Structural and Morphological Characteristics of Polyethylene Composites with Different Conductive Fillers

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Structural and morphological features of compositions based on LDPE which contains different types of fillers for creation of conductive polymer products are presented in this article. Different types of fine metallic fillers, such as Al, Br, Cu, and flake-like graphite were used in this work. Comparative assessment of morphometric characteristics of particulate fillers: area, perimeter, equivalent diameter, shape factor and their distribution on these indicators were performed by methods of optical microscopy and image analysis. Composite films based on LDPE, containing 5% vol. with different types of conductive fillers were obtained by pressing method. It was found that the nature of the filler quantitatively influences on the uniformity of distribution of its particles in composite films. The most structural homogeneity was observed in PE-Gr and PE-Cu composites, while the least - in PE-Br composite. It was shown that the increasing of average particle anisotropy for investigated fillers reduces their heterogeneity of distribution in composite films.

Keywords: conductive fillers, polymer compositions, image analysis, shape factor, mixing

The development of science and technology had required creation of new materials with specific physical and chemical properties. Conductive polymers are widely used in various products for electrical industry. Current conductivity can be possessed by polymeric compositions and polymers with *internal* self-conductivity, for example, linear polymers or cyclochain structure with conjugated bonds [1-5].

The problem of the formation of polymer materials with special electrical and technically important properties had appeared long years ago. The need in such materials was related, on one hand, with a much greater variety of their structural and physicochemical properties compared to the traditional inorganic semiconductors and metals, on the other hand - with possibility for continuous chemical modification. The importance of modification method which was associated with creation of composite polymer-based materials should be highlighted. This method has made it possible to modify the mechanical and electrical properties of these substances in the right direction [5-9].

Current conducting polymers are widely used in various fields of technology. Doped polymers are used as various additives including antistatic polyaniline layers for protection of computer disks [10]. Such kind of polymers had made interest for blocker surfaces [11], creation of optical fiber [12], in membrane technology for the separation of polar liquids and gases [13], for sensitive sensors in the lithographic processes and photographs [14].

Various types of inorganic fillers can be used to create conductive polymer compositions. The soot and its derivatives [15] such as carbon fibers [16], graphite [17] and metal powders are most widely used. These fillers have significantly different chemical properties which influences on level of adhesion between filler and polymer matrix and also on morphological characteristics of particles [18]. Last features of the crystal structure of fillers are related with methods of their preparation and grinding. For example, a form of aluminum powder particles can be quite different, ranging from the scaly-like and ending close to spherical [19].

The impact on the dispersion of conductive fillers and physical properties is not straightforward [20]. On the one hand, increasing of the particle size characteristics leads to achievement of more rapid percolation threshold, but on the other hand, it can significantly increase the heterogeneity of distribution for particles in the film and consequently impair on its physical and mechanical characteristics. This demonstrates the relevance of a comparative study of morphometric characteristics for specific types of conductive fillers that can be used to produce composite films and their distribution homogeneity in the polymer matrix [21].

The number of circumstances which are used in studying of impact of conductive fillers on the structure of composite films should be considered. First of all, it's dimensional characteristics of filler, their size distribution and the indexes of the particles shape. The specific index of share for largest fraction is also important. In the dimensional characteristics, the structure of composite films is significantly affects on level of interaction with the polymer matrix and the filler. It is rather depends on the ratio of the interaction forces on the border *filler-filler* and *filler-polymer.* Obviously, in a situation where the first value is greater than the second, even distribution of filler in the polymer matrix will be difficult.

The aim of the work was to study the structural and morphological features of compositions based on LDPE, containing various types of conductive fillers.

Experimental part

Objects of research are composite films based on polyethylene of high pressure mark 16803-070 (PE), containing about 5% of conductive fillers of various types. In these paper we had used powdered metal fillers: aluminum, brands PAP 1 (table 1) (*Al*), bronze brand BrO5S25 (table 2) (*Br*), copper brand PMS-1 (table 3) (*Cu*), and scale-like graphite brand RFL 99.5 (table 4) (*Gr*).

Mixing of the components was produced in two blade mixer with a volume of 1000 cm³ chamber for 5 min at a temperature 110^{0}C. Then, the mixture was placed in a heated mold at 160^{0}C. After 12 min. of holding in the mold, the composition was compressed using laboratory press at a pressure of 22 MPa.

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Table 1
THE MAIN PROPERTIES OF ALUMINUM POWDER

Properties	Value
Chemical composition, %:	-
The main components, at least:	-
Aluminum	95
Impurities, not more:	-
Iron	0.5
Silicon	0.4
Copper	0.05
Manganese	0.01
The moisture content	0.2
Bulk density, g/cm³	0.15-0.30

Table 2
THE MAIN PROPERTIES OF BRONZE POWDER

Properties	Value
Chemical composition, %:	-
The main components, at least:	-
Copper	66.8-73
Tin	4.0-6.0
Lead	23.0-26.0
Impurities, not more:	-
Zinc	0.5
Aluminum	0.02
Iron	0.2
Silicon	0.02
Phosphorus	0.05
Antimony	0.5
Bulk density, g/cm³	3.0-4.0

To determine the parameters of the filler and study the morphology of composite films was used optical polarizing microscope Biolam S-11 equipped by digital camera Canon PowerShot with adapter. Analysis of the digital imaging was performed using ImageJ [22]. As morphometric characteristics of particulate fillers in the work was used their area, perimeter, equivalent diameter and shape factor.

The equivalent diameter (D_e) is the theoretical diameter for each object if it was circular in shape.

$$D_e = \sqrt{\frac{4S}{\pi}}, \quad (1)$$

S - area of the object that had been analyzed.

Shape Factor (R) is measuring of the shape of a measured object. A perfect circle will have a shape factor of 1. A line's shape factor will approach zero.

$$R = 4\pi S/P^2, \quad (2)$$

P - perimeter of the object that had been analyzed.

Except average values of the size and shape of particles the distribution of these parameters also had been analyzed using histograms.

To study the uniform distribution of particles of different types of fillers in the films cluster method of image analysis [20] were used further statistical analysis of data [23]. For this method micrographs of films conventionally were

Table 3
THE MAIN PROPERTIES OF COPPER POWDER

Properties	Value
Chemical composition, %:	-
The main components, at least:	-
Copper	99.5
Impurities, not more:	-
Iron	0.018
Lead	0.05
Arsenic	0.003
Antimony	0.005
Oxygen	0.20
The moisture content	0.05
Bulk density, g/cm³	1.25-2.0

Table 4
THE MAIN PROPERTIES OF SCALE-LIKE GRAPHITE

Properties	Value
Density, kg/m³	2040
The current density, A/cm²	14
Tensile strength in bending, MPa	17.2
Hardness Rockwell B	35
Ash content,% (max)	13
Residue on net № 016, % (max)	40
Moisture,% (max)	1.0

divided on a given number of areas and the concentration of the dispersed phase in each cluster was determined. Uniformity of distribution of particles in the films was assessed to rate of mixing index ($K_{n.}$), which is the ratio of the standard deviation of the concentration of particles in clusters (S) to their average concentration in the sample ($P_{m.}$):

$$K_{n.} = (S/P_{m.})\cdot 100\%. \quad (3)$$

Results and discussions

Comparative morphometric analysis of conductive fillers of varied origin

Microphotographs of studied conductive fillers particles are presented in figure 1. They demonstrate that particles of varied origin have significant difference in both size and form.

Histograms of conductive filler particles distribution by equivalent diameter are presented in figure 2. As can be seen from presented results, Gr particles have the highest and significantly different particles distribution. While maximum particle size for Al, Br and Cu varies within 320-400 µm, particle size for Gr is approximately two times higher.

Histograms also show that for Br and Cu the share of particles smaller than 50 µm is approximately 60%, while for Al it is significantly higher and amounts to approximately 90%. For Gr, distribution by equivalent diameter is close to normal, and the biggest share of particles (approximately, 70%) are 200-400 µm in size. Share of very small particles (less than 100 µm) as well as big particles (more than 600 µm) in Gr is insignificant and is approximately 1%.

Histograms of spatial distribution of different filler particles are presented in figure 3. For convenience, the

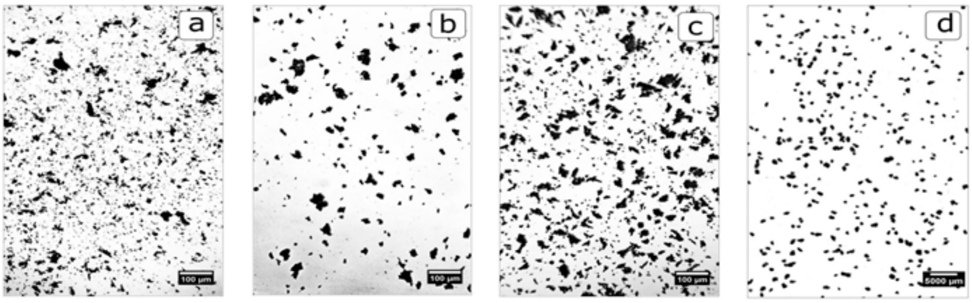

Fig. 1. Transmitted light microscopy images of conductive fillers: a) A1; b) Br; c) Cu; d) Gr

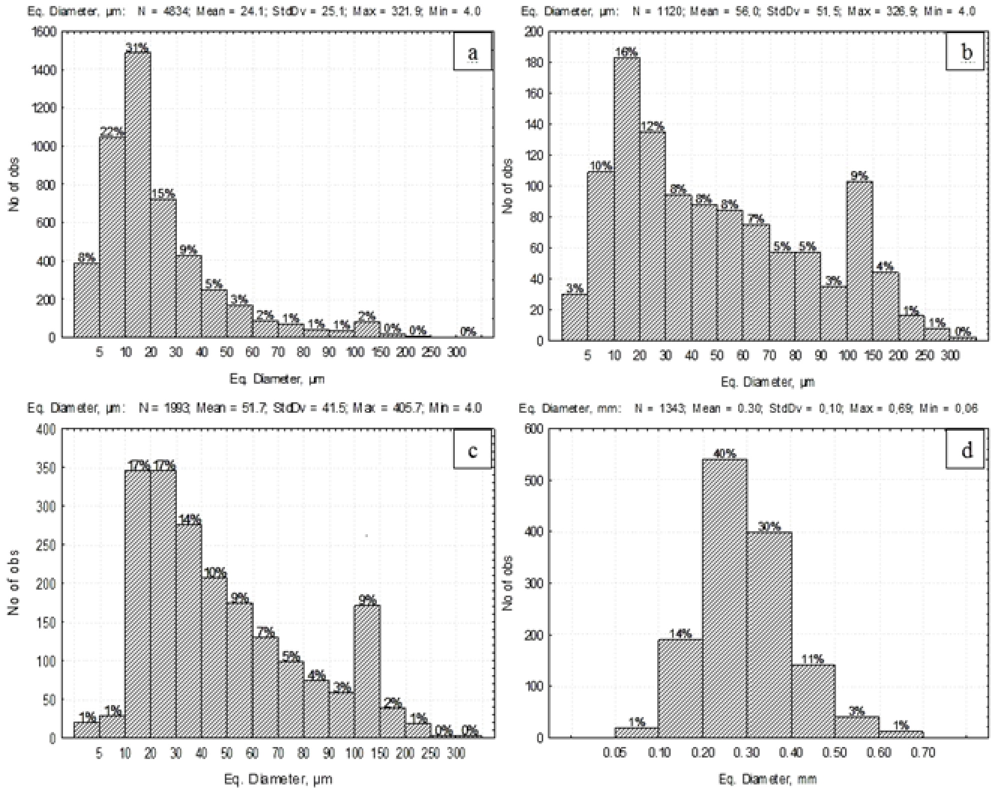

Fig. 2 Histogram of particle size distribution by diameter of conductive fillers: a) Al; b) Br; c) Cu; d) Gr

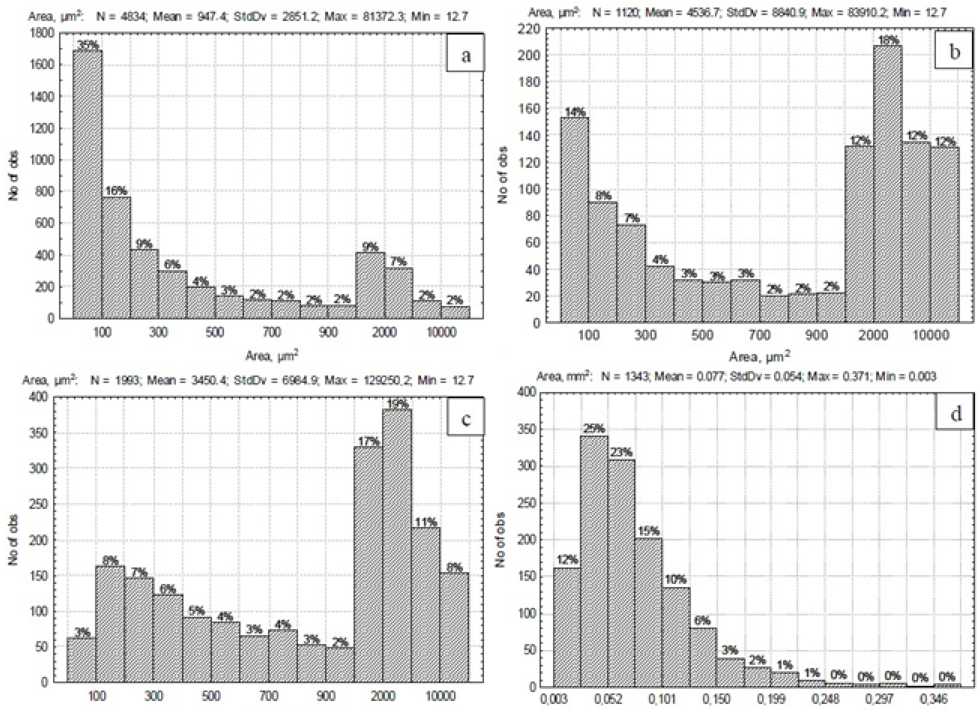

Fig. 3 Histogram of particle size distribution by area of conductive fillers: a) Al; b) Br; c) Cu; d) Gr

first three fillers (Al, Cu, Br) were analyzed in detail within 1000μm interval.

As can be seen from presented results, significant share of particles in researched fillers are of minimal area. E.g. for Al more than half of analyzed particles are less than 200 μm. The share of particles of the same size in Br and Cu is approximately two times lower. The share of particles bigger than 1000 μm is approximately 20% in Al, while in Br and Cu it is notably higher, e.g. in Br this share is more 50%.

Particles size in Gr is significantly bigger than in other three fillers. Analysis of distribution histogram (fig.3)

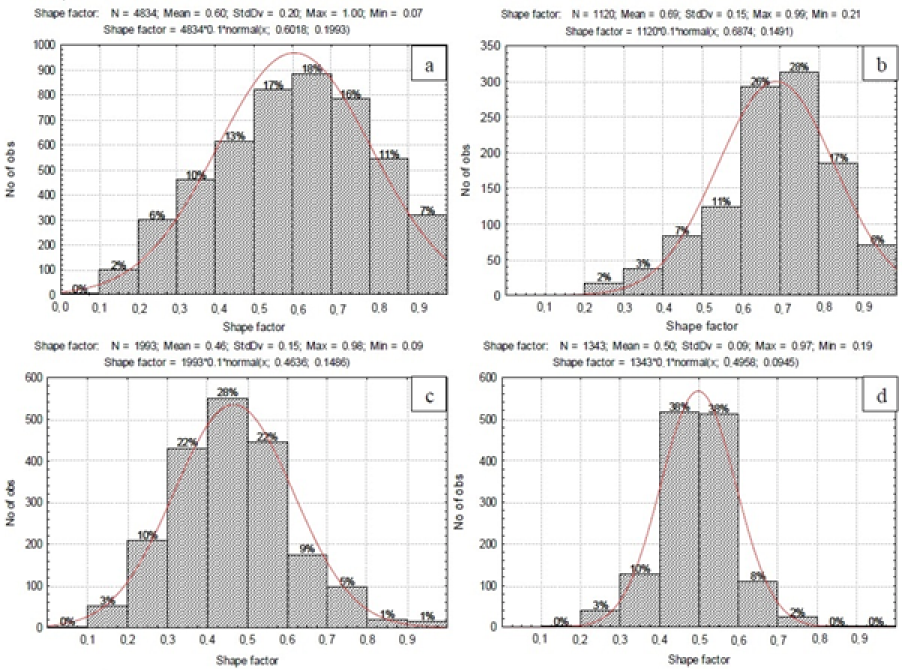

Fig. 4 Histogram of particle size distribution by shape factor of conductive fillers: a) Al; b) Br; c) Cu; d) Gr.

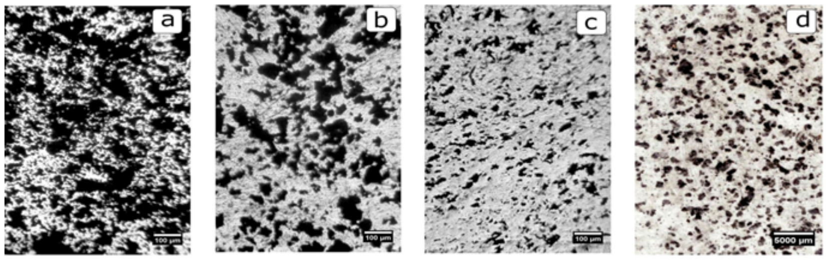

Fig. 5 Reflected light microscopy images of composite films based on PE, containing 5 vol. % of conductive fillers: a) Al; b) Br; c) Cu; d) Gr.

concludes that shares of under 0.05 mm^2 particles and of 0.05 to 0.10 mm^2 particles are approximately equal, and constitute more than 2/3 of volume content of the filler. Moreover, particles of more than 0.15 mm^2 in this filler sample have noticeable share of approximately 10%.

As a result, distribution by size characteristics shown in figure 2, 3 demonstrates that for Al, Br and Cu fillers these indicators are similar. At the same time, in Gr these indicators differ significantly both in distribution and in mean value.

Figure 4 demonstrates distribution histograms of conductive filler particles by form indicator. Conditionally, particles with shape factor of over 0.8 can be considered as approximate circular while particles with shape factor of under 0.2 can be considered highly anisometric.

More than half of particles in all studied fillers have shape factor within 0.4-0.8 interval. Characteristically, the share of near round particles (R>0.8) differs significantly for different types of fillers. Br and Al have the highest share (~23% and ~18% respectively), while for Gr and Cu this share is very low and amounts to less than 1-2%.

The share of highly anisometric particles (R<0.2) is low for all the studied fillers and does not exceed 2-3%. Cu has the highest share of these particles, while Gr has the lowest.

In general, it can be noted that the widest form distribution of the filler is observed in Al, while the narrowest is in Gr. However, the latter is also characterized by absence of both noticeably anisometric and near round particles.

Influence of conductive fillers nature on the structure of composite films

Figure 5 shows microphotographs of PE composite films containing 5% vol. conductive fillers of various types. It can be seen that the morphology and filler distribution depends greatly on its nature.

Samples containing Al are characterized by visible aggregation of filler particles. This can be a result of weak interaction on PE-Al margin compared to interaction between filler particles.

An earlier studies of PE filled films structure showed that during formation process filler aggregation and its migration towards film's surface can occur [6]. This can be due to filler's polymerophoby towards macromolecules of matrix polymer. Figure 5 shows that similar effect occurs in studied PE-Al composition. The result is Al particles aggregation and extremely high surface concentration of filler, which can be observed by microscopic examination. According to the quantitative analysis of images of the PE-Al film surface composition, with 5% vol. filler concentration it's average surface concentration is ~44%.

Comparing microphotographs in figure 1 and figure 5 shows that the filler like Br is also characterized by particles aggregation in composite film. At the same time, this fact is significantly less pronounced compared to Al composite films. This may be due to the larger particle size characteristics in Br, as well as different nature of interaction at polymer-filler margin. In composite films containing 5% vol. Cu and Gr, aggregation of the filler is practically nonexistent.

Thus, the same volume filling of different types of conductive fillers creates structures with significant differences in filler particles distribution in polymer matrix.

Results of the study of distribution uniformity of different filler particles in composite in composite films are shown in figure 6. Data comparison concludes that films containing Gr (K_n=21%) and Cu ($K_{n.}$=23%) are characterized by the highest uniformity. This can be due to lower aggregation of this type of particles which is visually evident in figure 5. Besides, this result may be due to the scale factor, since PE-Gr films have wider (compared to other films) analysis area.

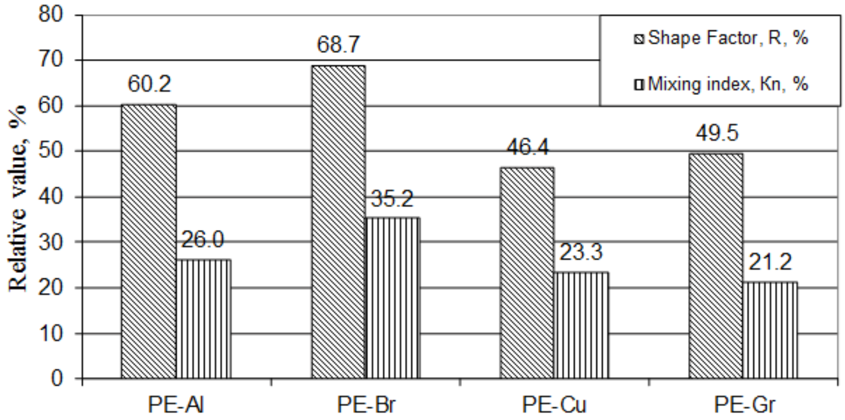

Fig. 6 Histogram for particle shape factor (R) and mixing index (K_n) for composite films with different types of conductive fillers.

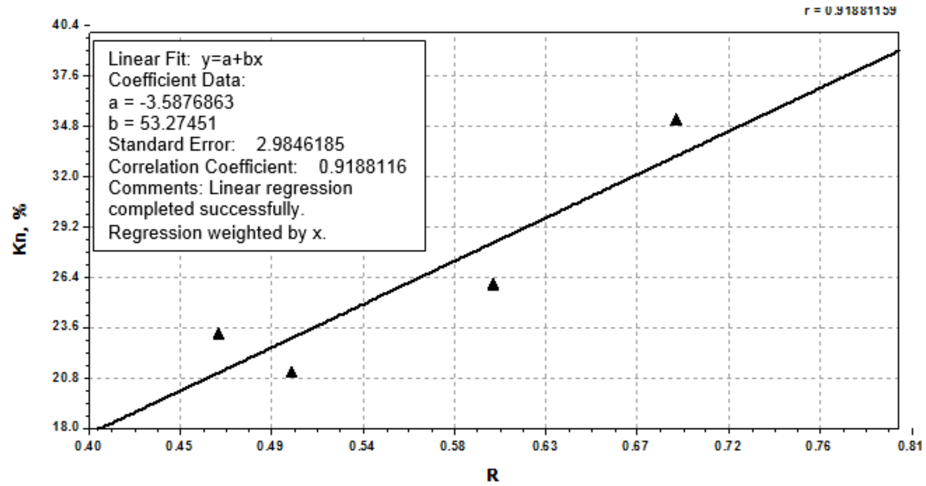

Fig. 7 Correlation between the shape factor (R) for filler particles and mixing index (K_n) in the composite films based on PE, containing 5 vol. % of conductive fillers

The «PE–Br» composition is characterized by the highest heterogeneity of particles distribution (K_n = 35%). Heterogeneity coefficient for «PE-Al» films is higher than for «PE–Gr» and «PE–Cu» films, but lower than for «PE - Br» composition.

As mentioned above, it is characteristic of «PE-Al» films to have high degree of filler aggregation. At the same time, «PE-Al» films have K_n value lower than «PE-Br» compositions, that can be explained by significantly smaller size of Al particles. As a result, the total number of filler particles in «PE-Al» compositions is higher than in «PE-Br» compositions while volume content is the same. Therefore, despite the forming of aggregates in PE films, a considerable number of small Aluminum particles are located between the aggregate spaces. It leads to certain concentration alignment in film and lowers its heterogeneity coefficient.

Comparison of studies of particles distribution uniformity in composite films and morphometric characteristics of fillers shows that the change of coefficient of particle distribution heterogeneity in composite films conforms with the change of its shape factor. These two indexes (K_n and R) are correlated (fig.7).

Thereby, increasing the mean value of anisometry in studied filler types increases the uniformity of their distribution in PE-based composite films.

Conclusions

Particles of different fillers that can be used in conductive polymer compositions were comparatively evaluated by optical microscopy and image analysis methods.

It was quantitatively established that nature of the filler influences the way particles are distributed in composite film. The most structural homogeneity was observed in PE-Gr and PE-Cu composites, while the least - in PE-Br composite.

Correlation between index of heterogeneity of particles distribution in composite films and index characterizing shape of particles was established. It was shown that the increase in the average value of the anisotropy of filler particles reduces heterogeneity of particles distribution in composite films.

Obtained results affirm that the shape factor of the filler particles should be considered when creating composite films with determined (predicted) level of homogeneity.

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