Розроблено електропровідні полімерні гібридні композити на основі емульсійного полівінілхлориду (ЕПВХ) та лінійного поліетилену (ПЕ). Досліджено залежність електропровідності моно- та бінарнонаповнених полімерних композитів від виду та вмісту наповнювачів. Визначено фізико-механічні характеристики отриманих полімерних композитів та запропоновано спосіб їх покращення. Наведено сфери застосування отриманих полімерних гібридних композитів (ПГК) відповідно до властивих їм значень електропровідності

Ключові слова: поліетилен, полівінілхлорид, графітизована сажа, вуглецеві волокна, порошок нікелю, мідні волокна

Разработаны электропроводящие полимерные гибридные композиты на основе эмульсионного поливинилхлорида (ЭПВХ) и линейного полиэтилена (ПЭ). Исследована зависимость электропроводности моно- и бинарнонаполненных полимерных композитов от вида и содержания наполнителей. Определены физико-механические характеристики полученных полимерных композитов и предложен способ их улучшения. Приведены области применения полученных полимерных гибридных композитов (ПГК) в соответствии со свойственными им значениями электропроводности

Ключевые слова: полиэтилен, поливинилхлорид, графитизированная сажа, углеродные волокна, порошок никеля, медные волокна

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DESIGN OF ELECTRICALLY CONDUCTING POLYMER HYBRID COMPOSITES BASED ON POLYVINYL CHLORIDE AND POLYETHYLENE

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1. Introduction

Today the issue of designing modern materials grows in importance, which is connected to the rapid development of new branches of science and technology. One of the solutions to this problem is to design new polymer materials or to improve the existing ones. The widespread applications call for creation of specific materials for specific needs of electric technology.

Designing electrically conducting polymer materials is not an easy task as today it has to meet a number of important requirements: ease of production, cost efficiency and effectiveness of operational properties. Most of the materials, already created, do not meet mentioned requirements, for example, carbon black-filled polymer composites obtain conducting state at the content of carbon black that is much larger than when introduction of carbon nanotubes, which in turn are difficult to evenly distribute in the polymer matrix. Thus, today there is a need to design electrically conducting polymer materials that will meet all the requirements. The solution may be to create electrically conducting polymer composite materials with a combined filler, which are still not sufficiently studied and may have promising properties, based on the properties of the constituing components of compositions.

2. Analysis of scientific literature and the problem statement

Electrically conducting polymers since their discovery and up to now have been an important subject of research, which is associated with the range of their applications, for example: as electrodes for solar panels [1], gas sensors that are made using electrically conducting polymers [2], membrane for methanol fuel systems [3], fuel elements and active electronic components [4], actuating mechanisms [5], electrostatic dispersion coatings [6], electromagnetic interference shielding [7] and others. At present, the properties of electrically conducting polymers are not ideal, that is why the studies are performed towards their improvement [8].

By their nature, only some polymers have high electrical conductivity and can be used in the above-mentioned areas, while all the others are usually good dielectrics. The most common way to design electrically conducting materials based on polymers-dielectrics is introduction of a variety of electrically conducting fillers, i.e. the creation of composite materials. Special attention is currently paid to carbon fillers. This type of fillers has a number of advantages: high electrical conductivity [9], relatively low density [10], ease of processing [11], etc. The most commonly used are carbon black [12], graphite [13], carbon fiber [14], carbon nanotubes [15]. Each of them has its own characteristics. Carbon black is cheap, a good electric conductor, it can be used as an agent for strengthening of electrical conducting properties of a different filler in a polymer composite [16]. However, the threshold of percolation is usually high for the carbon black. It is vice versa for carbon fiber and carbon nanotubes: high electrical conductivity, excellent mechanical properties, but their price is high. There is also a problem of even distribution of carbon nanotubes [17] as a filler in a polymer matrix. Negative impact is caused by the formation of aggregates that destroy the homogeneous structure of a composite. The research of metal-filled polymer systems is actively performed [18]. It is proven that the size and concentration of this type of filler significantly affects the electrical conductivity of a composite [19]. These composites can be used, for example, for the design of intelligent smart materials [20].

Most of the mentioned materials can be obtained by the classic methods of processing of polymers, while some of them require specific conditions of manufacturing, which complicates the process of their production.

Filled polymer materials have displayed excellent properties, though to achieve current conducting properties, it is necessary to overcome a number of obstacles, both structural and technological. That is why the idea of simultaneous introduction of several fillings, different in their properties, has been actively studied lately. With the introduction of only Ag nanoparticles in polypropylene that act as centres of crystallization of the polymer molecules, the formation of the beta form of polypropylene is induced. As a result, trans-crystals of polypropylene form around clusters of Ag particles, which worsens the electrical properties of a composite. Adding a small number of carbon nanotubes significantly improves electrical properties of the system of a hybrid composite. Nanotubes in this case act as bridges between the particles of Ag, thereby contributing to the creation of electrically conducting chains in a composite [21]. Another paper on composites based on polyethylene and polypropylene filled with modified carbon black, showed that adding a carbon fiber, at relatively small concentrations, significantly improved properties of electrically conducting composite. Carbon fiber connects not yet interconnected carbon black particles by bridges [22]. Obtained composites, based on epoxy resin containing hybrid fillers, showed that the gaps between the particles of the first filler were effectively filled with the second one with the formation of electrical conducting grid with low threshold of percolation when carbon nanotubes were added to the carbon black nanoparticles [23]. Thus, when introducing a layered silicate into a composite of polyamide-6 with carbon black, percolation threshold shifts towards the particles of carbon black of smaller volume. The interaction of the plates of a layered silicate with carbon black prevents the latter's aggregation and ensures the creation of a continuous conducting grid in a polymer matrix [24].

Thus, polymer composites with a combined filler, in other words polymer hybrid composites (PHC), represent a promising direction in the design of electrically conducting polymer materials with controlled properties.

3. The purpose and objectives of the study

The purpose of the research was to design electrically conducting hybrid polymer composites based on emulsion polyvinyl chloride (EPVC) and polyethylene (PE) with the use of fillers of varying nature and structure.

To achieve the set goal, the following tasks were solved:

– we studied the influence of composition of PE and EPVC composites on electrical and physical-mechanical properties;

– we defined the rational compositions of electrically conducting PE and EPVC composites, according to the purpose of application.

4. Materials and methods of research of the influence of composition and content of fillers on electrical and physical-mechanical characteristics of polymer hybrid composites

4. 1. The studied materials and equipment used in the experiment

Taking into account the above-mentioned, we selected for the research: polymer matrix – EPVC Vinnolit EP6854, plasticizer for EPVC – dibutylphthalat (DBPH) by GOST 8728–88, PE LLDPE, brand M3804RWP (SCG Chemicals), graft-polymer of polyethylene with maleic anhydride (GPMA), synthesized by extrusion method in the laboratory; fillers – carbon fiber (CaF), brand VMN-4 of length 1–2 mm and diameter 5 μm, carbon black, brand PUREBLACK SCD-205, nickel powder (NP), brand PNK – UT1, copper fiber (CoF), brand M1 (electrical) with a diameter of fiber 60 μm and length 1–2 mm.

The technology of PHC production includes the following stages: preparation of components, mixing all the components of the compositions, obtaining testing specimens by the method of sintering in a mold.

EPVC is used to obtain polymer products by a sintering method that allows obtaining specimens of polymer composites without any technological difficulties, including with several fillings, namely polymer hybrid composites (PHC). Composites based on PE were received by extrusion method. The content of the filler in composites reached 0,2–16 % of the entire volume at a ratio of fillers 1:1 in PHC.

CaF and carbon black are dried in advance in vacuum chamber at temperature 80°C for 5 hours to remove residual moisture. Mixing of components is carried out in two stages: first, the matrix in the form of powder is mixed with fillers in an one-step vane turbomixer of periodic action of Henschel type for 5 minutes, if the matrix is EPVC, then a plasticizer is added and the mixing is repeated for 3 min. When PE is used as a matrix, then after the mixing, a received mixture is extruded in a single-auger extruder (D=27 mm, L/D=30) with a static mixer. The sintering of the obtained compositions was carried out at temperature 190 °C for 2 min.

4. 2. Method of defining the indicators of the specimens' properties

Measurement of the electrical conductivity of the obtained specimens was performed according to GOST 6433.2–71. (Methods for determining electrical resistance at constant voltage) [25]. The specimens, selected according to requirements, of size 26×26 mm, were placed in a standardized two-electrode cell. Teraohmmeter E6–13A, connected to the cell, measured the resistance value of the specimens.

The specimens of electrically conducting compositions were obtained at a laboratory press at the temperature, accordingly, 190 °C for EPVC and 150 °C for PE and pressure up to 10 MPa. Before measuring the electrical conductivity, the specimens were kept for 48 hours at temperature 15–35 °C and relative air humidity 45–75 %, and we measured their thickness in at least 5 places with an accuracy of ±0.01 mm. For a better contact of the electrodes with flexible specimens we used aluminum foil with thickness 0.01 mm. The foil was placed between the electrodes and a specimen.

To determine electrical conductivity, a specimen was placed in the cell, between the electrodes, connected to the device for measuring resistance – Teraohmmeter E6–13A. After that, 100 V DC voltage was fed to the specimen. The value of the voltage of the power source was selected to ensure stable performance of electrometer with the smallest error. In this case, current value during the experiment did not exceed the values, with which the specimen used more than 0.1 W.

During the measurement, the compensation of the resistance of wires R_{wr} in the calibration mode of the device Teraohmmeter E6-13 is carried out (i. e. after this mode, in the calculation by formula it should be considered that the R_{wr}=0). The value of the cell R_c is determined during measurement in the absence of the specimen in an electrode device. By the results of the measurements, carried out in SE «Ukrmetrteststandard» (Kiev, Ukraine), this value of resistance is 0.025 Om (with accepted error ±0.4 %). Given the above-mentioned, resistance of a specimen is determined according to the following formula:

$$R = R_{ms} - 0{,}025. \quad (1)$$

Specific volume electric resistance (ρ_v) of specimens is calculated by the formula:

$$\rho_v = R_{sp} \cdot \frac{\pi \cdot d^2}{4 \cdot h}, \quad (2)$$

where R_{sp} is the electrical resistance of the specimen, Om; d is the specimen diameter, cm; h is the specimen thickness, cm.

After calculating the experimental values of electrical conductivity of polymer compositions depending on the concentration of a filler that correspond to points on the diagram (Fig. 1–4), we calculated corresponding theoretical values. The calculation was carried out according to percolation theory [26] by the following equation:

$$\sigma = \sigma_0 (\phi - \phi_c)^t, \quad (3)$$

where t is the critical index, equal to 1.6–1.9, σ_0 is the parameter of conductivity that describes percolation curve after the percolation threashold ($\phi > \phi_c$), ϕ is the volumentric content of a filler, vol. parts, ϕ_c is the volumetric content of a filler at the percolation threashold, vol.parts.

Measurement of tensile strength was conducted according to GOST 11262–80 [27]. The method is based on the tension test of a specimen with a set speed of deformation, by which a number of indicators is determined that characterize the physical-mechanical properties of the material. For measuring we applied a tensile machine of ZD-10 type for stretching a polymer specimen at a given speed, with the error of the unit not exceeding 1 %. Micrometer, calipers, a ruler to measure the size of a specimen. Specimens for testing were obtained by forming, or by mechanical processing of special workpieces.

During the stretching of a specimen, in the area of clamping, the plates of length 50 mm, thickness from 3 to 20 mm, strengthened the ends of it. Material of the pads was close to the tested material by the value of the module of elasticity. To test isotropic specimens, we used at least 5 specimens, and up to 5 specimens for anisotropic materials.

The value of the tensile strength at breaking σ_{pp} Mpa (N/mm^2) was calculated by the formula:

$$\sigma_{pp} = \frac{F_{pp}}{A_o}, \quad (4)$$

where F_{PP} is the loading at which a specimen breaks; A_0 is the area of initial cross section of a specimen, mm^2.

The value of the relative elongation at breaking ε_p (%) was calculated by the formula:

$$\varepsilon_p = \frac{\Delta l_p}{l_o} \cdot 100, \quad (5)$$

where Δl_p is the increase in the estimated length of a sample at the time of the break, mm; l_0 is the initial estimated length of a sample, mm.

The result was calculated by an arithmetic mean of at least 5 measurements.

5. Results of the study of the indicators of polymer hybrid composites

The results of the calculations of the electrical conductivity indicators for PHC based on plasticized EPVC are in Fig. 1, 2.

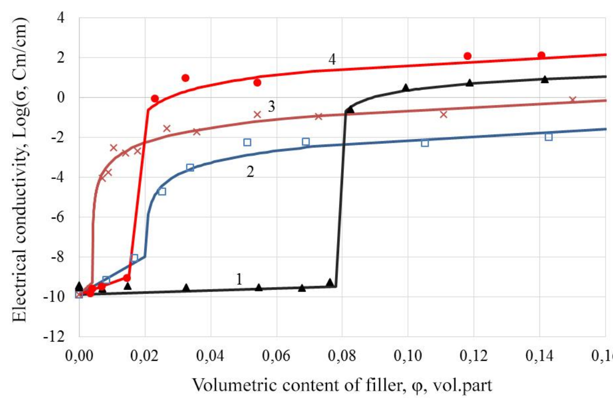

Fig. 1. Dependence of electrical conductivity of compositions based on plasticized EPVC on the content of a filler: 1 – NP, 2 – carbon black, 3 – CaF, 4 – CoF. Points — experimental values, lines – calculated according to the equation (3)

The above-presented figure shows that for the composites filled with CaF, electrical conductivity grows rapidly with increasing content of a filler. Volumetric content of CaF 0.004 vol. parts causes a dramatic increase in electrical conductivity of a composite, i. e. the threshold of percolation is observed. Further increase of the content of the CaF does not lead to significant changes in electrical conductivity. Such a sharp increase in electrical conductivity at such a low concentration of a filler can be explained by special geometric sizes of the filler. The ratio of the length of the CaF to its diameter l/d significantly affects the maximal possible degree of the filling (packing-factor F). Packing factor F is known to be a parameter that allows estimating the value of the threshold of percolation [28]. Since the fibrous fillers, in comparison with the dispersion ones, have lower F, then, accordingly, less volumetric concentration of a filler is needed for the formation of conducting structures in a polymer composite.

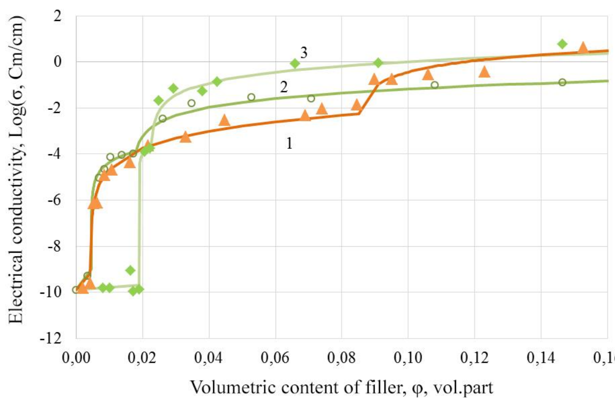

Fig. 2. Dependence of electrical conductivity of compositions based on plasticized EPVC on the content of a filler: 1 – NP/CaF, 2 – carbon black/CaF, 3 – carbon black/CoF. Points – experimental values, lines – calculated according to the equation (3)

For the composites filled with carbon black, the occurence of the threshold of percolation is observed at the content of a filler 0.02 vol. parts. As carbon black is a dispersed filler, then it has larger F compared to the fiber filler and to achieve the threshold of percolation, more volume concentration is necessary.

In the composites filled with NP and CoF, the dependence of electrical conductivity on the content of a filler is characterized by occurrence of percolation threashold at much larger concentrations compared to the content of CaF and carbon black, that can be explained by a lesser area of contact between the particles of fillers NP and CoF and less value of ratio l/d. Occurrence of the threshold of percolation happens at the content of NP 0.078 vol. parts and the CoF 0.015 vol. parts in the polymer matrix, but the values of electrical conductivity for these compositions are considerably larger due to the fillers' own high electric conductivity.

The above-attached dependency shows that the electrical conductivity for a composition, filled with hybrid filler carbon black/CaF, is significantly different from this dependence for mono-filled composites. For this system a double percolation threshold is characteristic. The first one occurs at the total content of the filler 0.0045 vol. parts, and the next one – at 0.017 vol. parts. This phenomenon can be explained by the presence of the effect of reinforcement during the interaction of the components between each other. The first threshold occurs due to the structure of the formed CaF, and then, with increasing concentration of binary filler, defining impact is caused by this very filler, as the main structure-creator of conducting grid in PHC. However, when increasing volume concentration of a binary filler up to the concentration of percolation threshold for carbon black-filled composites, the next threshold occurs, associated with a significant increase in the concentration of carbon black that creates, as a result, more branched conducting grid along with CaF. Thus, the binary content of CaF/carbon black has a better result than when filling with separate fillers. And the percolation threshold of 0.0045 vol. parts for the given composites reaches the value of 0.004 vol. parts, similar to the composites filled with CaF. For the composites filled with a mixture of NP/CaF and carbon black/CoF, the percolation threshold reaches 0.0042 vol. parts, and the second one – 0.085 vol. parts and 0.018 vol. parts, the second one – 0.022 vol. parts, respectively. A binary filling makes it possible to reduce the content of more electrically conducting, but economically inefficient filler – CaF, due to the introduction of a cheaper filler, carbon black, without affecting significantly the first percolation threshold of PHC compared to the composites filled with a monofiller.

The results of the calculations of the electrical conductivity indicators for the PE-based PHC are in Fig. 3, 4.

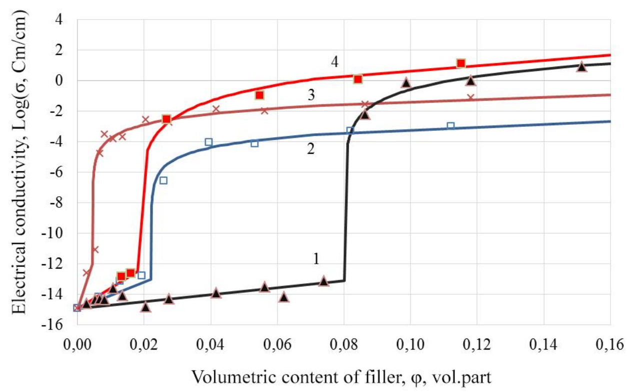

Fig. 3. Dependence of electrical conductivity of compositions based on PE on the content of a filler: 1 – NP, 2 – carbon black, 3 – CaF, 4 – CoF. Points are experimental values, lines – calculated according to the equation (3)

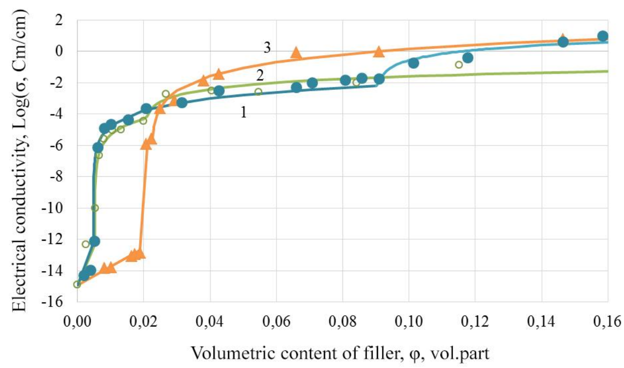

Fig. 4. Dependence of electrical conductivity of a composition based on PE on the content of a filler: 1 – NP/CF, 2 – carbon black/CaF, 3 – carbon black/CoF. Points – experimental values, lines – calculated according to equation (3)

It follows from Fig. 3 that for the PE-based composites, percolation threshold is observed at the content of CaF 0.0045 vol. parts and carbon black – 0.022 vol.parts, which is larger by 0.0005 vol. parts and by 0.002 vol. parts, respectively, compared to the EPVC– based composites. PE has a specific volume electrical resistance of 10^{15} Om·cm, which is several orders of magnitude larger than that of the EPVC, for which this value is 10^{10-11} Om·cm. The threshold of percolation for the composites filled with NP and CoF occurs at the content of 0.08 vol. parts and of 0.018 vol. parts, respectively.

The above-attached dependency shows that for a number of carbon black/CaF binary-filled PE-based composites also characteristic is a double percolation threshold. The first one occurs with the overall content of the filler of 0.0047 vol. parts, and the next one – of 0.02 vol. parts, which is higher than for the EPVC-based composites. With a filling of NP/CaF and carbon black/CoF, the first percolation threshold reaches 0.0052 vol. parts and 0.0189 vol. parts, and the second one – 0.09 vol. parts and 0.0219 vol. parts, respectively, which is not practically different from the value for a monofiller.

Physical and mechanical properties of EPVC and PE-based composites are presented in Fig. 5–8.

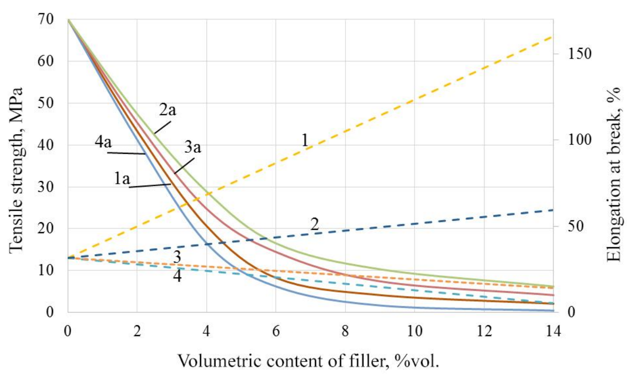

Fig. 5. Dependence of the tensile strength (lines 1–4) and elongation at break (lines 1–4) of polymer composites based on plasticized EPVC on the content of a filling: 1, 1a – CaF, 2, 2a – CoF, 3, 3a – NP, 4, 4a – carbon black

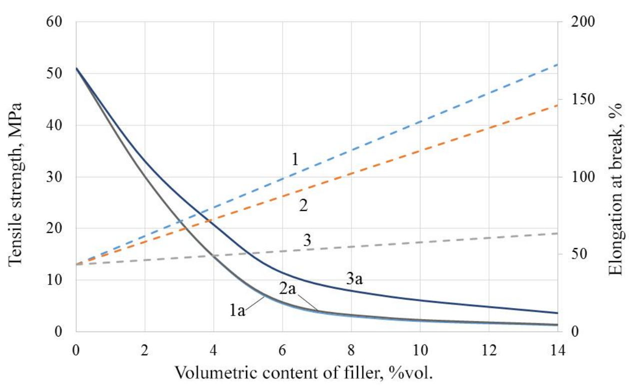

Fig. 6. The dependence of the tensile strength (lines 1–3) and elongation at break (lines 1a – 3a) of polymer hybrid composites based on plasticized EPVC on the content of a filling: 1,1a – NP/CaF, 2, 2a – carbon black/CaF, 3, 3a – carbon black/CoF

Carbon fibres, compared to copper, have higher anisotropy and mechanical characteristics that can improve the mechanical properties of the obtained composites. The composites, filled with CaF, as was expected, have the highest tensile strength at break. The lowest values of this indicator refer to the composites filled with dispersion fillers – NP, carbon black. Relative elongation monotonically decreases with increasing concentration of a filler.

CoF compared to CaF have a much lower tensile strength. Therefore, the CaF/NP-based composites have the highest tensile strength at break. Relative elongation decreases with a filling with fibrous fillers, especially CaF, as well as with the introduction of a large amount of dispersed filler – carbon black.

To enhance the physical and mechanical properties of PHC with fillers of carbon black/CaF, NP/CoF, their composition was introduced with a compatibilizer (5 % of the mass) – graft-polymer GPMA. The mechanism of obtaining GPMA is in Fig. 9 [29].

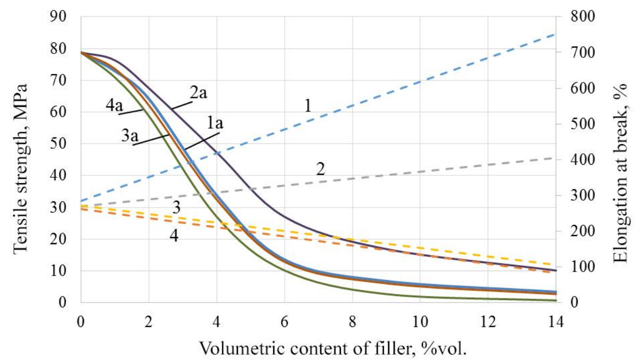

Fig. 7. Dependence of the tensile strength and (lines 1–4) and elongation at break (lines 1–4a) of polymer composites based on PE on the content of a filler: 1, 1a – CaF, 2, 2a – CoF, 3, 3a – NP, 4, 4a – carbon black

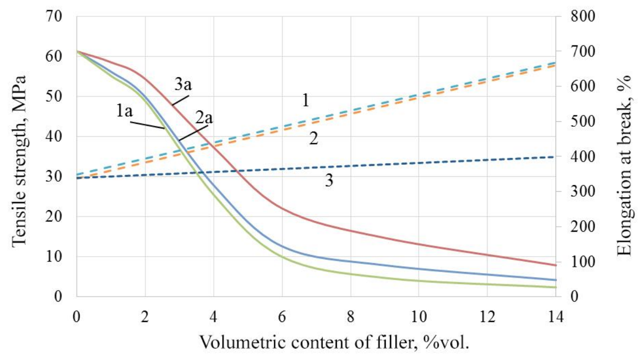

Fig. 8. Dependence of the tensile strength and (lines 1–3) and elongation at break (lines 1a – 3a) of polymer hybrid composites based on PE on the content of a filler: 1, 1a – NP/CaF, 2, 2a – carbon black/CaF, 3, 3a – carbon black/CoF

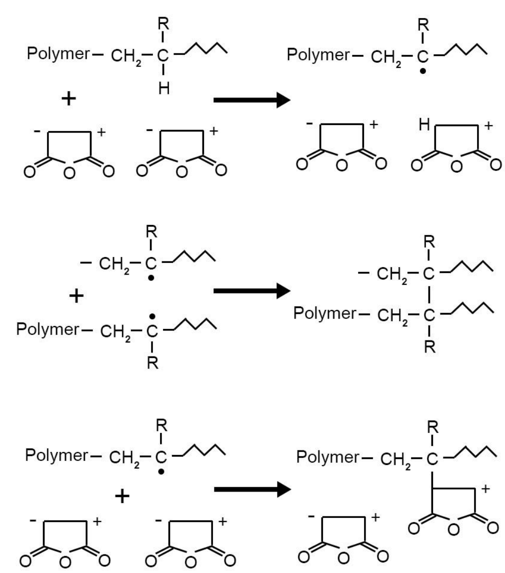

Fig. 9. Mechanism of the process of obtaining polyethylene-based maleic graft-polymer

Physical and mechanical properties of the obtained PE-based composites with a compatibilizer are in Fig. 10.

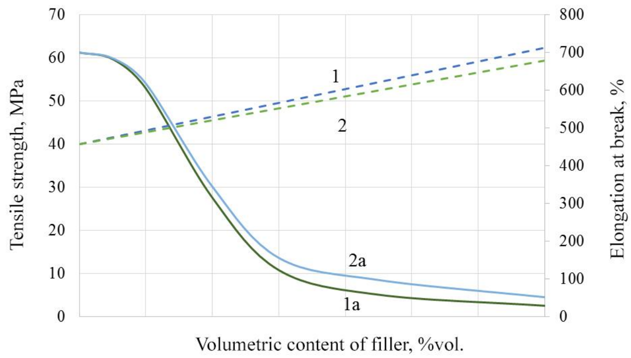

Fig. 10. Dependence of the tensile strength and (lines 1, 2) and elongation at break (lines 1a, 2a) of polymer hybrid composites based on PE + 5 % of the mas. of compatibilizer on the content of a filler: 1, 1a – NP/CaF, 2, 2a – carbon black/CaF

It follows from Fig. 10 that when adding the obtained compatibilizer in the amount of up to 5 % of the mass, there is a significant improvement of the physical and mechanical properties, namely, tensile strength at stretching increased by 1.3 times, and relative elongation at break – by 1.1 times, since a compatibilizer increases adhesion bonds between polymer matrix and a filler.

5. Discussion of results of the study of influence of fillers on electrical and physical-mechanical characteristics of polymer hybrid composites

The possibility of creating PHC based on PVC and PE was shown. It was found that the properties of PHC are significantly affected by both the type of filler and its contents, and the type of polymer matrix. PE-based PHC have 10–20 MPa larger tensile strength than the corresponding EPVC-based PHC while the PHC percolation threshold occurs, accordingly, later at the content of a filler by 0.02–0.07 % vol. The greatest influence on the properties of PHC is produced by the filler CaF. Increasing CaF content significantly improves both electrical conductivity and a tensile strength at break of PHC. Thus, percolation threshold for the EPVC/PE-based PHC, filled with carbon black/CaF, is observed, respectively, at the contents of 0.45 % vol./ 0.47 % vol.; filled with NP/CaF – relatively to the content of 0.42 % vol./ 0,52 % vol., while for the compositions of carbon black/CoF – 1.8 % vol./ 1.89 % vol., respectively. And the PHC tensile strength on both polymer matrices with the filler carbon black/CaF, NCP/CaF is almost two times larger than that of filled with carbon black/CoF.

To improve the mechanical properties of the PE-based PHC, they were modified by introduction of a compatibilizer of the graft-polymer-GPMA in the amount of 5 % of the mass. Such PHCs have shown strength gain by almost 1.5 times.

6. Conclusions

The studies have shown the possibility to design polymer materials such as PHC, based on PVC and PE. It was found that the electrical conductivity indicators of PHC are larger than when only dispersed fillers are introduced and they are close to the values of the composites with fibrous fillers only. It was determined that the properties of PHC are significantly influenced by the type of a filler and its contents, and the type of polymer matrix. PE-based PHC have a 10–20 MPa larger tensile strength than the corresponding EPVC-based PHC while the PHC percolation threshold occurs, accordingly, later, at the content of a filler by 0.02–0.07 % vol. The combination of two different in structure, anisothropy and shape fillers allows creating more efficiently electrically conducting structures in polymer matrix, cutting costs on expensive fibrous filler.

To improve the mechanical properties of the PE-based PHC, they were modified by introduction of a compatibilizer of the graft-polymer-GPMA in the amount of 5 % of the mass. Such PHCs have shown strength gain by almost 1.5 times.

The EPVC-based PHC with the content of hybrid filler of carbon black/CF at 4–16 % vol. have electrical conductivity of 10^{-2}–10^{-1} Cm/cm and can be used for the manufacture of electromagnetic shielding materials. The EPVC-based PHC with the content of hybrid filler NP/CaF at 9–16 % vol. have electrical conductivity of 10^{1} Cm/cm and can be used for the manufacture of current- conducting elements.

Designed PHC outperform existing materials by their mechanical properties. However, we failed to achieve the effect of synergy with a combination of the two types of fillers in the desinged PHC. Obviously, it is is necessary to change the ratio of dispersed and fibrous fillers in favor of the fibrous one, or introduce a third filler, or change a polymer matrix. Research in this direction will probably be the next stage of a scientific study.

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