation and melt flow index. An improvement of flow melt creates some technological advantages to the examined highly filled nanocomposites organosilicone compound acidified by acetic intended for their processing by methods of extrusion and casting under pressure.

The authors [58–60] have considered the influence of mineral fillers (talc, quartz, clinoptilolite, etc) that resulted in organosilicone compounds based on physical-mechanical properties of composite materials. In all cases a noticeable improvement of properties of finished composite materials was noted. So, for example, it found that the maximum value of breaking stress was achieved in nanocomposites with 10% mass content of talc and apprete. An increase of heat-stability of nanocomposites with growth of content of finished talc was interpreted by the existence of the possible covalent bond of silanes with tertiary carbon atoms or double bonds available in the structure of polypropylene.

On the basis of the above-mentioned, it may be concluded that the problem of improvement of the electret and physical-mechanical characteristics of the polymer composite materials on the whole will mainly be identified by the concentration of reacting components of the mixture, structure of the initial polymer matrix due to its molecular weight and molecular-weight distribution, content of functional groups with conjugated double bonds, sizes of filler nanoparticles and its composition. The investigation of nanosized filler particles once again confirms great opportunities of structure regulation and properties of the composite materials. It becomes obvious that the most perspective direction of material preparation with high electrical properties will be formed in the process of mechanical-chemical synthesis of the composite materials with the use of combined variants of their modification. The possibility of wide variation in the structure of polymer nanocomposites opens up new possibilities of selective influence on change of their properties.

REFERENCES

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характеристик композитов. Большое место удалено исследованию нанополимерных композитов с использованием большого набора дисперсных минералов. Использование гибридных полимерных нанокомпозитов открывает новые и перспективные возможности широкого их использования в производстве токопроводящих материалов. Возможность химического связывания частиц минерального наполнителя с полимерной матрицей с использованием связующих с сопряженными двойными связями – это инновационные подходы в деле создания высокопроводных и теплостойких электропроводящих композитов. Очевидно, что наиболее перспективное направление получения материалов с высокими электретными свойствами будет основываться на процессе механо-химического синтеза композитных материалов.

Ключевые слова: полиэтилен, электропроводящие полимерные композиции, удельное объемное сопротивление, нановолокно, графит, электрет, технический углерод, углеродные волокна, электропроводность

YÜKSƏK ELEKTROFİZİKİ VƏ FİZIKİ-MEXANİKİ XASSƏLİ KOMPOZİTLƏRİN ALINMASI HAQQINDA

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Мəгалада электрет əяхəлəр өмүрдəлүү өлкөдө композициясы материалдарын таддыйгы өө ишлүүлөөсинин өдөрүүдө ичүүлүк ичинде сүзөлүүдү көрсөтүү өчүрүнү марат дүйнөсүнү дайындык өө материалдарын электриккөүчөрилийинин түшүрүктөө өчүрүүгү яңылык, электрет əяхəлəрini өө тәсилизөөлөк өчүрү. Мыңып эчкөлүүдү көрсөтүү өчүрүнү, термопластдар, реактопластдар өө резин мүмкүнлөрүн дүйнө, графит, минералдар өө металдар кимдөө əяхəлəр дүйнөсүнү дүйнөдө, дүйнө амалдагы материалдар өө электромагнит өрткөлөрү, резисторлор өө дүйнөлүү өө электриккөүчөрилий медиаалар амалдагы мүмкүнчүлүк. Мүмкүнчүлүк нөфүрү мүнөздө дүйнөсүнү табып, үзүккө физик-механик əяхəлəрга өмүрдəлүү алынышын ичиндө өчүрүлүк. Полиолөө вө дүйнө дүйнөдөрүс композициясы материалдарын мүңүн иштөөлөрүнү дүйнөсүнү электриккөүчөрилий материалдарын алынышын дайын маалыматтар берирулүү. Мəгалада ишүүлөрдөн бирини композициясы электрет əяхəлəрini ичүүлөөдөрү пайдалануу мүмкүнчүлүк алынышын ичиндө ишүүдү ичүүлүк дисперсиялык өмүрдəлүү металдык өчүрү төшөөлөк өчүрү. Коньяк көлөңүсү өчүрүлүк рагби вө ватырында минерал дүйнөсүнүн вө полимер мараттывун кимдөө əяхəлəрдө алынышын ичиндө үзүккө мүмкүнчүлүк вө истилия даярды электриккөүчөрилий композициясы алынышыннда инноватив табиисиз мүмкүнчүлүк өчүрүлүү. Мүмкүнчүлүк эңбөлөрү көрсөтүү өчүрү електрет əяхəлəрге өмүрдəлүү материалдарын алынышын пепсивтив истигимөт композит материалдарын механик-кимдөө əяхəлəрдө ишүүлөөдөрү өчүрүлүү.

Açar səslər: полиолөөлүк, электрет, электриккөүчөрилий, композит материалдар, механик-кимдөө əяхəлəр, графит, физик-механик əяхəлəр