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Influence of particle aspect ratio and ability to aggregate on electrical conductivity of fiber-forming polymer composites

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Abstract. Fiber-forming polymer composites filled with carbon nanoparticles of three types (carbon black is a spherical filler; carbon nanofibers and carbon nanotubes are anisotropic nanoparticles) were produced by melt technology. Electrical conductivity of the fiber-forming polymer composites was measured; a function of the filler concentration and the percolation thresholds were determined. It was found that an increase in the aspect ratio of carbon nanoparticles leads to a decrease in the percolation threshold. The correlation between the axial ratio, stiffness, filler concentration and electrical conductivity of the percolation cluster in fiber-forming polymer composites was analysed.

Keywords: polymer composites, carbon particles, fiber-forming, electrical conductivity, percolation threshold, aspect ratio, aggregate.

Introduction

In recent decades electrically conductive composite materials based on polymer matrices have been in the spotlight of a range of technological fields from aircraft and tool engineering to medicine. The interest arises from the fact that electrical characteristics of such composites are close to the properties of metals, whereas mechanical properties and processing methods are typical for plastics.

The special properties of composites depend on filler concentration of nanoparticles and the shape of filler particles dispersed in the polymer matrix. The latter characteristic for nanocomposite materials is usually difficult to assess. For this reason, it is important to attempt establishing a correlation between the particle aspect ratio, ability to aggregate, and electrical conductivity of the composite material, which can be measured using simple methods. The presence of aggregates in the polymer matrix leads to a decrease in mechanical characteristics of electrically conductive polymer composites. Therefore, it is the electrical conductivity values of the composite material that make it possible to evaluate the quality of the technology used to introduce electrically conductive nanoparticles into the polymer and the dispersion degree of the filler. Polymer composites filled with dispersed carbon particles (especially carbon

nanotubes) are of special interest to both theoretical and applied science because the use of carbon nanotubes allows changing electrical conductivity in a wide range of values and improving mechanical characteristics of polymer matrices (Kymakis et al. 2002; Moskalyuk et al. 2012; Tarfaoui et al. 2017).

The percolation theory formulated for a continuous medium is often used to describe electrical properties of a composite material filled with electrically conductive particles (Fig. 1). According to this theory, each point of the space corresponds to electrical conductivity $\sigma = \sigma_f$ with the probability $p = \vartheta_f$ and to electrical conductivity $\sigma = \sigma_m$ with the probability $1 - p$. Here, ϑ_f is the fraction of conducting particles in the bulk of the polymer matrix; σ is electrical conductivity; and the indices f and m denote the filler and the matrix, respectively (Kinloch et al. 2018; Moskalyuk et al. 2012; Tarfaoui et al. 2017).

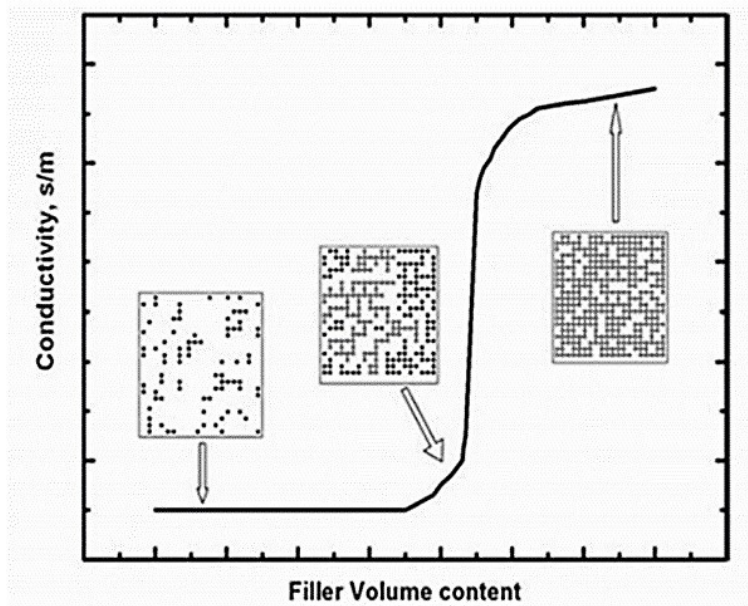


Fig. 1. Dependence of the polymer composites conductivity on the filler content

The percolation threshold in this case is equal to the minimum fraction of the space occupied by conducting regions at which the system is still conducting (Kinloch et al. 2018). Electrical conductivity of the composite material increases non-monotonically: the most dramatic change in electrical conductivity occurs, as a rule, in a narrow range of filler concentrations, which suggests a dielectric–metal transition or a percolation transition when the quantity ϑ_f is equal to the percolation threshold (Kinloch et al. 2018; Moskalyuk et al. 2012). At filler concentrations above and below the percolation threshold, dependence of the composite material electrical conductivity on the concentration of the carbon filler differs significantly. At low concentrations of the filler (the first horizontal section in Fig. 1), all conductive particles introduced into the polymer matrix are combined into finite-size clusters that are isolated from each other. With increasing concentration of conductive particles, the average cluster size also increases. At $\vartheta_f = \vartheta_f^*$, most of the clusters at first isolated from each other are combined into an infinite cluster, penetrating the entire system with the formation of a conduction channel (Kinloch et al. 2018; Matos et al. 2019; Moskalyuk et al. 2012). With the further increase in the concentration of the conducting filler, the volume of the endless cluster increases as a result of absorption of the final clusters, especially the largest ones. Thus, the average size of the final clusters decreases (Kinloch et al. 2018; Matos et al. 2019; Moskalyuk et al. 2012).

The description of the correlation between physical and geometric analyses is the main task of percolation theory. One of the simplest approaches and, consequently, the most studied one is the description of structures based on regular lattices. In this approach, the identification of nodes and links that have a certain fraction $(1-p)$ of randomly selected nodes (along with outgoing links) or a part of randomly selected links is performed. The answer (cut) is determined in such a way that the grid breaks into two parts. During the node identification, nodes are blocked (network nodes are destroyed) (Matos et al. 2019). Percolation on a square grid is just one of possible patterns. It is also possible to study percolation on triangular and hexagonal grids, trees, as well as on more complex (three-dimensional) lattices,

for example, cubic ones. The grid does not have to be regular. Random lattice processes are also considered (Kovacs et al. 2007).

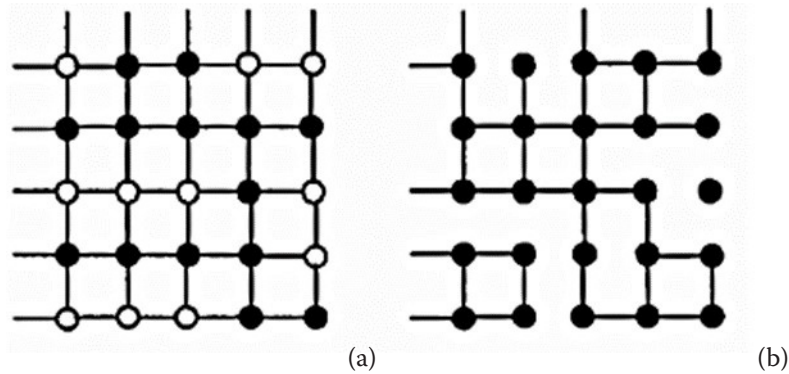


Fig. 2. The knot problem (a) and the connection problem (b) on a square lattice

The analysis of the topology of an infinite cluster showed that it contributes to infinite clustering and permittivity, but not to conductivity (Kovacs et al. 2007; Matos et al. 2019). Such chains were called “dead ends”. An infinite cluster without dead ends was called a skeleton of an infinite cluster. A skeleton of an infinite cluster was first described in the Shklovskii–De Gennes model (Efros, Shklovskii 1976; Li et al. 2006; Ukshe et al. 2020). It is an irregular lattice with an average distance between nodes, depending on the proximity of the filler concentration to the percolation threshold.

$$\begin{aligned} \sigma_c &= \sigma_f (\vartheta_f - \vartheta_f^*)^\beta, \text{ if } \vartheta_f > \vartheta_f^* \\ \sigma_c &= \sigma_f (\vartheta_f - \vartheta_f^*)^\beta, \text{ if } \vartheta_f < \vartheta_f^* \\ \sigma_c &\approx \sigma_f X^\delta, \text{ if } \vartheta_f \approx \vartheta_f^*, \end{aligned}$$

where $X = \sigma_2/\sigma_1 \ll 1$; Table 1 provides the parameters α , β , and $\delta = \beta / (\alpha + \beta)$ for different flow models.

Table 1. Parameters of some percolation models near the percolation threshold

	Cn	α	β	δ
Three-dimensional connection problem (cubic lattice)	0.25	1	1.6	0.67
Two-dimensional connection problem (square lattice)	0.5	1	1.1	0.51
Three-dimensional flow model (continuous medium)	0.145	1	1.4	0.65

In the case of a polymer composite filled with anisotropic electrically conductive fillers (e. g., carbon nanotubes), the conductive cluster may consist of randomly oriented anisometric particles (fibers, cylinders). Electrical conductivity of such a polymer composite is always anisotropic (Kinloch et al. 2018; Kymakis et al. 2002; Moskalyuk et al. 2012; Tarfaoui et al. 2017). Polymer composites filled with anisotropic fillers usually have a considerably lower percolation threshold than polymer composites filled with spherical or spheroidal particles. Electrical properties of composite materials with anisotropic spheres or isotropic elongated particles were previously investigated in detail (Kinloch et al. 2018; Kymakis et al. 2002; Moskalyuk et al. 2012; Tarfaoui et al. 2017).

The aim of this study was to investigate electrical conductivity of fiber-forming polymer composites filled with two types of carbon nanoparticles: spherical particles with an aspect ratio 1—carbon black—and particles with a high aspect ratio—carbon nanofibres and carbon nanotubes—in which the L/D is 10 times different from each other. Nanoparticles used in the study vary in size, shape (aspect ratio) and hardness. Hardness of the filler is crucial for the effective introduction of nanoparticles into the fiber-forming polymer matrix and ensuring high conductivity because only hard particles are able to maintain their original shape when introduced into the polymer matrix (Kinloch et al. 2018; Moskalyuk et al. 2012; Tarfaoui et al. 2017). For example, this property is observed in such carbon particles as carbon black and carbon nanofibers which have the necessary rigidity. Unlike them, such flexible structures as

carbon nanotubes, which have the highest aspect ratio of all carbon particles, can retain their original shape in the bulk of the polymer matrix or may lose it. If carbon nanotubes take the form of globules, spirals or aggregates, the optimal values of electrical conductivity in the polymer composite cannot be achieved, and this can also lead to a deterioration in mechanical properties (Kymakis et al. 2002; Moskalyuk et al. 2012). An attempt was made to relate the shape of the carbon nanoparticles dispersed in the fiber-forming polymer to the threshold concentration of the percolation cluster formation and electrical conductivity of a percolation cluster at the percolation threshold.

The aim of this study was to obtain fiber-forming polymer composite based on polypropylene matrix filled with different types of carbon particles using melt technology and investigate the influence of particle aspect ratio and ability to aggregate on electrical conductivity of composites.

Sample preparation and experiment

The fiber-forming polymer matrix was isotactic polypropylene Balen 01270 (Ufa Petroleum Refinery, Bashneftkhim, Ufa). The density was 0.9 g/cm³; melt flow rate (MFR) was 27–30 g/10 min.

Carbon black (CB) P-805 E, graphitised carbon nanofibers (CNF) VGCF-H by Showa Denko K. K., Japan, and multi-walled carbon nanotubes (CNT) CTube-100 by CNT Co., LTD, Korea, were used as fillers for fiber-forming polymer composites. The parameters of the carbon nanoparticles used are presented in Table 2.

Table 2. Parameters of the carbon fillers used

Characteristic	Carbon black P-805 E	Carbon nanofibers VGCF	Multi-walled carbon nanotubes CTube-100
Aspect ratio (L/D ratio)	~1	~30	~400
Electrical resistivity, S/m	10 ⁻¹	10 ⁻²	10 ⁻⁵ –10 ⁻¹

Carbon black is a cluster consisting of primary particles with an average size of ~80 nm and has an almost spherical or ellipsoidal shape with an aspect ratio of order unity. Carbon nanofibers have the form of rigid cylinders from 100 to 150 nm in diameter, which are characterised by a moderate aspect ratio of ~30. Carbon nanotubes are flexible fibers from ~10 to ~40 nm in diameter with a very large axial ratio average ~400.

The samples of fiber-forming polymer composites were prepared using melt blending technology with a DSM Xplore 5 ml Twin Screw Microcompounder (Netherlands). Dispersion of the filler in the polymer melt was carried out for 5 minutes at a temperature of 200°C and a screw rotation speed of 75 rpm. Then the fiber was extruded through a round die installed at the exit of the Twin Screw Microcompounder chamber. Immediately after leaving the spinneret, the fiber-forming polymer material was rapidly cooled and wound at a constant speed on coils of the receiver device. Composite fibers had a diameter of 400 μm.

The current–voltage characteristics of the fibers were measured at a direct current in the voltage range from –100 to +100 V using an automated setup based on a Keithley 6487 picoammeter and an AKIP_1124 programmable power supply.

The dispersion quality of nanoparticles in the bulk of the polypropylene matrix was controlled by examining the fracture surfaces of the samples of the composite fibers with a Supra 55 scanning electron microscope (Carl Zeiss, Germany). In order to remove the charge of static electricity and to improve the contrast, gold was evaporated onto the surface under investigation.

Results and discussion

The change in electrical conductivity of the fiber-forming polymer composites according to the filler concentration with different morphologies and sizes (CB, CNF, CNT) is presented in Fig. 3. Pure polypropylene has electrical conductivity of ~10⁻¹⁴ S/m.

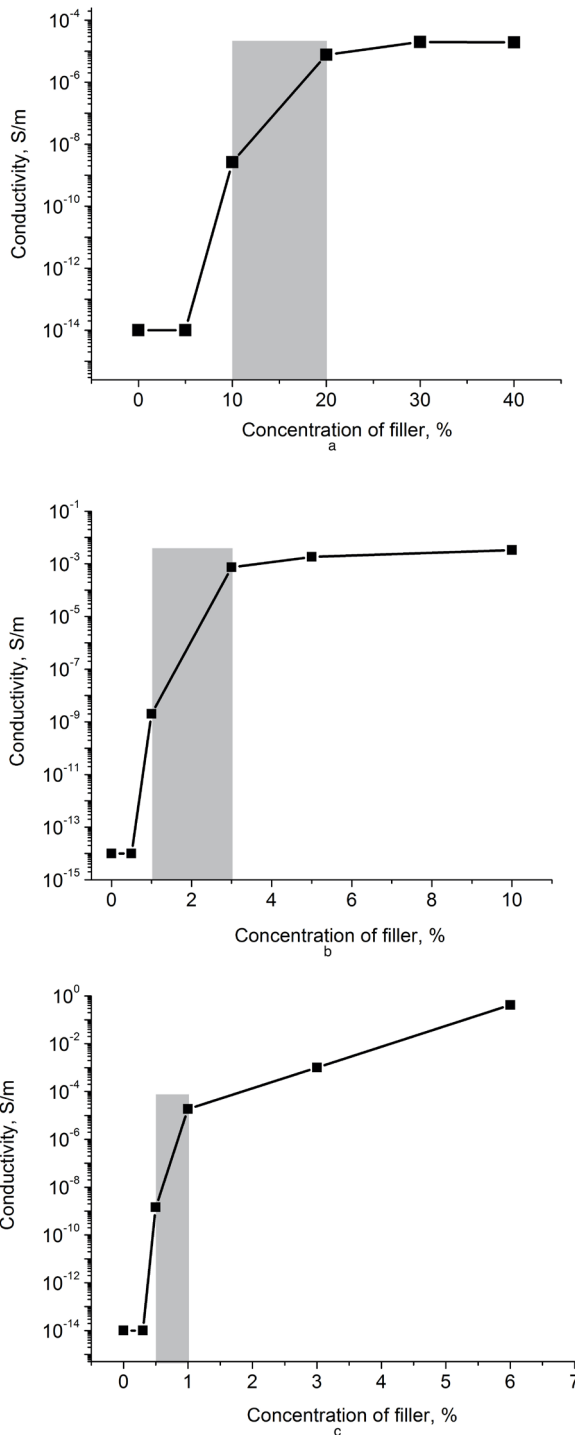


Fig. 3. Change in electrical conductivity of composite materials based on polypropylene according to the concentration of (a) carbon black, (b) graphitised carbon nanofibers, (c) multi-walled carbon nanotubes. The percolation threshold is highlighted in colour

Fig. 3 shows three clearly distinguishable sections in the concentration dependences of electrical conductivity for all fiber-forming polymer composite materials: the first one is a horizontal section where the filler concentration is not sufficient to form an electrically conductive cluster in the volume of the polymer matrix; the second one is a steep section with a sharp increase in electrical conductivity with an increase in filler concentration, i.e. a conducting cluster is formed; and the third section is the smoothed part of the increase in electrical conductivity with an increase in filler concentration above the percolation threshold. Cryo-cleavage micrographs of fiber-forming polymer composite fibers are presented in Fig. 4.

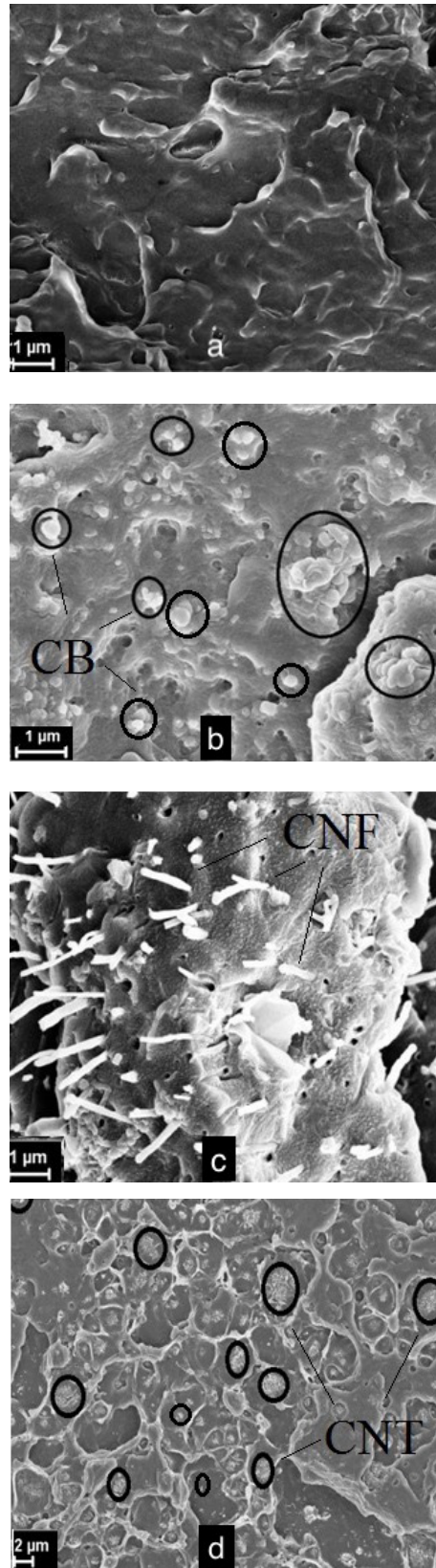





Fig. 4. Cleavage micrographs of (a) pure polypropylene fibers and (b) polypropylene filled with 20% carbon black, (c) 10% graphitised carbon nanofibers and (d) 6% multi-walled carbon nanotubes

As can be seen from Fig. 4b, carbon black is dispersed in a fiber-forming polypropylene matrix both at the size of the primary particles and with the formation of conglomerates up to 2 microns in size. With an increase in the filler concentration, conglomerate sizes also increase. Carbon nanofibers up to the

maximum filling, dispersible in a fiber-forming polypropylen composites, retain their original shape (Fig. 4c). At the same time more flexible carbon particles (carbon nanotubes) with a high aspect ratio demonstrate the ability to aggregate (Fig. 4d). The average aggregate size is 2 microns.

Summarising the above results, the filler concentration and shape of the percolation cluster for the fiber-forming composite fibers are listed in Table 3. The nanoparticle concentration at the percolation cluster was determined in the middle of the increasing straight-line section.

Table 3. Filler concentration and shape of the percolation cluster for the fiber-forming composite fibers

Reference parameter	CB	CNF	CNT
Filler concentration of the percolation cluster, wt%	15	2	0.75
Piece shape of the percolation cluster			

Based on the $\sigma(\theta)$ dependence, percolation thresholds are established for fiber-forming polymers filled with carbon nanoparticles with a typical axial ratio: 10–20 wt% for CB, 1–3 wt% for CNF and 0.5–1.0 wt% for CNT (Fig. 3, the percolation threshold is highlighted in colour). In the case of carbon black (particles with L/D ratio~1), the conductive cluster is a chain of their conglomerates. For CNF (hard particles with L/D~30), a conducting cluster is formed due to contacts between individual particles. For CNT (flexible particles with a high aspect ratio L/D~400), a conducting cluster is formed of single particles and their aggregates.

The nanoparticle concentrations determined at the percolation threshold and after the percolation threshold at the maximum concentration of carbon nanofillers are listed in Table 4. Electrical conductivity at the percolation cluster was determined in the middle of the increasing straight-line section.

Table 4. Electrical conductivity of the fiber-forming composite fibers

Reference parameter	CB	CNF	CNT
Electrical conductivity of the percolation cluster, S/m	$\sim 10^{-7}$	$\sim 10^{-6}$	$\sim 10^{-6}$
Electrical conductivity at the maximum concentration of carbon nanofillers, S/m	$\sim 10^{-4}$	$\sim 10^{-3}$	$\sim 10^0$

In the case of fiber-forming composites filled with spherical carbon particles, electrical conductivity of the percolation cluster is $\sim 10^{-7}$ S/m; for composites filled with anisotropic particles (CNF and CNT), electrical conductivity of the percolation cluster is an order of magnitude higher. Thus, an increase in the axial ratio of CNT in comparison with CNF does not lead to an increase in electrical conductivity of the percolation cluster. For carbon black particles with L/D~1 electrical conductivity at the maximum filler concentration is $\sim 10^{-4}$ S/m. With aspect ratio increased by thirty times (CNF) electrical conductivity at the maximum filler concentration is $\sim 10^{-3}$ S/m. For carbon particles L/D~400 (CNT) electrical conductivity at the maximum filler concentration is $\sim 10^0$ S/m.

The following conclusions can be drawn from the data presented in Fig. 3 and in Tables 3 and 4. An increase in the aspect ratio of nanoparticles leads to a decrease in the threshold concentration of the filler and electrical conductivity of the percolation cluster increases by an order of magnitude. Thus, the effect is observed when comparing the results obtained for fiber-forming polymer composites filled with carbon black and carbon nanofibers, the aspect ratio of which is 30 times different (Kinloch et al. 2018; Moskalyuk et al. 2012; Tarfaoui et al. 2017). An increase in the concentration of CB and CNF above the percolation threshold does not any further lead to an increase in electrical conductivity of fiber-forming composites. This effect means that the contribution to electrical conductivity from the conducting

clusters formed upon the introduction of additional carbon particles above the percolation threshold is significantly less than conductivity of the polymer composite formed during the formation of the percolation threshold (Kinloch et al. 2018; Moskalyuk et al. 2012).

Comparison of the data obtained for fiber-forming polymer composites filled with CNF and CNT has demonstrated that an increase in the aspect ratio of carbon nanoparticles by 10 times decreases the percolation threshold. It should be noted that the percolation threshold in composites filled with carbon nanotubes is usually lower than the values obtained in this study. Since the CNT conductivity is at or lower than that of CNF (Table 2) and the aspect ratio is 10 times greater than that of CNF, we can conclude that flexible carbon particles (nanotubes) do not retain an elongated, almost straight shape when dispersed into a fiber-forming polymer matrix, which does not allow to obtain an effective increase in electrical conductivity of the polymer (Fig. 4d). Therefore, the technology used to introduce nanoparticles into a fiber-forming polymer is suitable only for the preparation of a composite with rigid (i.e. not flexible) nanoparticles, such as CB and CNF, while its usage for flexible carbon structures (carbon nanotubes) is not justified. Microphotography shows that carbon nanotubes do not generally retain their straight shape when introduced into a fiber-forming polymer matrix; instead, they form dense clusters and globules. Therefore, the final sizes of electrically conducting particles and their aspect ratio change and differ significantly from the original ones (Kinloch et al. 2018; Moskalyuk et al. 2012; Tarfaoui et al. 2017). Future studies should lead to the development of alternative ways to introduce flexible carbon nanoparticles into a fiber-forming polymer matrix. This will allow us to use such unique particles more efficiently in order to create electrically conductive polymer composites.

Thus, it is impossible to draw conclusions about the effect of electrically conductive fillers on electrical conductivity of the fiber-forming polymer matrix based on their aspect ratios only. It is necessary to confirm that the nanoparticles dispersed in the polymer matrix retain a shape that is close to rectilinear.

Conclusions

Fiber-forming polymer composites filled with carbon nanoparticles with different aspect ratio (carbon black, graphitised carbon nanofibers and multi-walled carbon nanotubes) were obtained in laboratory conditions using a twin-screw microextruder. Electrical conductivity of the fiber-forming polymer composite was measured. The dependence of electrical conductivity of the filler concentration has a threshold character. The percolation thresholds were observed at concentration 10–20 wt% for spherical particles (carbon black), at concentration 1–3 wt% for anisotropic nanoparticles and 0.5–1.0 wt% in the case of carbon nanofibers and carbon nanotubes. The percolation threshold can be shifted towards the lower filler concentrations with an increase in the aspect ratio of electrically conductive nanoparticles. In this case, electrical conductivity of the percolation cluster can increase by one order of magnitude. To use electrically conductive nanoparticles with a high aspect ratio as efficiently as possible when creating fiber-forming polymeric composites, it is necessary to take into account not only the L/D of fillers, but also the nature of their dispersion in the polymer matrix. Flexible nanoparticles with a high aspect ratio should maintain an almost rectilinear shape when dispersed into a polymer matrix.

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