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Article

Composite High-k Films Based on Polyethylene Filled with Electric Arc Furnace Dust and MWCNT with Permittivity Synergetic Effect

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Abstract: The production of three-phase composites is a relevant and effective approach to obtain materials with the required mechanical and dielectric properties. In this work, dust, which is a waste product of steelmaking and is formed during the gas cleaning of electric arc furnaces at the production base of Severstal, was used as a functional filler for the low-density polyethylene polymer matrix. The fractional, elemental, qualitative, and quantitative phase composition of the native dust was studied using laser diffraction, energy-dispersive X-ray phase analysis, and X-ray fluorescence spectrometry. An increase in the permittivity of the dust was achieved due to its reduction in a hydrogen atmosphere and, as a consequence, a change in the elemental and phase composition causing an increase in the concentration of metallic iron. Composite films were obtained using a blending roll mill at temperatures of 130 and 140 °C. The concentration of the main filler was 18.75, 37.5, and 75 wt.%. Additionally, a conductive additive in the form of MWCNTs was introduced into the composition of the composites in an amount of 0.25 wt.%. The uniformity of the filler distribution in the polymer matrix was assessed from electron micrographs. The dielectric properties of fillers and composite films based on polyethylene filled with electric arc furnace dust and MWCNTs were studied using impedance spectroscopy in the frequency range of 10–10^6 Hz. The use of reduced dust at a concentration of 25.8 vol.% combined with 0.25 wt.% MWCNTs in the composition of the composite film provided an increase in ε' to 13.5 at $\tan\delta = 0.038$. Thus, three-phase polymer matrix composites based on LDPE using dust as a filler with a conductive microadditive of MWCNTs have a synergistic effect, which manifests itself in an increase in the permittivity and a decrease in dielectric losses.

Keywords: three-phase composites; electric arc furnace dust; LDPE; permittivity; dielectric loss; synergism

1. Introduction

Electric arc furnace dust (EAFD) is one of the most common metallurgical waste products. It is a finely dispersed powder which settles on the air filters of workshops and consists mainly of metal oxides and carbon [1]. In addition to various iron compounds, the native dust may contain compounds of volatile metals such as zinc, nickel, lead, cadmium, and chromium [2]. Due to the high content of volatile heavy metals, the dust of electric arc steel-smelting furnaces is classified as a substance of hazard class I [3]. In this regard, for further application, various methods are used to reduce the possible danger, for example, stabilization by binding with mineral binders [4] or reduction by heating, in which volatile metals evaporate from the material [5].

EAFD is popular in the production of various structural materials, improving their properties and binding heavy metal compounds. EAFD is used in the production of cement concretes [6], asphalt concretes [7], ceramics [8], glass ceramics and glazes [9], and even ink [10]. EAFD can be used in agriculture for soil deoxidation due to the content of oxides of alkali and alkaline earth metals [11]. Due to the relatively high content of zinc oxide, dust can be a low-cost and effective H_2S adsorbent [12]. Additionally, it can be used as a filler to improve the mechanical properties of polymer composites, such as tensile strength and hardness similar to fly ash particles [13,14], as well as reducing flammability. Thus, dust has been used as a filler for unsaturated polyester resin [15], EVA–polyethylene–butene blends [16], etc. Several studies use EAFD-polymer systems as a phase change material (PCM) due to their high thermal energy storage (TES) capacity as latent heat from the phase change [17–19]. In addition, there are works devoted to the creation of EAFD polymer matrix composites based on epoxy resins [15] and unsaturated polyester resin [20] and the study of their mechanical properties. The presence of a large amount of iron in the composition of EAFD and the finely dispersed form of the powder make it possible to use it as a filler that provides effective absorption of electromagnetic radiation in various wavelength ranges.

Low-density polyethylene (LDPE) was used as the polymer matrix in this study. The choice is due to its favorable mechanical and dielectric properties, as well as the easy process for the production of composites based on it due to the good dispersion of filler particles in the polymer volume. Pure polyethylene is characterized by a permittivity of about 2.3 in the frequency range of 10–10^5 Hz with a dielectric loss tangent of not more than 2.3×10^{-3} [21]. Unlike HDPE, there is almost no difference in dielectric loss between LDPE which is aged after working under high voltage for a long time and unaged LDPE [22]. This expands the potential areas of application of composites based on it. An additional advantage is that polymer matrix composites based on it have a wide range of applications [23,24]. A Composites based on LDPE filled with cenospheres typically shows the permittivity less than 2.3 at frequency range of 1–10 kHz [25].

In recent years, much attention has been paid to the creation and study of three-phase polymer matrix composites. The type of the polymer matrix, the nature of the dielectric and conductive fillers, their concentration, as well as the method of combination and introduction into the polymer can be varied. Therein, it is possible to directionally control the dielectric properties of the resulting composite. For the example of Epoxy/$K_{1.6}(Ni_{0.8}Ti_{7.2})O_{16}$/CNT, PVDF/$K_{1.6}Fe_{1.6}Ti_{6.4}O_{16}$/MWCNT, PTFE/$K_{1.6}Fe_{1.6}Ti_{6.4}O_{16}$/CB systems, it is shown that the simultaneous use of a ceramic filler with the structure of hollandite and a small amount of carbon additive/coating contributes to a synergistic effect. It manifests itself in the form of an increase in the permittivity and a decrease in the dielectric loss of the composite material. The carbon-containing component of the composite (mainly carbon nanotubes) is combined with the ceramic filler immediately before being introduced into the polymer matrix through the mechanical mixing of dry powders using a vibrating micromill or in the form of alcohol dispersions, followed by the evaporation of the solvent. Another approach is the deposition of a carbon coating using carbon black as a result of annealing in an argon atmosphere. In all cases, the addition of a conductive material at an optimal concentration of ceramic filler provides an increase in the value of ε' by a factor of 3–10 relative to a pure polymer, depending on its type and composition of the composite [26–28].

In this regard, the aim of this work was to study the dielectric characteristics (permittivity and dielectric loss tangent) of composites based on EAFD and EAFD reduced in a stream of hydrogen and polyethylene, as well as these composites with small additions of Taunit-M MWCNTs. Owing to their high conductivity, unique morphology, and nanosizesd particles, MWCNTs are often used both independently and as part of various composites. Within the framework of this work, it is important and interesting to consider the distribution and interaction of MWCNTs relative to the main filler (EAFD) and the polymer matrix, as well as the influence of these factors on the dielectric properties of three-phase composites with a new composition.

2. Materials and Methods

2.1. Materials

As the main object of study, steelmaking wastes obtained during the gas cleaning of electric arc furnaces at the production base of PAO Severstal were chosen (electric arc furnace dust—EAFD, Cherepovets, Russia). To increase the permittivity, Taunit-M MWCNTs manufactured by the LLC NanoTechCenter (Tambov, Russia) were introduced into the composites. Low-density polyethylene (LDPE) LB7500N (LG Chem, Seoul, Republic of Korea) was used as a polymer matrix. The compounding of the composite components was carried out on a blending roll mill (UBL-6175-BL, Dongguan BaoPin International Precision Instruments Co., Ltd., Dongguan, China) at a temperature of 130 and 140 °C for a cold and hot roll, respectively, for 15 min.

2.2. EAFD Reduction

To increase the permittivity, EAFD was treated with heating in a hydrogen flow, providing the reduction of iron oxide and a decrease in the content of a number of impurities, including zinc, sodium, and potassium chlorides. The optimal reduction temperature was chosen based on the results of thermogravimetric analysis and was 900 °C. After heat treatment in a reducing atmosphere, the elemental composition of the reduced samples was studied. The mass fraction of Fe increased from 34.4% to 56.5%. The sample after this procedure was named as reduced EAFD or reduced dust.

2.3. Methods

The study of the microstructure and elemental composition was carried out using a Tescan Vega 3 scanning electron microscope (Brno, Czech Republic) equipped with an X-Act Oxford Instruments (High Wycombe, UK) energy-dispersive analysis attachment. The phase composition was studied using a Difrey 402 X-ray diffractometer (Saint Petersburg, Russia). X-ray fluorescence spectrometry combined with X-ray diffraction on an ARL 9900 Workstation instrument (Durham, NC, USA) performed quantitative elemental analysis. To study the fractional composition of the EFSC dust, the laser diffraction method implemented in the Analysette 22 analyzer (Idar-Oberstein, Germany) was used.

To study the dielectric properties of the native and reduced dust the powders were placed in a cylindrical mold with a diameter of 12 mm and subjected to pressing at a pressure of 10 MPa. As a result, discs with a thickness of ~1.5 mm were obtained. In the case of composite from films 1 mm thick and 8 cm wide, disks 15 mm in diameter were cut out. Contacts 12 mm in diameter were deposited on both sides using conductive glue ≪Kontaktol≫ (Keller). An Impedance Analyzer Novocontrol Alpha AN, (Novocontrol Technologies GmbH & Co. KG, Montabaur, Germany) was used to measure the dielectric properties via impedance spectroscopy. The frequency ranged from 0.01 Hz to 1.00 MHz with a voltage amplitude of 100 mV. The permittivity (ε', ε'', and ε), conductivity (σ), and dielectric losses (tan δ) were found from the experimental values of the real and imaginary parts of the impedance (Z' and Z'') using the standard computing operations.

3. Results and Discussion

The fractional composition of the native dust was represented by particles from 0.1 to 3 μm, while according to the laser diffraction data (Figure 1), the particle distribution was bimodal with maxima at 0.5 and 8 μm. The second mode indicated a tendency to the agglomeration of dust particles in the aquatic environment. In this case, the average particle size of the dust sample was about 1 μm.

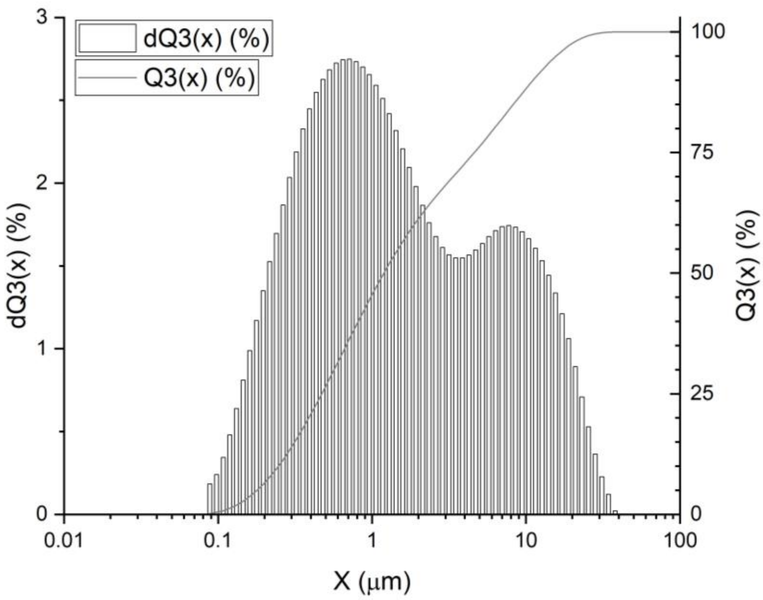

Figure 1. Particle size distribution of the native dust.

The results of elemental analysis of the native and reduced EAFD are presented in Table 1.

Table 1. Elemental composition of the native and reduced dust.

Element		Fe	O	C	Ca	Mg	Mn	Si	Zn	Na	Cl	K	Al	Cr	P	Pb	S
Mass fraction, %	Native	34.4	28.4	5.2	2.1	0.8	2.5	1.2	17.5	3.0	2.0	1.1	0.3	0.2	0.2	1.1	0.5
	Reduced	56.5	23.5	7.4	6.2	1.2	3.8	1.8	<0.1								

Because of reduction, the size and morphology of dust particles (Figure 2b) remained virtually unchanged compared to native dust particles (Figure 2a), which was confirmed by the results of electron microscopy. Both the native (Figure 2c) and reduced (Figure 2d) dust were well distributed in the structure of the polymer matrix, which was well observed in the SEM micrograph of a brittle cleavage of the composite with a composition of 75 wt.% reduced dust and 0.25 wt.% MWCNT.

The method of X-ray fluorescence spectroscopy combined with X-ray diffraction was used to quantify the phase composition (Figure 3).

From the results presented in Figure 3, we can conclude that the sample mainly consisted of the $ZnFe_2O_4$ and Fe_3O_4 phases, the mass fractions of which were 42.5% and 28.25%, respectively, and the mass fraction of the zinc oxide phase was 5.6%. A quantitative analysis of the phase composition was carried out using an X-ray fluorescence wave spectrometer ARL 9900, which made it possible to study the phase composition using X-ray diffraction simultaneously with X-ray fluorescence analysis, followed by the software processing of the results and a nonstandard calculation of the phase content.

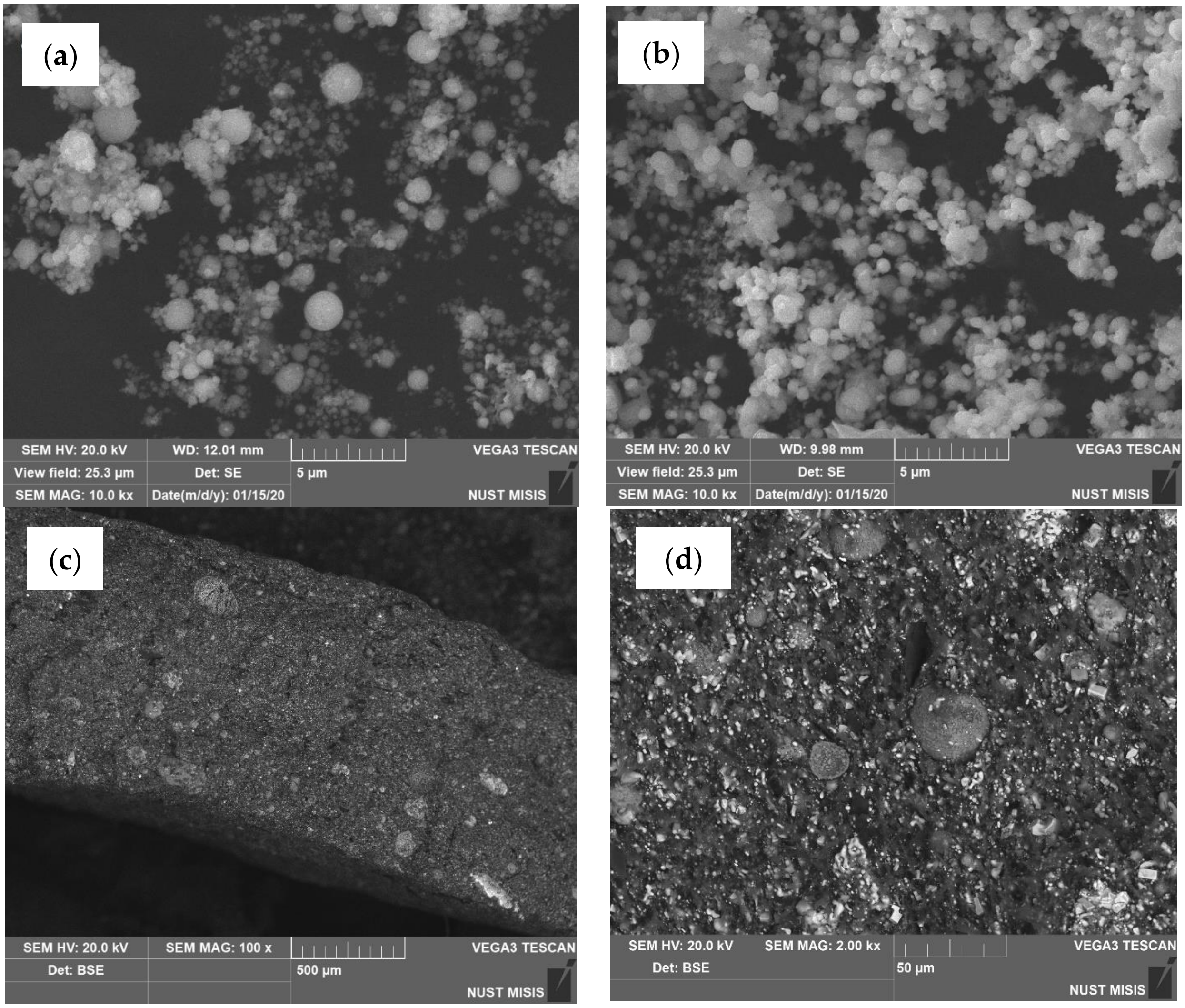

Figure 2. SEM micrographs of (**a**) the native and (**b**) reduced dust powder and (**c**), (**d**) composite based on the dust (75 wt.% with MWCNT).

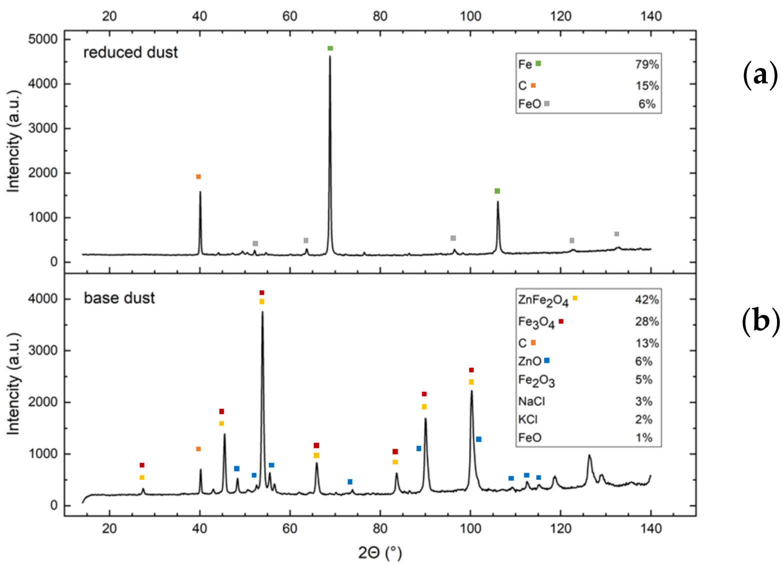

Figure 3. XRD data on reduced dust (**a**) and base dust (**b**) and with phase composition.

3.1. Dielectric Properties

The frequency dependences of permittivity and dielectric loss tangent of composite films based on LDPE, dust (native and reduced), and MWCNT are shown in Figures 4 and 5.

In the range of 10–10^6 Hz, the permittivity of the investigated polymer matrix composites of various compositions was predominantly a frequency-independent value. The exception was samples of composite films based on LDPE filled with 75 wt.% dust both without (Figure 4a,b) and with the addition of an MWCNT (Figure 4c,d), the ε′ of which slightly increased with decreasing frequency. Several regularities were observed: (1) the permittivity of the composite films increased with an increase in the proportion of filler in the composition of the polymer matrix; (2) at the maximum filler fraction, the permittivity of the composite films increased more efficiently with the introduction of reduced dust (Figure 4b) compared to native dust (Figure 4a); (3) an additional increase in the permittivity of the composite films was achieved by adding MWCNTs to both the native (Figure 4c) and reduced dust (Figure 4d).

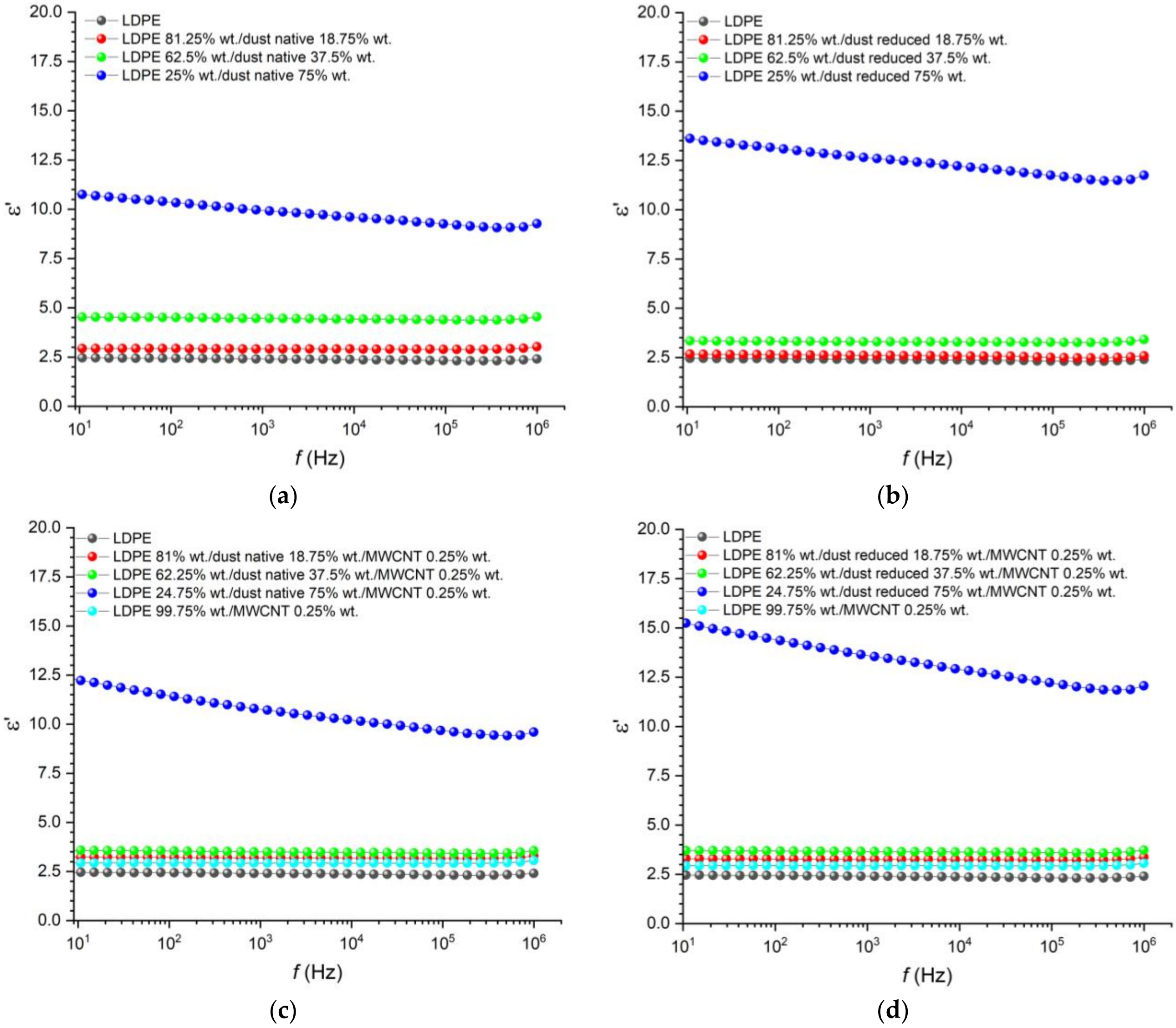

Figure 4. The frequency dependence of permittivity of composite films based on LDPE filled with (**a**) native dust, (**b**) reduced dust, (**c**) native dust /MWCNT, and (**d**) reduced dust /MWCNT.

The dielectric losses of composite films based on LDPE filled with native dust (Figure 5a), reduced dust (Figure 5b), native dust/MWCNT (Figure 5c), and reduced dust/MWCNT (Figure 5d) naturally increased with the addition of a filler compared to the initial LDPE; the increase in tan δ is especially typical for composites with a maximum filler concentration in the low-frequency region. The behavior of the frequency dependences was similar for all the studied samples with small maxima in the region of 10^2 and 10^5 Hz.

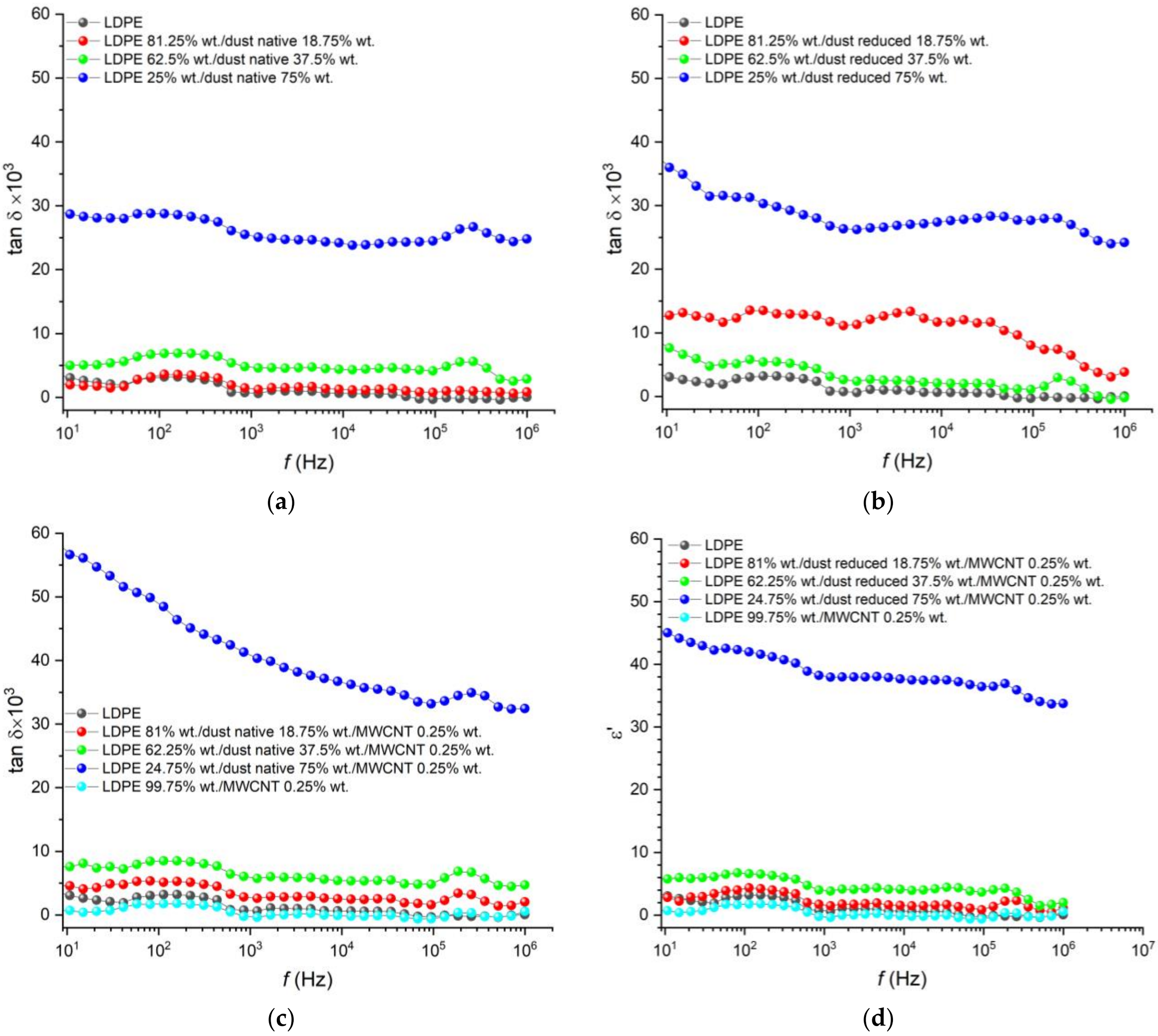

Figure 5. The frequency dependence of dielectric loss tangent of composite films based on LDPE filled with (**a**) native dust, (**b**) reduced dust, (**c**) native dust /MWCNT, and (**d**) reduced dust /MWCNT.

The frequency dependences of the conductivity of composite films based on LDPE, dust (native and reduced), and MWCNT are shown in Figure 6.

All the obtained samples were characterized by the same behavior of the frequency dependence of conductivity. The conductivity value linearly increased with increasing frequency in the range of 10–10^6 Hz. With an increase in the concentration of native dust, the conductivity of the polymer composites gradually increased (Figure 6a). In the case of composite films filled with the reduced dust, the conductivity sharply (by an order of magnitude) increased at a concentration of 75 wt.% (Figure 6b). With the introduction of MWCNT microadditives in addition to the native dust, the polymer composite films had a similar conductivity value in the entire frequency range, except for the concentration of the main filler of 75 wt.% (Figure 6c). The trend for composites with the composition of LDPE/reduced dust/MWCNT did not change relative to the composites with the composition of LDPE/reduced dust (Figure 6d).

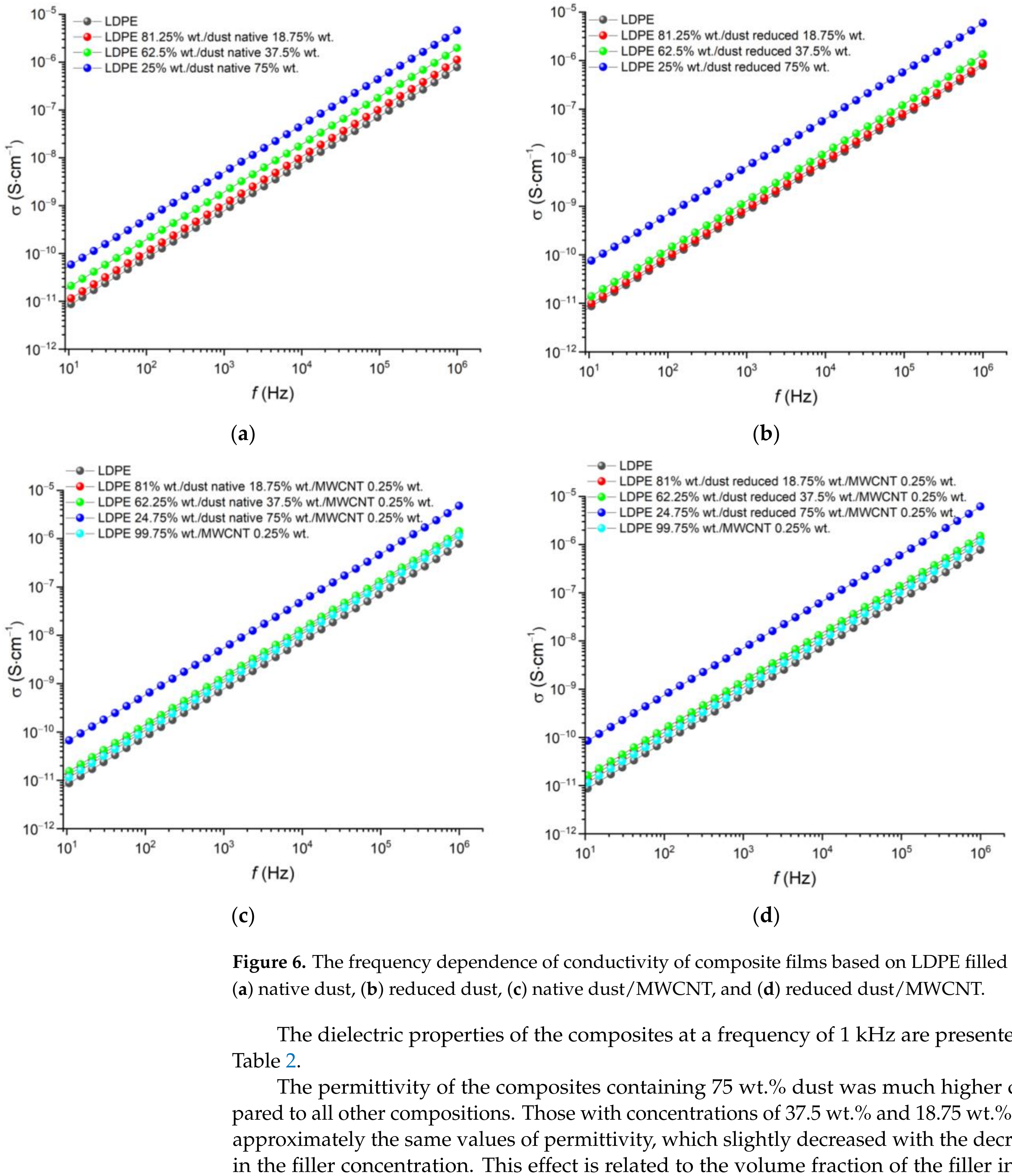

Figure 6. The frequency dependence of conductivity of composite films based on LDPE filled with (**a**) native dust, (**b**) reduced dust, (**c**) native dust/MWCNT, and (**d**) reduced dust/MWCNT.

The dielectric properties of the composites at a frequency of 1 kHz are presented in Table 2.

The permittivity of the composites containing 75 wt.% dust was much higher compared to all other compositions. Those with concentrations of 37.5 wt.% and 18.75 wt.% had approximately the same values of permittivity, which slightly decreased with the decrease in the filler concentration. This effect is related to the volume fraction of the filler in the material; assuming that the spheres have a regular shape and a uniform distribution, we should find a percolation threshold at a concentration of 16 vol.% (±10%). Based on the true densities of the oxide and metallic iron (for the calculations, we tentatively took the values of 5.1 and 7.8 g/cm^3; it made no sense to use more accurate values due to the spread of concentrations and the nonideal structure and composition of the spheres themselves), the volume fractions of both oxide and metal spheres at a mass concentration of 75% for all compositions (depending on the density and the presence of MWCNT, from 26% to 35%) were significantly higher than the percolation threshold, and 37.5 wt.% and 18.75 wt.% were lower (depending on the density). The values of the permittivity for polyolefins filled with oxide fillers range from single units to several tens. The most studied is the dielectric properties of polymer composites with nano- or micron-sized perovskite-type ceramics (predominantly $BaTiO_3$) [29–31]. A commercially available polymer filled with high-k ceramic showed a relatively high permittivity of 10–36 [32].

Table 2. The dielectric properties of the composites at 1 kHz.

Component Content, wt.%/vol.%				The Dielectric Properties	
LDPE	**Native Dust ($\approx Fe_2O_3$)**	**Reduced Dust ($\approx Fe^0/Fe_2O_3$)**	**MWCNT (Taunit-M)**	**ε (1 kHz)**	**tan(δ) (1 kHz)**
100	-	-	-	2.4	0.0013
-	100	-	-	54.6	0.2784
81.25/96.09	18.75/3.91	-	-	2.9	0.0012
62.5/90.43	37.5/9.57	-	-	4.5	0.0046
25/65.38	75/34.62	-	-	9.9	0.0251
81/95.92	18.75/3.92	-	0.25/0.16	2.6	0.0026
62.25/90.22	37.5/9.59	-	0.25/0.19	3.3	0.0057
24.75/64.93	75/34.72	-	0.25/0.35	12.6	0.0403
-	-	100	-	$\approx 10^3$	
81.25/97.41	-	18.75/2.59	-	3.2	0.0113
62.5/93.53	-	37.5/6.47	-	3.5	0.0024
25/74.29	-	75/25.71	-	10.7	0.0262
81/97.24	-	18.75/2.60	0.25/0.16	3.3	0.0015
62.25/93.32	-	37.5/6.49	0.25/0.20	3.7	0.0038
24.75/73.80	-	75/25.80	0.25/0.39	13.5	0.0380
99.75/99.87	-	-	0.25/0.13	2.9	0.0013

The introduction of MWCNT naturally increased the permittivity by about 0.5–1. The obtained results are noticeably inferior to a number of the best published permittivity values, which are of the order of 100 to 200 at 1.5 vol.% of MWCNTs, depending on the frequency [32]. However, the values of ε of the order of 15–17 can provide the material with a number of practical applications in cable sheaths and devices for electronics and electrical engineering, while the developed composites are produced based on extremely low-cost waste from widespread steel-smelting furnaces used both in full-cycle combines and in small enterprises processing secondary metal.

The results, which are interesting for interpretation, show the dependences of the dielectric loss tangent. A comparison of the value of tan(δ) for composites with and without the MWCNT shows that for the material based on the native dust, an increase in dielectric losses was observed, and on the contrary, for composites based on reduced ones, a decrease was observed.

A significant influence on the contribution of MWCNT to the value of permittivity and dielectric loss is exerted by the uniformity of their distribution in the composite, which can change due to significant changes in viscosity during rolling due to a change in the volume fraction of spheres from ~35 to ~2 vol.%, as well as MWCNT themselves from 0.13 to 0.39 vol.% (due to significant differences in the densities of the material at equal mass concentrations; volumetric ones will differ). It is important to note that the permittivity and dielectric losses of LDPE with an MWCNT and without spheres have almost the same values as with spheres at a concentration of the latter below the percolation threshold.

A certain contribution to the dielectric losses can be made by the relaxation of nonelectronic charge carriers, associated with a higher residual moisture content of oxide spheres compared to metal spheres, while MWCNTs can contribute to this process by providing electronic conductivity and charge recombination.

Dielectric losses in composites are most often caused by relaxation losses, electrical conductivity, and inhomogeneity (additional relaxation losses and migratory polarization). The reduced dust had an electrical conductivity that was orders of magnitude higher than before reduction. At the same time, the volume concentration of the reduced spheres turned out to be lower, which means that the average intervals of the dielectric polymer medium between them increased. It can be assumed that the MWCNT-free composites containing reduced dust exhibited greater losses due to the higher conductivity relative to the unreduced ones. At the same time, the addition of MWCNTs in the composites with reduced dust increased the homogeneity by reducing the migration polarization and localizing mobile charge carriers at the points of contact of the MWCNT particles/dust, which was not observed for the unreduced dust.

3.2. Synergistic Effect

A photograph of composite films based on LDPE and their preparation for the study of dielectric properties is shown in Figure 7a. It is seen that the introduction of dust and MWCNTs in the specified amounts allows maintaining the flexibility of the polymer.

Compacted reduced dust samples showed a high permittivity and dielectric loss tangent, which confirms the presence of a metallic phase with conductor properties (Figure 7b).

A comparison of the dielectric properties of composite films at a frequency of 1 kHz is shown in Figure 7c,d. The addition of only an MWCNT in an amount of 0.25% to polyethylene did not lead to a significant change in the dielectric properties; however, a simultaneous increase in the permittivity and loss tangent was observed. There are few works devoted to the production and study of two-phase composites based on LDPE and MWCNTs. The obtained values of the permittivity of the composite produced in this study are in good agreement with those in the literature at the same CNT content (ε'~3.0 at 1 kHz) [33–35].

The composites filled with 18.75% dust exhibited a slight increase in the permittivity and a simultaneous increase in the dielectric loss tangent. At the same time, for this concentration of reduced dust, the permittivity values obtained were lower than for the native dust, and the loss tangent for the reduced dust was much higher than for a pure polymer and polymer filled with native dust. This can be explained by differences in the adhesion of the polymer to the filler, which, for the reduced dust, caused an increase in the porosity and loss tangent. The addition of MWCNTs changed the balance of permittivity and the dielectric loss tangent; the sample with reduced dust had a significantly lower loss tangent with a simultaneous increase in permittivity. For the native dust, a simultaneous increase in the permittivity and loss tangent was observed, which leads to the conclusion that at a concentration of 18.75% dust, a greater synergistic effect from the addition of dust and MWCNTs was observed for the reduced sample.

For samples filled with 37.5 wt.% of dust, a higher permittivity was found for those filled with native dust without MWCNTs. In this case, the loss tangent for samples with native dust was higher than for reduced ones. It should be noted that the addition of the MWCNT for the sample with native dust led to a decrease in the permittivity and an increase in the loss tangent. For the sample with reduced dust, an increase in the permittivity and loss tangent was observed with the addition of the MWCNT. So, a positive effect in a three-phase composite at a concentration of 37.5 wt.% dust for dielectric properties can be noted only for reduced dust.

For the samples filled with 75 wt.% dust, as noted earlier, the concentration exceeded the percolation threshold. A comparison of the permittivity and loss tangent for the samples without the MWCNT shows that both parameters for reduced dust were higher and amounted to 9.9 and 0.0251, respectively. However, the addition of the MWCNT increased the permittivity difference more significantly, and the loss tangent of the sample with reduced dust became smaller than that of the native one. However, dielectric losses showed high values of 0.0380.

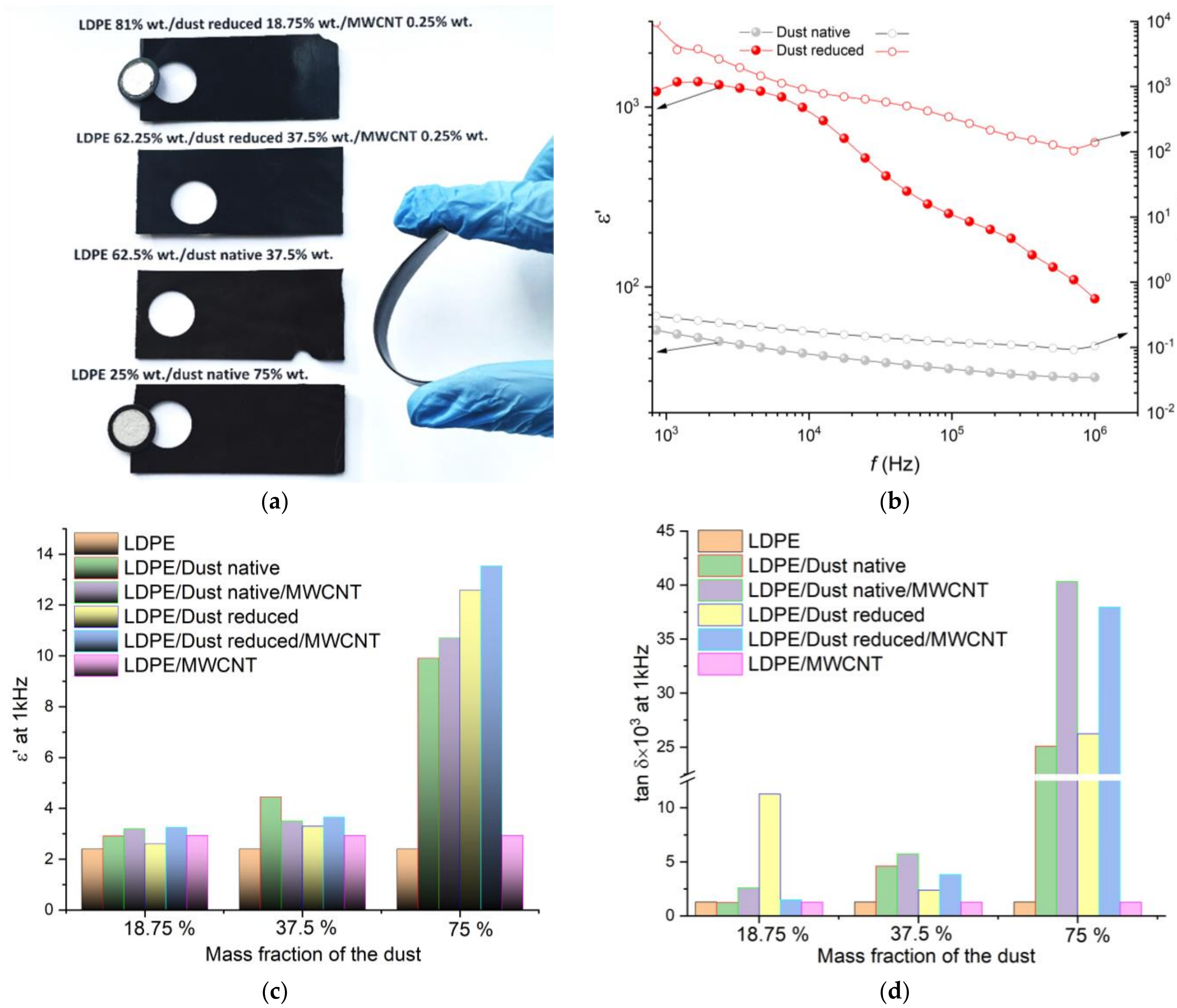

Figure 7. Images of composite films based on (**a**) filled LDPE, (**b**) the frequency dependence of dust permittivity, (**c**,**d**) permittivity and dielectric loss tangent of composite films with different qualitative and quantitative composition at 1 kHz.

The addition of the MWCNT demonstrated the presence of a synergistic effect on the dielectric properties, which was more pronounced for the samples with reduced dust. The studied materials can be used for the production of high-permittivity polymer compounds and power cable materials.

4. Conclusions

In this work, composite films based on a widely used polyethylene polymer matrix and metallurgical production waste electric arc furnace dust as a functional filler with MWCNT microadditives were fabricated and studied. The phase composition of native dust was mainly represented by $ZnFe_2O_4$ and Fe_3O_4 crystalline phases. The particles were characterized by a size of less than 1 µm and were capable of forming larger agglomerates up to 8 µm. The influence of the qualitative and quantitative composition of the composite films on the dielectric properties was studied in the frequency range of 10–10^6 Hz at room temperature. To optimize the permittivity and dielectric losses, the native dust was reduced in a hydrogen atmosphere, and the MWCNT conductive component was added to the composition of the composites. The conductivity values of the obtained composite films varied slightly depending on the concentration and type of filler. An influence of the composition of the composites was observed on the permittivity and dielectric loss tangent. These characteristics increased with the increase in the filler concentration in the polymer matrix. It was noted that even at the highest concentration of the filler, the LDPE retained its flexibility. The composite films based on LDPE filled with reduced dust were characterized by a more noticeable increase in permittivity due to the high individual ε' values. In the case of using reduced dust as a filler with 0.25 wt.% carbon additive, a synergistic effect was manifested for a concentration of 75 wt.% to the greatest extent, providing an increase in the permittivity up to 13.5 with a dielectric loss tangent of 0.038.

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