

# Strengthened Electrically Conductive Composite Materials Based on Ultra-High-Molecular-Weight Polyethylene Reactor Powder and Nanosized Carbon Fillers

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**Abstract**—Electrically conducting samples of polymer composites of different compositions based on the reactor powder of ultra-high-molecular-weight polyethylene (UHMWPE) with a special morphology filled with fine powders of graphite, carbon nanotubes (CNTs), and electrically conducting carbon black (CB) are investigated. Strengthened oriented electrically conductive polymer composites possessing high tensile strength and conductivity values are obtained by the compaction of mechanical mixtures of the polymer and fillers powders, followed by the uniaxial deformation of materials under homogeneous shear conditions. Changes in the electrical conductivity of oriented composite materials during reversible “tension–contraction” cycles along the orientation axis direction are studied. The influence of the type of nanosized carbon filler on the electrical conductivity and mechanical properties of strengthened conductive composites oriented under homogeneous shear conditions is investigated.

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## INTRODUCTION

Electrically conducting polymer composites containing nanosized filler of various types (nanotubes, graphene, fullerenes, finely dispersed graphite, or carbon black (CB)) are of great interest for both scientific studies and multiple practical applications [1–6]. Based on them, materials that are cheap, light, and resistant to aggressive media may be developed with the electrical resistivity changing, depending on the filling degree and filler type, over wide range:  $10^9$ – $10^{14}$  Ohm cm for antistatic materials,  $10^5$ – $10^9$  Ohm cm for electromagnetic radiation absorbing materials, and  $10^3$  Ohm cm for semiconducting materials.

Among a large number of various polymer matrices used for the design of filled electrically conductive polymer composites [1–6], a special place belongs to ultra-high-molecular-weight polyethylene (UHMWPE), possessing a complex of valuable exploitation characteristics such as low bulk density, chemical resistance to aggressive gaseous and liquid media, hydrophobicity, abrasive resistance, physiological inactivity, cold endurance, X-ray radiation tolerance, etc.

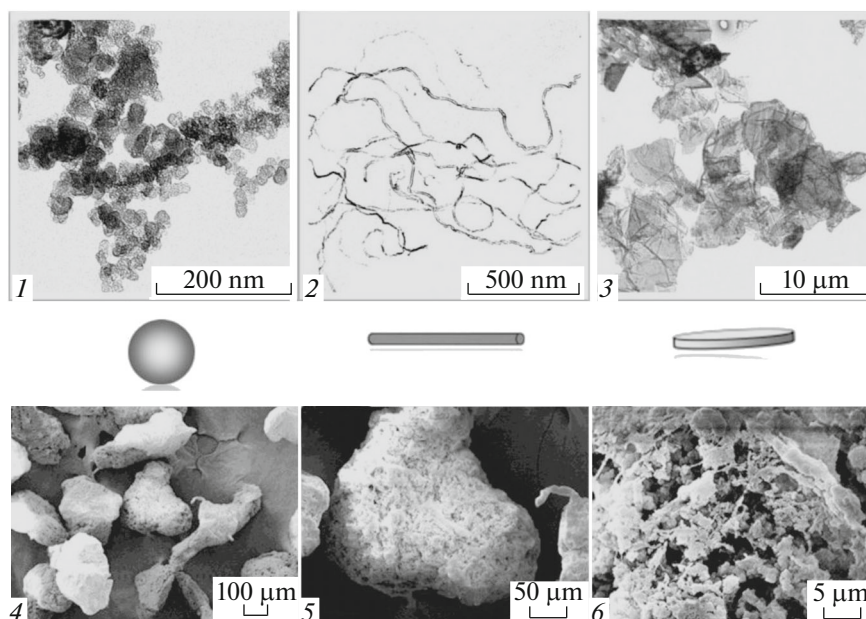
The main drawback of polymers of this class is the difficult processing of both the polymers themselves

and filled systems on their basis into final products, since the UHMWPE melt is nonfluid. Nevertheless in a series of papers [7–13], the preparation and properties of UHMWPE-based conductive composites with various carbon fillers have been described.

The analysis of experimental data obtained so far for filled conductive polymer composites makes it possible to conclude that, in order to extend the range of applicability of these materials, it is necessary to enhance their tensile characteristics. The uniaxial tensile strength and elongation at the break of these composites are, as a rule, very low at the filler volume fraction values that provide a high level of material electrical conductivity.

It is known [14] that an efficient and rather universal way of to strengthen polymer materials is orientation stretching. However, the orientation stretching of polymer composite materials filled with various finely dispersed fillers is often accompanied by their brittle failure already in the initial stages of deformation [15–17], thus preventing the use of this approach for the enhancement of tensile characteristics of composite materials.

The complexity of the problem under discussion, especially for high concentrations of conductive filler



**Fig. 1.** Electron micrographs of nanodispersed carbon fillers ((1) CB, (2) CNT, and (3) NG) and the reactor powder of UHMWPE [21] at different magnifications ((4)  $\times 100$ , (5)  $\times 300$ , and (6)  $\times 3000$ ).

in the system, is revealed by sporadic attempts to obtain high-strength conductive oriented fibers of UHMWPE composites with carbon nanotubes (CNTs) using sophisticated and costly processing technologies of solution [18] or gel spinning [19].

The possibility of obtaining strengthened electrically conducting UHMWPE-based composites by means of a uniaxial shear deformation of room-temperature compacted mechanical mixtures of the UHMWPE reactor powder, possessing a special morphology, with nanosized carbon particles of various types is described in the present work. The uniaxial tensile strength of the oriented electrically conductive composites exceeds that of nonoriented composites of the same composition by an order of magnitude.

The main aim of the paper is to study the effect of the type of nanosized carbon filler on the electrical conductivity and mechanical properties of the strengthened conductive composites prepared under uniaxial shear conditions.

Some preliminary results of the investigation were published earlier [20].

## MATERIALS AND METHODS

Electrically conductive samples of polymer composites of various compositions based on a polymer matrix prepared from the initial finely dispersed UHMWPE reactor powder [21] possessing a nodular morphological structure ( $MW = 5 \times 10^6$ , bulk density of the reactor powder  $0.058 \text{ g/cm}^3$ ) are investigated.

This choice of the initial reactor powder type for the subsequent continuous extrusion of the UHMWPE

polymer matrix makes it possible to achieve a continuous solvent-free solid-state (below melting temperature) extrusion of high-strength (tensile strength above 2.5 GPa) and high-modulus (elastic modulus up to 150 GPa) oriented materials with the structure and thermodynamic characteristics described, e.g., in [21–26].

Model systems used as fillers in the present work include nanodispersed graphite (NG), CNTs, and electrically conductive CB, being qualitatively different types of nanosized electrically conductive particles.

NG particles are in the form of thin plates with a high aspect ratio; CNTs are highly stretched one-dimensional structural formations, having also a high aspect ratio; and CB particles are globular structures which may be roughly approximated by spheres. Particles of these types are often used as electrically conducting fillers for various polymer matrices [13, 27–29].

To fill the composites, commercially available electrically conductive CB of the brand P 267-E, Nanocyl™ NC 7000 CNTs [30] and Grade AO-3 NG (Graphene Laboratories) were used [31].

Electron micrographs of carbon fillers particles and the reactor UHMWPE powder are presented in Fig. 1.

It is known that nanosized carbon particles (CNTs, graphene, etc.) possess a high surface energy [29, 30–32], leading to the aggregation of nanoparticles and preventing their homogeneous distribution in a polymer matrix, regardless of the mixing method selection [29, 37].

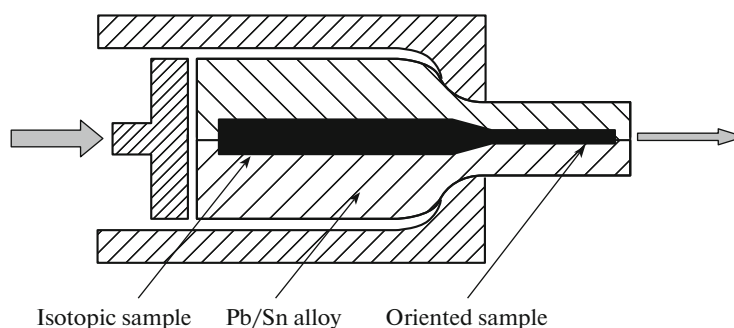


Fig. 2. Scheme of the device for homogeneous shear of materials [15].

In the present work, the following approach was employed in order to “standardize” the preparation conditions for composite materials with various types of carbon fillers and to decrease the sizes of their aggregates.

The initial mixing of the fine dispersed UHMWPE reactor powder and a filler of one kind or another was carried out by means of their simultaneous addition at predefined proportions to a non-solvent liquid (hexane or heptane), followed by their dispersal under a short ultrasonication, resulting in a homogeneous distribution of filler particles over the polymer surface (the “powdering” effect, see also [13, 29]). The mechanical method of the initial mixing of the polymer and filler used in the work allows conductive composite materials to be obtained with a lower percolation threshold than that provided by solution or melt methods of the initial mixing. The superiority of this approach was proven earlier by both experiments [8, 12, 13, 29, 38–40] and calculations based on the models suggested for this case [41–43].

The suspension of particles of the UHMWPE reactor powder coated with carbon filler particles was filtered and dried until the dispersion medium was completely removed. The initial compacted nonoriented  $\sim 0.5$ -mm-thick plates of UHMWPE/CB-m, UHMWPE/CNT-n, and UHMWPE/NG-k conductive composite materials (m, n, and k are the filler content, wt %) were prepared by the cold molding of the obtained blend of UHMWPE and filler particles at room temperature ( $20^\circ\text{C}$ ) in a special mold under the pressure 200 MPa and cut into pieces for their subsequent orientation stretching.

In order to enhance tensile characteristics of the compacted samples, they were uniaxially oriented at room temperature in a special appliance [15], providing a combination of compression deformation with an homogeneous shear of a sample placed between clads made of a plastic Pb/Sn alloy (Fig. 2).

The final deformation of the material characterized by the relative uniaxial deformation  $\varepsilon_d = ((l_d - l_0)/l_0) \times 100\%$ , where  $l_d$  and  $l_0$  are the lengths of the oriented

and initial nonoriented composite samples, respectively, was varied by means of extrusion of samples through conical dies of different diameters.

Stress–strain characteristics of materials (tensile strength  $\sigma_p$  and elongation at break  $\varepsilon_p$ ) were determined from deformation curves “stress ( $\sigma$ )–strain ( $\varepsilon$ )” for the prepared nonoriented composite samples and oriented samples with different  $\varepsilon_d$  values in the stretching mode at room temperature with the initial deformation rate  $0.2 \text{ min}^{-1}$  using Tinius Olsen H1KS and Shimadzu AGS-10 universal testing machines.

For composites, showing additional orientation strengthening under subsequent tests, the uniaxial tensile yield stress was taken for the tensile strength  $\sigma_p$ , and the brittle failure stress was used in all other cases.

Direct current electric conductivities of the formed nonoriented plates and oriented composite samples were determined by means of the four-probe method of the resistance measurement, as well as by the two-probe method with the use of a 34401A multimeter (Agilent).

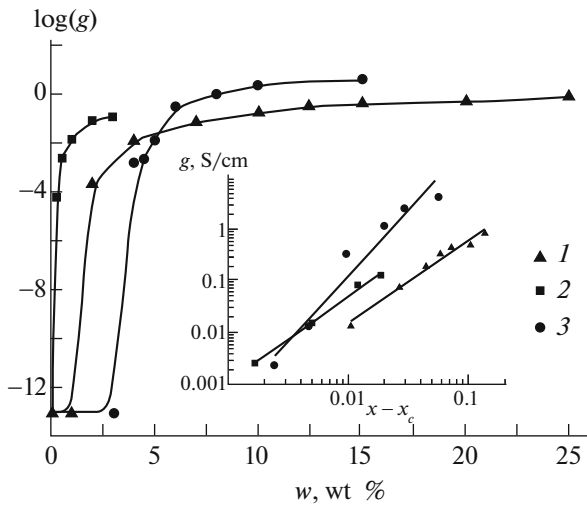
Wide angle X-ray diffraction patterns were registered on a Bruker NANOSTAR setup with a two-dimensional detector of  $\text{CuK}_\alpha$ -radiation.

Electron microscopic investigations of carbon-fillers powders at different magnifications were performed using JSM-35, JSM 6460 LV (Jeol), and LEO Gemini 1530 (Zeiss) scanning microscopes with an SDD detector (Thermo Scientific). The low-temperature chipping method at liquid nitrogen temperature was employed to prepare bulk composite samples.

## ELECTRICALLY CONDUCTIVE PROPERTIES OF COMPOSITES

Changes in electrically conductive properties of composite materials consisting of conducting and insulating components, depending on the conducting component content, have been described in numerous publications on the percolation theory [44–47].

In Fig. 3, dependences of the specific conductivity of UHMWPE/CB, UHMWPE/CNT, and



**Fig. 3.** Dependences of the specific conductivity  $g$  of nonoriented composites (1) UHMWPE/CB, (2) UHMWPE/CNT, and (3) UHMWPE/NG on the filler weight content  $w$ . The inset shows an approximation of the concentration dependences of the specific conductivity by the percolation equation.

UHMWPE/NG composites under investigation in the present work on the filler content (filling degree) are presented. The dependences make it possible to determine the so-called “percolation threshold,” i.e., the filler content at which the specific conductivity increases by about several orders of magnitudes.

According to [44–47], parts of an S-shaped curve for the dependence of conductivity on the filler content may be approximated by the percolation equation

$$g = g_0(x - x_c)^s, \quad (1)$$

where  $g$  is the specific conductivity of a composite,  $x$  is the volume content of a conductive filler,  $x_c$  is the percolation threshold, and  $s$  is the critical index characteristic of the above-threshold part of the conductivity dependence on the filler content. The critical index  $s$  characterizes the dimension of the spatial distribution of the conducting filler in the composite matrix. Thus, e.g., the index values  $s = 1.6–2$  correspond to the three-dimensional distribution of the filler and  $s = 1–1.3$  corresponds to a two-dimensional system [45].

The approximation of the dependences shown in Fig. 3 via percolation equation (1) made it possible to

determine the values of percolation thresholds  $x_c$  and critical indexes  $s$  for each type of filler in the UHMWPE matrix. The results are presented in the table.

Based on the values obtained by us (the table), it may be concluded that the spatial distribution for two types of investigated fillers, CNT and CB, is three-dimensional. This result agrees with data [48], but it differs from results [18, 26, 45], where a two-dimensional character of the conductive filler distribution was found for composites with components blended preliminarily by means of a method similar to that used in the present work.

For a third of the fillers investigated in the present work, NG, the critical index value  $s = 2.5$  is beyond the range of theoretically predicted values. We suppose that a possible reason for the observed disagreement between the experimental data and theoretical predictions in this case is the presence of aggregates of the filler particles in the prepared samples of electrically conductive UHMWPE/NG samples, which is difficult to take into account exactly when the corresponding model system is formulated and analyzed.

Samples with a filler content certainly exceeding the percolation threshold were selected from the whole series of the prepared nonoriented composites with different filler types for the subsequent analysis and investigations: UHMWPE/CB-20, UHMWPE/CNT-3, and UHMWPE/NG-10. The selected electrically conductive composite samples were uniaxially oriented under homogeneous shear (HS) conditions in order to prepare strengthened composite materials.

Dependences of the change in conductivity of initially highly conductive nonoriented composites with different fillers selected for subsequent analysis on the value of their relative uniaxial deformation  $\varepsilon_d$  under HS conditions are presented in Fig. 4.

For all systems, a decrease in the conductivity with increasing  $\varepsilon_d$  was observed. For UHMWPE/CB and UHMWPE/CNT composites, the conductivity increased smoothly with  $\varepsilon_d$ , while for UHMWPE/NG the dependence had a threshold character.

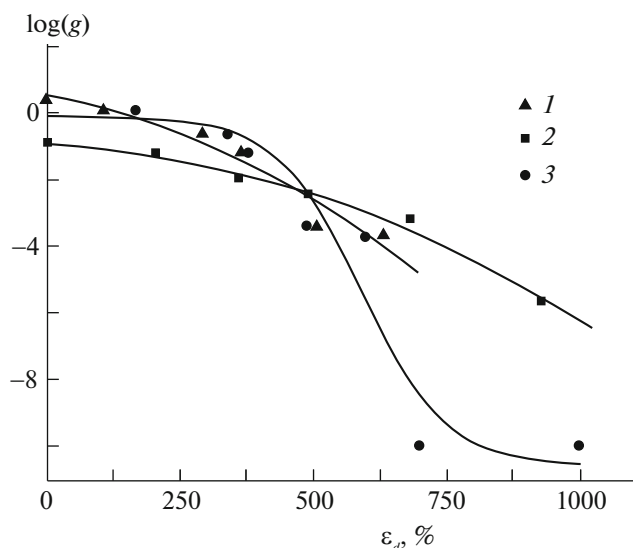
Using electrically conducting UHMWPE/NG composites as an example, it was shown that the percolation threshold shifts towards higher values with an increase in the magnitude of the preliminary relative uniaxial deformation  $\varepsilon_d$  of the samples (Fig. 5).

## MECHANICAL PROPERTIES OF COMPOSITES

Nonoriented samples of UHMWPE-based electrically conducting composites with above-threshold values of the filler concentration obtained in the present work are characterized by low values of stress–strain characteristics. In particular, the values of tensile strength  $\sigma_p$  are only 5–20 MPa, whereas elongations at break  $\varepsilon_p$  do not exceed 10%. Such low values of

Percolation threshold values of the filler volume fraction  $x_c$  and critical indexes  $s$  for UHMWPE/CB, UHMWPE/CNT, and UHMWPE/NG composites

Filler	$x_c$ , volume fraction	$s$
CB	$0.015 \pm 0.005$	$1.6 \pm 0.1$
CNT	$0.0015 \pm 0.005$	$1.68 \pm 0.09$
NG	$0.018 \pm 0.006$	$2.5 \pm 0.3$



**Fig. 4.** Dependences of the specific conductivity  $g$  of composites (1) UHMWPE/CB-20, (2) UHMWPE/CNT-3, and (3) UHMWPE/NG-10 on the relative uniaxial deformation value  $\varepsilon_d$  under HS conditions.

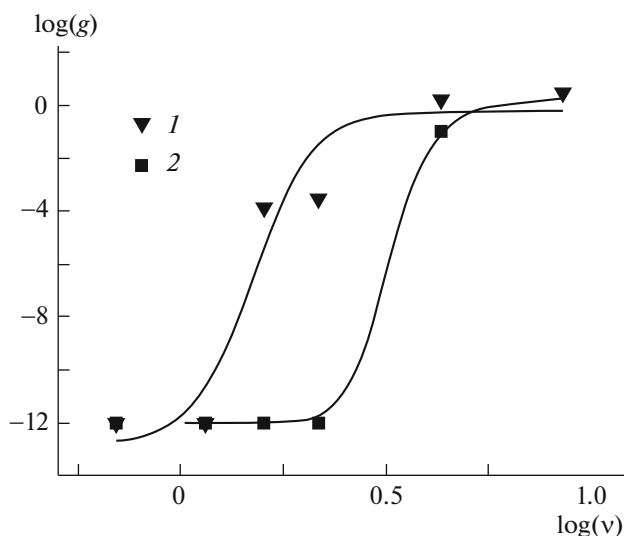
these characteristics are typical of both UHMWPE-based nonoriented composites [7, 11, 12, 28, 29, 39] and carbon-containing composites with PE of other types as the polymer matrix [49, 50].

An additional orientation under HS conditions [15] of UHMWPE-based nonoriented electrically conductive composites with above-threshold values of the filler concentration results in an essential enhancement of their tensile characteristics, as follows from the dependences of tensile strength for UHMWPE/CB, UHMWPE/CNT, and UHMWPE/NG composites and a pure UHMWPE on the value of their relative uniaxial deformation  $\varepsilon_d$  under HS conditions presented in Fig. 6.

It should be noted that the strengthening of the polymer matrix is as efficient for the pure UHMWPE matrix (curve 4 in Fig. 6) as for the UHMWPE matrix of carbon-containing composites (curves 1–3 in the same figure).

Using UHMWPE/NG composite as an example, it was also shown (Fig. 7) that, at a fixed value of the preliminary relative uniaxial deformation  $\varepsilon_d$ , an insignificant decline of the composite tensile strength  $\sigma_p$  is observed with an increase in the conductive filler content in the system, allowing its content in the composite to rise up to a level that provides high conductivity without a noticeable deterioration of tensile characteristics of the electrically conducting composite.

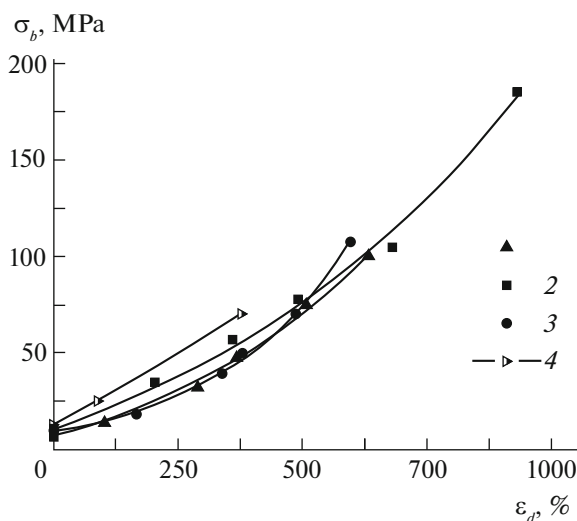
Indeed, a comparison of Figs. 4 and 6 shows that, for the values of the relative uniaxial deformation  $\varepsilon_d$  under HS conditions at which the conductivity is still high, the tensile strength values  $\sigma_p$  of oriented compos-



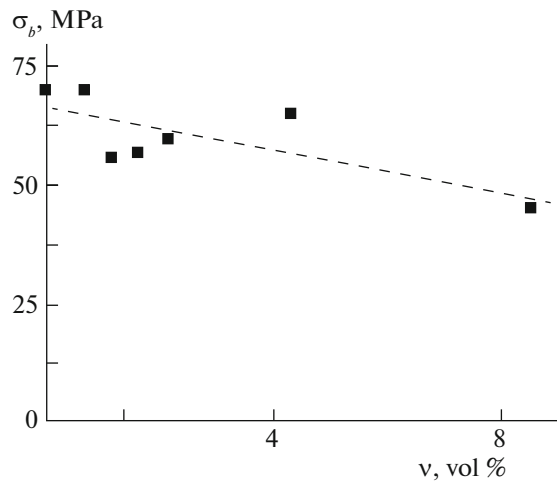
**Fig. 5.** Dependences of the specific conductivity  $g$  of the composite UHMWPE/NG on the volume fraction  $\nu$  of NG for samples with a fixed relative uniaxial deformation value under HS conditions  $\varepsilon_d$ : (1) 0 and (2) 350%.

ites essentially (by an order of magnitude and more) exceeds those for nonoriented composites.

It is obvious that, using the suggested approach and combining parameters such as filler type, its content in the initial nonoriented composite, and the value of the relative uniaxial deformation under HS conditions, it is possible to obtain electrically conductive composites with an optimized complex of electrical conductivity and stress–strain properties.



**Fig. 6.** Dependences of the tensile strength  $\sigma_p$  of composites (1) UHMWPE/CB-20, (2) UHMWPE/CNT-3, (3) UHMWPE/NG-10, and (4) pure UHMWPE on the relative uniaxial deformation value  $\varepsilon_d$  under HS conditions.



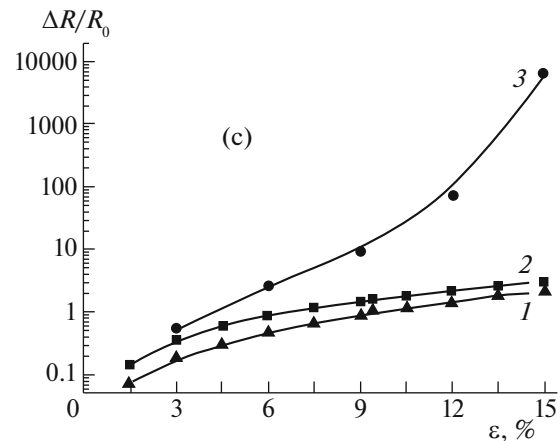
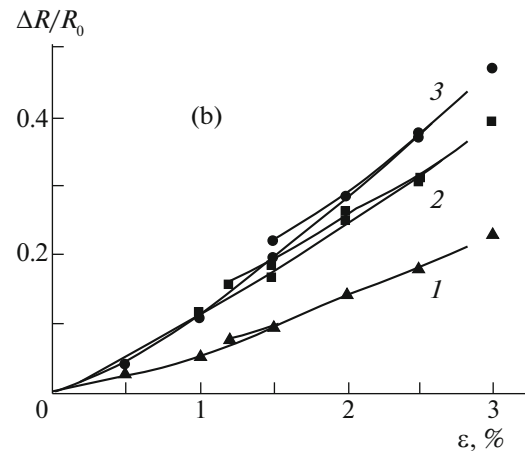
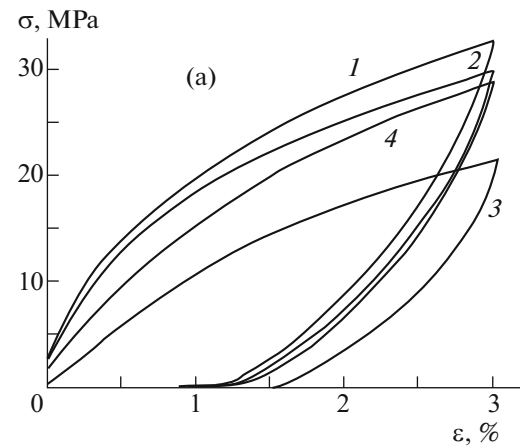
**Fig. 7.** Dependence of the tensile strength  $\sigma_p$  of the composite UHMWPE/NG on the volume fraction  $\nu$  of NG for samples with a fixed relative uniaxial deformation value under HS conditions

Thus, e.g., in the present work, the initially nonoriented electrically conducting UHMWPE/NG-35 composite was subsequently orientated under HS conditions up to the deformation value  $\varepsilon_d = 600\%$  to obtain a strengthened electrically conducting composite with the tensile strength  $\sigma_p = 80$  MPa and specific conductivity  $g = 10$  S/cm. Such materials are of interest for further practical applications.

#### LOW UNIAXIAL DEFORMATIONS OF ORIENTED COMPOSITES

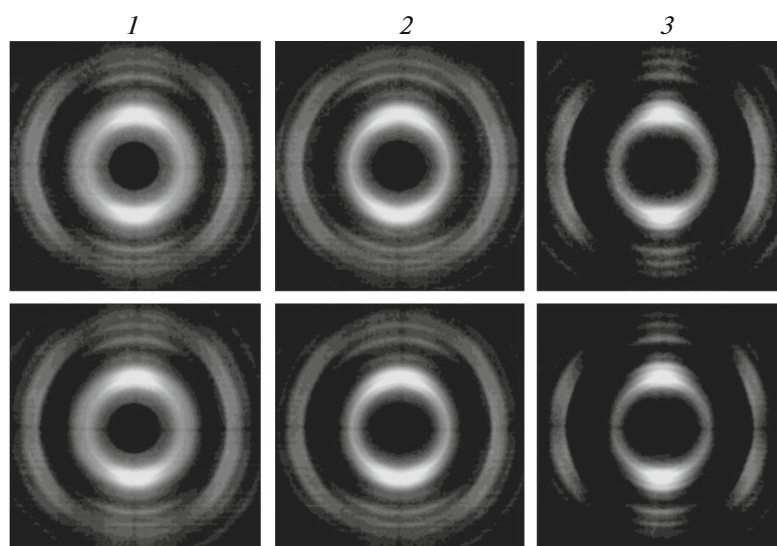
Tests of oriented electrically conducting composites preliminarily stretched uniaxially under HS conditions showed a significant decrease in the initially high conductivity of the composites at a low additional strain deformation along the preliminary orientation axis (the so-called elastic loading range).

For a more detailed investigation of this phenomenon, reference nonoriented UHMWPE/NG-9, UHMWPE/CNT-2, and UHMWPE/CB-10 samples with approximately the same conductivity level were prepared (see Fig. 3). The prepared samples were subsequently orientated under HS conditions up to the same relative uniaxial deformation value  $\varepsilon_d = 350\%$ . Thus obtained oriented 100-mm-long composite samples were fixed with clamps of a universal testing machine, avoiding any electrical contact with the clamps, and subjected to a low (1–15%) additional tensile-compression deformation  $\varepsilon$  along the preliminary orientation axis while simultaneously measuring the electrical resistance of the materials. The effect magnitude was characterized by the relative change in the sample resistance  $\Delta R/R_0$ , where  $\Delta R = R - R_0$ ,  $R$  is



**Fig. 8.** Deformation curves  $\sigma$ – $\varepsilon$  in cycles “tension–contraction” (a), dependences of the relative change in the resistance  $\Delta R/R_0$  in the range of low (up to 3% (b)) and high (up to 15% (c)) relative elongation  $\varepsilon$  upon deformation for composites (1) UHMWPE/CB-10, (2) UHMWPE/CNT-2, (3) UHMWPE/NG-10, and (4) pure UHMWPE.

the current resistance value and  $R_0$  is the initial value of the composite resistance. The measurement results are presented in Fig. 8.



**Fig. 9.** X-ray diffraction patterns of nonoriented samples of composites compacted in the mold: (1) UHMWPE/CB-20, (2) UHMWPE/CNT-3, and (3) UHMWPE/NG-10. The primary beam direction is perpendicular (top row) and parallel (bottom row) to the sample plane.

As can be seen from the data presented in Figs. 8a and 8b, at the uniaxial deformation values below a few percents, the relative change in resistance of all investigated composites is practically linear and reversible, up to the reversibility of the deformation itself. Proportionality coefficients between the relative gain in resistance and the relative elongation for composites with different filler types are close to each other; the minimal coefficient values being observed for UHMWPE/CB and the maximal ones are being observed for UHMWPE/NG composites. It is worth noting that some results obtained in the studies of low deformations of nonoriented polymer electrically conducting composites with CB and CNT fillers were described earlier [51, 52].

An increase in deformation  $\varepsilon$  up to 10% and above leads to an obvious deviation between the deformation dependence of the relative gain in resistance for composites with NG and analogous dependences for composites with other filler types (Fig. 8c). While composites with CNT and CB show a continuous linear increase in resistance with the deformation value, the UHMWPE/NG composite resistance grows by several orders of magnitude.

#### STRUCTURE AND TEXTURE OF COMPOSITES

In order to explain the aforementioned specific features of changes in electrically conductive properties of UHMWPE/NG composites upon their deformation, i.e., the loss of conductivity of oriented composites both above a certain threshold deformation  $\varepsilon_d$  of the material under HS conditions (Fig. 4) and at low uniaxial tensile deformations (Fig. 8c), X-ray and

electron microscopic studies of nonoriented and oriented UHMWPE-based composite samples with different filler types were carried out.

In Fig. 9, wide-angle X-ray diffraction patterns are presented for nonoriented samples compacted in a mold.

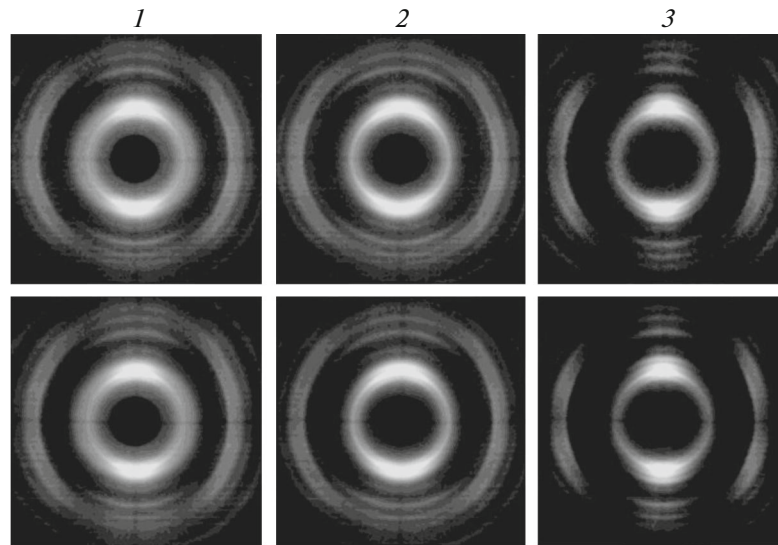
It is seen that the orientation of NG particles in the polymer matrix is characterized by a planar texture, the basal (002) planes of polycrystals of the graphite phase being arranged in the sample plane perpendicularly to the direction of load applied at the sample molding during its preparation.

Wide-angle X-ray diffraction patterns for oriented composites of the same composition are shown in Fig. 10.

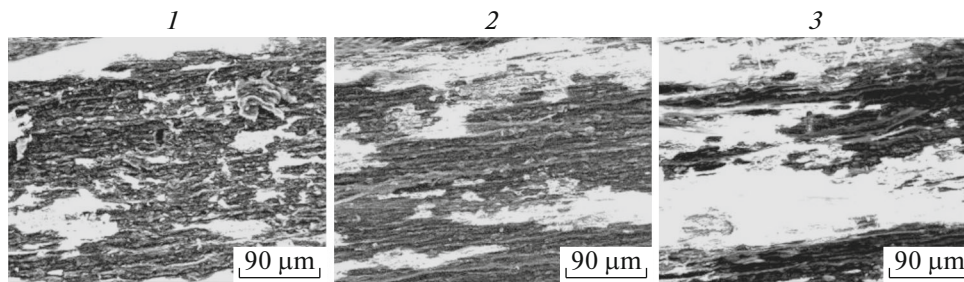
It is seen that a planar texture of NG particles formed in the nonoriented UHMWPE/NG sample in the stage of its compaction in the mold is preserved in the oriented sample as well. It is established that a planar texture of NG particles is present in all investigated samples of composites of this type, regardless of the composition, up to the maximum deformation under HS conditions  $\varepsilon_d = 1500\text{--}1600\%$  attained in our experiments. In UHMWPE/CB and UHMWPE/CNT composites, no texturing of the conductive component was observed.

A planar texture of NG in oriented composites was also found on micrographs of longitudinal chips of UHMWPE/NG-10 samples obtained by scanning electron microscopy (Fig. 11). In this case, no metal deposition on the chip surface was performed deliberately in order to reveal (“contrast”) conducting and insulating regions of the composite structure.

Conducting NG regions are seen (in black in the micrographs) with the longitudinal dimensions many



**Fig. 10.** X-ray diffraction patterns of oriented composites: (1) UHMWPE/CB-20, (2) UHMWPE/CNT-3, and (3) UHMWPE/NG-10. The primary beam direction is perpendicular (top row) and parallel (bottom row) to the sample plane. The orientation axis is horizontal.



**Fig. 11.** Electron micrographs of the surface of longitudinal chips of oriented UHMWPE/NG-10 composites. The relative uniaxial deformation value under HS conditions  $\varepsilon_d = (1)$  350%, (2) 500%, and (3) 900%. The chip plane is perpendicular to the sample plane. The orientation axis is horizontal. Magnification is  $\times 300$ .

times exceeding the size of individual NG particles (Fig. 1). These regions consist of stacks of separate plates arranged perpendicularly to the sample plane. With an increase in the relative uniaxial deformation under HS conditions  $\varepsilon_d$ , conducting regions move apart and, finally, become separated by insulating UHMWPE regions (in white in the micrographs).

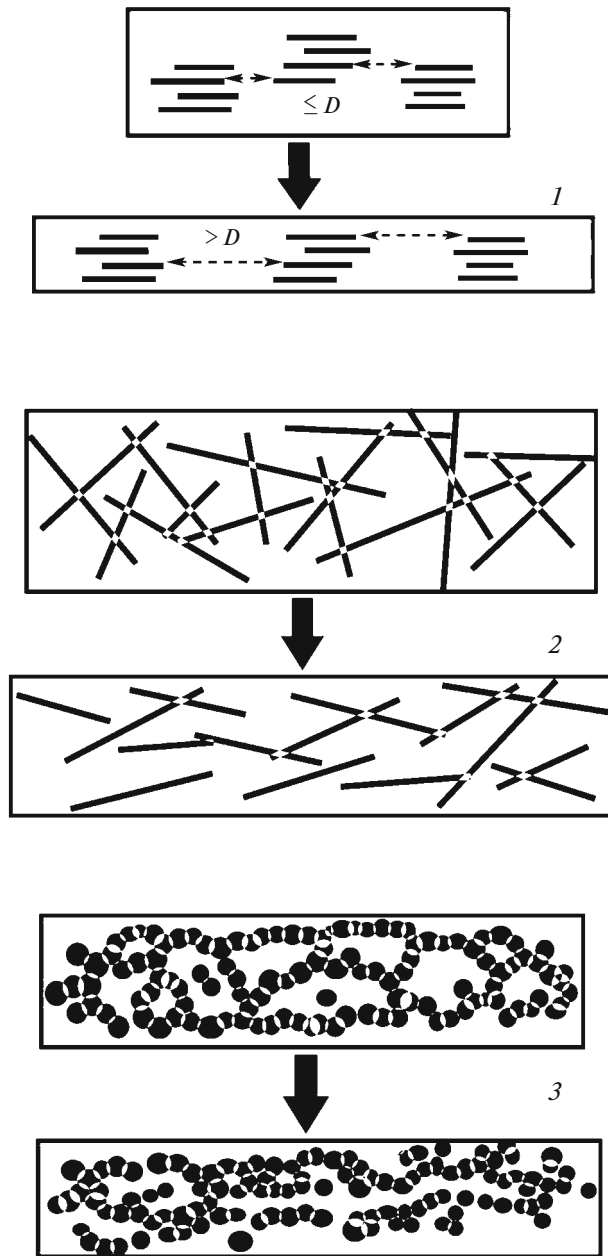
We suppose that a heterogeneous structure of the UHMWPE/NG composite, containing large discrete aggregates of the conducting component as stacks of NG plates, may be the main reason for the abovementioned features of changes in its electrically conductive properties upon its orientation or elastic deformation. The observed abrupt decrease in its conductivity may be explained by the assumption that, during the deformation process, a certain average distance (D) between conducting regions is attained when the mechanisms of electron transfer from one conducting region to another become inefficient (Fig. 12, scheme 1). The-

oretical descriptions of this phenomenon based on different models may be found in a number of publications (e.g., the IPD “average interparticle distance” model [53]).

For UHMWPE composites with the two other electrically conducting fillers, CNT and CB, the characteristic dimensions of fillers particles are essentially lower than the sizes of NG aggregates (see Fig. 1). In this case, a real three-dimensional spatial distribution of filler particles in the polymer matrix becomes possible (Fig. 12, schemes 2 and 3). It should be remembered that this character of CNT and CB particles distribution in the polymer matrix is also confirmed by the data presented above in Fig. 3.

It is known that a decrease in conductivity upon deformation of composites with a three-dimensional character of the spatial distribution of an electrically conducting filler of CNT or CB types in the polymer matrix is due to an orientation of CNTs or CB particle





**Fig. 12.** Scheme of changes in the mutual arrangement of electrically conducting regions upon the orientation of UHMWPE-based polymer composites for fillers of different types: (1) NG, (2) CNT, and (3) CB.

clusters along the deformation direction [54–57], leading to a reduction in the number of conducting pathways in the composite. Upon that, individual particles or particle clusters move apart, but this process may be partially compensated for by merging of neighboring particles or particle clusters during their orientation and closing along the direction perpendicular to the deformation [54]. As a result, the destruction of conducting pathways for composites with a three-

dimensional character of the filler spatial distribution in the polymer matrix occurs not as abruptly as that for composites with discretely arranged large aggregates of the filler. Therefore, the conductivity of these materials decreases slowly upon their orientation or deformation, being still at a high level even for large deformation values.

## CONCLUSIONS

The results of our investigation show that uniaxial deformation under homogeneous shear conditions is an efficient method of enhancing stress–strain characteristics of electrically conducting composite materials based on the reactor UHMWPE powder and nanosized carbon fillers such as CNTs, NG, and CB. Due to the orientation of the polymer matrix under homogeneous shear conditions, the tensile strength values of the composites increase by more than an order of magnitude when compared to those for non-oriented electrically conducting composites of identical compositions.

In the present paper, the effect of the nanosized carbon filler type on the electrical conductivity and mechanical properties of strengthened electrically conducting composites prepared under homogeneous shear conditions is studied.

It is demonstrated that, using the suggested approach and combining parameters such as the filler type, its content in the initial nonoriented composite, and the value of the relative uniaxial deformation under HS conditions, it is possible to obtain electrically conductive composites with an optimized complex of electrical conductivity and stress–strain properties.

The phenomenon of a significant reversible increase in the electrical resistance of composites, occurring when uniaxially oriented samples undergo stretching in the direction of the orientation axis of the composite material, and its subsequent recovery, occurring when the applied load is released, revealed in the present work may find interesting applications for the creation of prototypes of new electromechanical devices like peculiar electrical “gates” controlling the current strength in electric circuits via an applied mechanical load or “load–displacement” transducers fully exploiting the chemical resistance and other important operational characteristics of the matrix polymer–UHMWPE.

The facile approach described in the present paper makes it possible to obtain electrically conducting polymer composite materials with a relatively low filling degree possessing a complex of high conducting and tensile characteristics; therefore, it is highly promising for practical applications.

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## REFERENCES

- J. C. Huang, "Carbon black filled conducting polymers and polymer blends," *Adv. Polym. Tech.* **21** (4), 299–313 (2002).
- M. Moniruzzaman and K. I. Winey, "Polymer nanocomposites containing carbon nanotubes," *Macromolecules* **39** (16), 5194–5205 (2006).
- J. N. Coleman, U. Khan, W. J. Blau, and Y. K. Gun'ko, "Small but strong: a review of the mechanical properties of carbon nanotube-polymer composites," *Carbon* **44** (9), 1624–1652 (2006).
- M. H. Al-Saleh and U. Sundararaj, "A review of vapor grown carbon nanofiber/polymer conductive composites," *Carbon* **47** (1), 2–22 (2009).
- T. Kuilla, S. Bhadra, D. H. Yao, N. H. Kim, S. Bose, and J. H. Lee, "Recent advances in graphene based polymer composites," *Prog. Polym. Sci.* **35** (11), 1350–1375 (2010).
- E. N. Kablov, S. V. Kondrashov, and G. Yu. Yurkov, "Prospects of using carbonaceous nanoparticles in binders for polymer composites," *Nanotechnol. Russ.* **8** (3–4), 163–185 (2013).
- A. Bhattacharyya, S. Chen, and M. Zhu, "Graphene reinforced ultra-high molecular weight polyethylene with improved tensile strength and creep resistance properties," *eXPRESS Polym. Lett.* **8** (2), 74–84 (2014).
- J. F. Gao, Z. M. Li, Q. J. Meng, and Q. Yang, "CNTs/UHMWPE composites with a two-dimensional conductive network," *Mater. Lett.* **62**, 3530–3532 (2008).
- S. R. Bakshi and J. E. Tercero, "Synthesis and characterization of multiwalled carbon nanotube reinforced ultra high molecular weight polyethylene composite by electrostatic spraying technique," *Compos Part A: Appl. Sci.* **38**, 2493–2499 (2007).
- X. Hao, G. Gai, Y. Yang, Y. Zhang, and C. W. Nan, "Development of the conductive polymer matrix composite with low concentration of the conductive filler," *Mater. Chem. Phys.* **109**, 15–19 (2008).
- M. O. Lisunova, Ye. P. Mamunya, N. I. Lebovka, and A. V. Melezhyk, "Percolation behaviour of ultrahigh molecular weight polyethylene/multi-walled carbon nanotubes composites," *Eur. Polym. J.* **43**, 949–958 (2007).
- C. Zhang, C. A. Ma, P. Wang, and M. Sumita, "Temperature dependence of electrical resistivity for carbon black filled ultra-high molecular weight polyethylene composites prepared by hot compaction," *Carbon* **43** (12), 2544–2553 (2005).
- H. Pang, T. Chen, G. Zhang, B. Zeng, and Z.-M. Li, "An electrically conducting polymer/graphene composite with a very low percolation threshold," *Mater. Lett.* **64**, 2226–2229 (2010).
- I. M. Ward, *Mechanical Properties of Solid Polymers*, 2nd ed. (1983).
- A. S. Kechek'yan, E. S. Mikhailik, K. Z. Monakhova, T. S. Kurkin, O. T. Gritsenko, M. A. Beshenko, and A. N. Ozerin, "Effect of preliminary compression and uniform shear on the deformation behavior of a filled polymer nanocomposite in orientation stretching," *Dokl. Chem.*, No. 1, 94–97 (2013).
- G. Carotenuto, S. De Nicola, M. Palomba, D. Pullini, A. Horsewell, T. W. Hansen, and L. Nicolais, "Mechanical properties of low-density polyethylene filled by graphite nanoplatelets," *Nanotechnology* **23** (8), 485705 (2012).
- S. Y. Fu, X. Q. Feng, B. Lauke, and Y. W. Mai, "Effects of particle size, particle/matrix interface adhesion and particle loading on mechanical properties of particulate-polymer composites," *Compos. Part B: Eng.* **39** (6), 933–961 (2008).
- P. Ciselli, R. Zhang, Z. Wang, C. T. Reynolds, M. Baxendale, and T. Peijs, "Oriented UHMW-PE/CNT composite tapes by a solution casting-drawing process using mixed-solvents," *Eur. Polym. J.* **45**, 2741–2748 (2009).
- S. Ruan, P. Gao, and T. X. Yu, "Ultra-strong gel-spun UHMWPE fibers reinforced using multiwalled carbon nanotubes," *Polymer* **47**, 1604–1611 (2006).
- O. V. Lebedev, A. S. Kechek'yan, V. G. Shevchenko, T. S. Kurkin, M. A. Beshenko, and A. N. Ozerin, "Strengthened electrically conductive composites based on ultra high molecular weight polyethylene filled with fine graphite," *Dokl. Chem.* **456** (2), 87–90 (2014).
- A. N. Ozerin, S. S. Ivanchev, S. N. Chvalun, V. A. Aulov, N. I. Ivancheva, and N. F. Bakeev, "Properties of oriented film tapes prepared via solid-state processing of a nascent ultrahigh-molecular-weight polyethylene reactor powder synthesized with a post-metallocene catalyst," *Polymer Sci. Ser. A* **54** (12), 950–954 (2012).
- T. Kanamoto, T. Ohama, K. Tanaka, M. Takeda, and R. S. Porter, "Two-stage drawing of ultra-high molecular weight polyethylene reactor powder," *Polymer* **28** (9), 1517 (1987).
- S. Akira, K. Hirofumi, I. Yoshimu, Y. Shigeki, and M. Kazuo, *Eur. Patent No. EP0376423* (1990).
- V. I. Selikhova, Yu. A. Zubov, E. A. Sinevich, S. N. Chvalun, N. I. Ivancheva, O. V. Smol'yanova, S. S. Ivanchev, and N. F. Bakeev, *Polym. Sci. USSR* **34**, 151 (1992).
- Y. L. Joo, O. H. Han, H. K. Lee, and J. K. Song, "Characterization of ultra high molecular weight polyethylene nascent reactor powders by X-ray diffraction and solid state NMR," *Polymer* **41** (4), 1355–1368 (2000).
- Y. L. Joo, H. Zhou, S. G. Lee, H. K. Lee, and J. K. Song, "Solid-state compaction and drawing of nascent reactor powders of ultra-high-molecular-weight polyethylene," *J. Appl. Polym. Sci.* **98**, 718–730 (2005).
- R. A. Antunes, M. C. L. de Oliveira, G. Ett, and V. Ett, "Carbon materials in composite bipolar plates for polymer electrolyte membrane fuel cells: a review of the main challenges to improve electrical performance," *J. Power Sources* **196**, 2945–2961 (2011).

28. W. Bauhofer and J. Z. Kovacs, "A review and analysis of electrical percolation in carbon nanotube polymer composites," *Compos. Sci. Technol.* **69**, 1486–1498 (2009).
29. P. C. Ma, N. A. Siddiqui, G. Marom, and J. K. Kim, "Dispersion and functionalization of carbon nanotubes for polymer-based nanocomposites: a review," *Compos Part A: Appl. Sci.* **41**, 1345–1367 (2010).
30. www.nanocyl.com
31. https://graphene\_supermarket.com
32. A. Peigney, C. Laurent, E. Flahaut, R. Bacsá, and A. Rousset, "Specific surface area of carbon nanotubes and bundles of carbon nanotubes," *Carbon* **39** (4), 507–514 (2001).
33. K. S. Subrahmanyam, S. R. C. Vivekchand, A. Govindaraj, and C. N. R. Rao, "A study of graphenes prepared by different methods: characterization, properties and solubilization," *J. Mater. Chem.* **18**, 1517–1523 (2008).
34. Z. M. Li, S. N. Li, M. B. Yang, and R. Huang, "A novel approach to preparing carbon nanotube reinforced thermoplastic polymer composites," *Carbon* **43**, 2413–2416 (2005).
35. S. N. Li, B. Li, Z. M. Li, Q. Fu, and K. Z. Shen, "Morphological manipulation of carbon nanotube/polycarbonate/polyethylene composites by dynamic injection packing molding," *Polymer* **47**, 4497–4500 (2006).
36. Z. M. Li, X. B. Xu, A. Lu, K. Z. Shen, R. Huang, and M. B. Yang, "Carbon black/poly(ethylene terephthalate)/polyethylene composite with electrically conductive in situ microfiber network," *Carbon* **42**, 428–432 (2004).
37. L. A. Pranger, "Self-assembly and reactive molding techniques for controlling the interface and dispersion of the particulate phase in nanocomposites," *ProQuest* (2008).
38. K. Kalaitzidou, H. Fukushima, and L. T. Drzal, "A route for polymer nanocomposites with engineered electrical conductivity and percolation threshold," *Materials* **3**, 1089–1103 (2010).
39. J. Du, L. Zhao, Y. Zeng, L. Zhang, F. Li, P. Liu, and C. Liu, "Comparison of electrical properties between multi-walled carbon nanotube and graphene nanosheet/high density polyethylene composites with a segregated network structure," *Carbon* **49**, 1094–1100 (2011).
40. S. H. Foulger, "Reduced percolation thresholds of immiscible conductive blends," *J. Polym. Sci. Polym. Phys.* **37**, 1899–1910 (1999).
41. Y. P. Mamunya, V. V. Davydenko, P. Pissis, and E. V. Lebedev, "Electrical and thermal conductivity of polymers filled with powders," *Eur. Polym. J.* **38**, 1887–1897 (2002).
42. N. Lebovka, M. Lisunova, Y. P. Mamunya, and N. Vygornitskii, "Scaling in percolation behaviour in conductive–insulating composites with particles of different size," *J. Phys. D: Appl. Phys.* **39**, 2264–2271 (2006).
43. F. Lux, "Models proposed to explain the electrical conductivity of mixtures made of conductive and insulating materials," *J. Mater. Sci.* **28**, 285–301 (1993).
44. A. R. Blythe and D. Bloor, *Electrical Properties of Polymers*, 2nd ed. (Cambridge Univ. press, 2005).
45. D. Stauffer and A. Aharony, *Introduction to percolation theory*, 2nd ed. (Taylor & Francis, 1992).
46. M. Sahimi, *Applications of Percolation Theory* (Taylor & Francis, London, 1994).
47. S. Kirkpatrick, "Percolation and conduction," *Rev. Mod. Phys.* **45** (4), 574–582 (1973).
48. H. Pang, C. Chen, Y. Bao, J. Chen, X. Ji, J. Lei, Z. and M. Li, "Electrically conductive carbon nanotube/ultrahigh molecular weight polyethylene composites with segregated and double percolated structure," *Mater. Lett.* **79**, 96–99 (2012).
49. M. Sarikanat, K. Sever, E. Erbay, F. Güner, I. Tavman, A. Turgut, Y. Seki, and I. Özdemiř, "Preparation and mechanical properties of graphite filled HDPE nanocomposites," *Arch. Mater. Sci. Eng.* **50** (2), 120–124 (2011).
50. K. Q. Xiao, L. C. Zhang, and I. Zarudi, "Mechanical and rheological properties of carbon nanotube-reinforced polyethylene composites," *Compos. Sci. Technol.* **67**, 177–182 (2007).
51. R. Zhang, M. Baxendale, and T. Peijs, "Universal resistivity-strain dependence of carbon nanotube/polymer composites," *Phys. Rev. B* **76**, 195433 (2007).
52. J. N. Aneli, G. E. Zaikov, and L. M. Khanashvili, "Effects of mechanical deformations on the structuring and electric conductivity of electric conducting polymer composites," *J. Appl. Polym. Sci.* **74**, 601–621 (1999).
53. J. Li and J. K. Kim, "Percolation threshold of conducting polymer composites containing 3D randomly distributed graphite nanoplatelets," *Compos. Sci. Technol.* **67**, 2114–2120 (2007).
54. F. Du, J. E. Fischer, and K. I. Winey, "Effect of nanotube alignment on percolation conductivity in carbon nanotube/polymer composites," *Phys. Rev. B* **72**, 121404-1–121404-4 (2005).
55. F. Du, R. C. Scogna, W. Zhou, S. Brand, J. E. Fischer, and K. I. Winey, "Nanotube networks in polymer nanocomposites: rheology and electrical conductivity," *Macromolecules* **37**, 9048–9055 (2004).
56. E. K. Hobbie, H. Wang, H. Kim, and S. Lin-Gibson, "Orientation of carbon nanotubes in a sheared polymer melt," *Phys. Fluids* **15** (5), 1196–1202 (2003).
57. H. Kim and C. W. Macosko, "Processing-property relationships of polycarbonate/graphene composites," *Polymer* **50**, 3797–3809 (2009).

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