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Electrical conductivity of composites based on ultra-high molecular weight polyethylene modified with a mixture of graphene nanoplates and iodized carbon nanotubes

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Abstract: In this work, a series of samples of composite materials based on ultra-high molecular weight polyethylene and a hybrid filler containing graphene nanoplates and iodized multi-walled carbon nanotubes (MWCNTs) were obtained by pressing followed by sintering. The resulting nanocomposites were studied by X-ray phase analysis and Raman spectroscopy. The iodine concentration in the modified MWCNTs was determined by energy dispersive X-ray fluorescence analysis. Assessment of the structural features of nanomaterials using X-ray phase analysis indicates the absence of iodine in the interlayer space of graphene sheets, while a change in the surface is observed. Raman spectroscopy data indicate an insignificant destructive effect of iodine on the surface of the nanomaterial. The study of electrical conductivity showed that when using iodine-modified MWCNTs as a filler, the percolation threshold shifts to lower filler concentrations, in comparison with nanocomposite samples containing unmodified nanotubes. An increase in the concentration of graphene nanoplates contributes to a twofold decrease in the percolation threshold. The maximum electrical conductivity of 5.4×10^{-4} S·cm^{-1} was achieved in ultra-high molecular weight polyethylene nanocomposites containing 3 wt. % iodinated multi-walled carbon nanotubes and 1 wt. % graphene nanoplates.

Keywords: nanomaterials; carbon nanotubes; graphene; modification; iodine; nanocomposites; polymers; ultrahigh molecular weight polyethylene; electrical conductivity.

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Электропроводность композитов на основе сверхвысокомолекулярного полиэтилена, модифицированного смесью графеновых нанопластинок и йодированных углеродных нанотрубок

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Аннотация: Получены серии образцов композиционных материалов на основе сверхвысокомолекулярного полиэтилена и гибридного наполнителя, содержащего графеновые нанопластинки и йодированные многостенные углеродные нанотрубки (МУНТ) посредством методов прессования с последующим спеканием. Полученные

нанокомпозиты исследованы методами рентгенофазового анализа и рамановской спектроскопии. Концентрацию йода в модифицированных МУНТ определяли посредством энергодисперсионного рентгенофлуоресцентного анализа. Оценка структурных особенностей наноматериалов при помощи рентгенофазового анализа указывает на отсутствие йода в межслоевом пространстве графеновых листов, при этом наблюдается изменение поверхности. Данные рамановской спектроскопии указывают на незначительное деструктивное воздействие йода на поверхность наноматериала. Исследование электрической проводимости показало, что при использовании в качестве наполнителя модифицированных йодом МУНТ происходит смещение перколяционного порога в область меньших концентраций наполнителя, в сравнении с образцами нанокомпозитов, содержащих немодифицированные нанотрубки. Увеличение концентрации графеновых нанопластин способствует снижению перколяционного порога в два раза. Максимума электрической проводимости 5.4×10^{-4} См/см удалось достичь в нанокомпозитах сверхвысокомолекулярного полиэтилена, содержащих 3 масс. % йодированных многостенных углеродных нанотрубок и 1 масс. % графеновых нанопластинок.

Ключевые слова: наноматериалы; углеродные нанотрубки; графен; модифицирование; йод; нанокомпозиты; полимеры; сверхвысокомолекулярный полиэтилен; электропроводность.

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1. Introduction

Polymers filled with electrically conductive particles are a promising material for obtaining composites that reduce the impact of electromagnetic fields on electronic components of computer technology and biological objects [1–8]. The high resistance of polymers to external influences (temperature, humidity, etc.) allows them to be used as parts of household appliances, structural blocks and assemblies in equipment for air, sea and land applications.

Carbon nanomaterials, due to their high electrical conductivity, mechanical strength, and chemical resistance, are effective fillers for electrically conductive polymer composites [9]. In this case, the intrinsic conductivity of the nanodispersedfiller and the tunneling magnetic resistance between its individual dispersed particles limit the conductivity of the composite material. In this regard, it is very important to develop new modifications of nanocarbon fillers, the composition and structure of which will contribute to the formation of a conducting cluster with the lowest electrical resistance in the volume of the polymer matrix.

Previously, the authors of [10] compared the electrical conductivity, percolation threshold, and dielectric properties of epoxy composites filled with graphene nanoplates (GNPs) and multi-walled carbon nanotubes (MWCNTs). It is shown that the percolation network, regardless of the type of filler and matrix, is formed at a filler concentration of 3.0 wt. %.

The electrical and mechanical properties of composites are also determined by the methods of combining the carbon filler (MWCNTs and graphene) and the polymer matrix. In [11], the electrically conductive and mechanical properties of composites based on carbon nanostructures (MWCNTs, GNPs, and their mixtures) and polylactide obtained by extrusion, 3D printing, and hot pressing were studied. At the same time, the samples obtained by extrusion and hot pressing showed the highest electrical conductivity. The authors of the work believe that with these methods of forming composites, the distance between the filler particles turns out to be noticeably smaller, the contribution of the tunnel effect decreases, and the overall electrical conductivity of the materials increases. Attention should be paid to the large difference between the electrical percolation threshold values, which for composites with MWCNTs and GNPs in this work are 1.5 and 6–9 wt. %, respectively.

Works [12–15] present the facts that additionally indicate that the type of matrix and filler, as well as the nature of their interaction, affect the value of the percolation threshold.

The authors of [16] focused their attention on the study of conductive and mechanical properties of epoxy composites with MWCNTs / GNP hybrid fillers. It has been established that at a mass ratio of MWCNTs : GNPs equal to 8 : 2, the bending strength of the composite increases and the electrical percolation threshold decreases. The authors believe that the presence of oxygen-containing functional groups on the surface of GNPs contributes to the uniform distribution of the filler in the matrix. In addition, based on the data on the electrical conductivity of composites containing GNPs (2.1×10^{-5} S·m^{-1}), MWCNTs (4.3×10^{-3} S·m^{-1}) and

hybrid filler MWCNTs/GNP (9.1×10^{-3} $S\cdot m^{-1}$), a synergistic effect of a mixture of carbon nanostructures on the properties of materials has been demonstrated.

The authors of [17] note that one-dimensional MWCNTs bridge the gaps between GNPs in a thermoplastic polyurethane (TPU) matrix, contributing to the formation of additional pathways. Therefore, the addition of GNPs can improve the electrical conductivity of the resulting nanocomposite and lower the percolation threshold. The MWCNTs/GNP(3 : 1)/TPU composite shows better electrical performance compared to MWCNTs/TPU and GNP/TPU nanocomposites with the same content of the same type of filler.

The above information can be summarized as follows:

– the formation of a percolation cluster in polymer nanocomposites is affected by the nature of the polymer matrix and filler, as well as the nature of the filler distribution;

– the synergistic effect of hybrid fillers on the properties of composites is observed only at a certain ratio of MWCNTs and GNPs;

– electrophysical properties depend on the formation method of composites filled with MWCNTs and GNPs.

Taking into account numerous data, it can be assumed that the possibilities of the original (unmodified) MWCNTs to increase the electrical conductivity of composites are practically exhausted. Modification of MWCNTs with silver [18, 19], nitrogen [20, 21], polyaniline [22–28], halogens [29–32], etc., makes it possible to achieve better performance in this respect.

In this work, ultra-high molecular weight polyethylene (UHMWPE) was chosen as a polymer matrix, which is characterized by wear resistance, resistance to aggressive media, low friction coefficient, high impact strength and low embrittlement temperature, which makes it possible to use products based on it, including under extreme operating conditions [33]. The aim of the research was to obtain composites with antistatic properties based on this polymer. Mixtures of GNPs with original and iodine-modified MWCNTs were tested as fillers. Composites were obtained by pressing followed by sintering.

2. Materials and Methods

2.1. Characteristics of initial materials and reagents

Powdered UHMWPE (Hi-zex, China) and isopropyl alcohol (Laverna Co., Russia) were used to obtain samples of polymer composites. The filler components were GNPs Taunit GM and MWCNTs Taunit-M (NanoTechCenter Ltd., Tambov). Their electronic images are shown in Fig. 1.

GNPs Taunit-GM were obtained by a modified Hummers method by treating crystalline graphite with a solution of ammonium persulfate in sulfuric

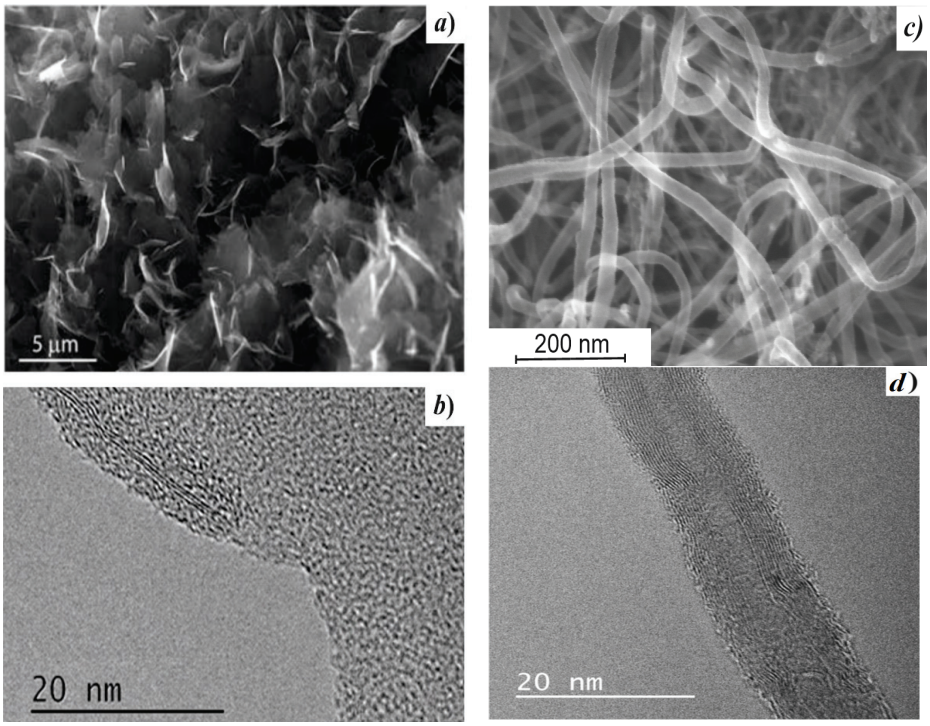

Fig. 1. Electronic images of Taunit GM graphene nanoplates (*a*, *b*) and Taunit-M carbon nanotubes (*c*, *d*) [36]

Table 1. Characteristics of GNPs Taunit GM [36]

Parameter	Value
Number of graphene layers	3 – 5
Thickness of nanoplates, nm	2 – 3
Size of nanoplates in plane, μm	2 – 10
Oxygen content, wt. %	9 – 13
Sulfur content, wt. %	≤ 0.7

Table 2. Characteristics of MWCNTs Taunit-M [36]

Parameter	Value
Outerdiameter, nm	10 – 30
Inner diameter, nm	5 – 15
Length, μm	≥ 2
Total amount of impurities, %	
– initial	≤ 5
– after cleaning	≤ 1
Specific surface, $m^2 \cdot g^{-1}$	≥ 270
Bulk density, $g \cdot cm^{-3}$	0.025 – 0.06

acid followed by washing and ultrasonic dispersion in an aqueous solution of surfactant (aminocumulene) [34]. MWCNTs were obtained by CVD synthesis on a $Co,Mo/MgO,Al_2O_3$ catalyst [35].

Characteristics of GNPs Taunit GM and MWCNTs Taunit-M are presented in Tables 1 and 2, respectively. Crystalline iodine (Component-Reaktiv, Russia) was used to modify MWCNTs.

2.2. Method for modifying MWCNTs with iodine

MWCNTs powder was mixed with crystalline iodine. The content of I_2in the resulting mixture in different experiments ranged from 5 to 15 wt. %. Then it was placed in a sealed glass container and kept in a heating cabinet for 2 hours at a temperature of 120 °C. The iodine-modified carbon nanotubes are hereinafter referred to as MWCNTs-I.

2.3. Method for obtaining nanocomposites

GNPs, MWCNTs, and MWCNTs-I were added to 1 g of UHMWPE at the concentrations indicated in Table 3. 1 mL of isopropyl alcohol was added to the resulting composition, after which it was stirred until homogeneous. The mixture was dried in an oven at 40 °C. The dried material was pressed on a tablet press (FluxanaVaneox, Germany). Pressing was carried out at 25 °C with a load of 5 tons. Compressed pellets with a diameter of ~12 mm and a height of about 3 mm were sintered at a temperature of 170 °C for 2 h. Series of composite samples were obtained. Composites of the first series contained 0.5 wt. % GNPs and 0.1–3 wt. % MWCNTs. MWCNTs-I were used in the composites of the second series. Composites of the third and fourth series contained 1 wt. % GNPs. The designations and compositions of the obtained series of nanocomposite samples are given in Table 3.

2.4. Characterization of MWCNTs and composites

The iodine concentration in the modified Taunit M MWCNTs was determined by energy dispersive X-ray fluorescence analysis using an ARL QUANTX spectrometer (Thermo Fisher Scientific, Switzerland).

X-ray phase analysis of the samples was carried out using an ARL Equinox 1000 diffractometer (Thermo Fisher Scientific, USA) with a radiation wavelength of 1.5406 Å. Shooting time – 600 s.

Raman spectra were obtained on a DXR Raman Microscope (Thermo Fisher Scientific, USA) with an excitation laser wavelength of 532 nm.

Table 3. Designation of nanocomposite sample series

Designation of a sample series	Concentration, wt. %		
	MWCNTs	MWCNTs-I	GNPs
1	0.1; 0.2; 0.5; 1; 2; 3	–	0.5
2	–	0.1; 0.2; 0.3; 0.4; 0.5; 1; 2; 3	0.5
3	0.1; 0.2; 0.5; 1; 2; 3	–	1
4	–	0.1; 0.2; 0.3; 0.4; 0.5; 1; 2; 3	1

The electrical conductivity of nanocomposites was measured according to Russian Standard R50499-93 using an E6-13A teraohmmeter (Punane-Ret, Estonia). The value of electrical conductivity (σ) was calculated by the formula: $\sigma = 4h/\pi d^2 R$, where h, d are the thickness and diameter of the sample, respectively, R is the electrical resistance.

3. Results and Discussion

3.1. The study of the properties of iodine-modified MWCNTs

The X-ray diffraction patterns of the original and iodine-modified MWCNTs (Fig. 2) are similar.

The shift in the position of the (002) peak for MWCNTs-I samples is insignificant (Table 4). The interplanar distances can also be considered unchanged, which indicates that iodine molecules and atoms do not penetrate between the graphene layers of nanotubes, but cause surface changes.

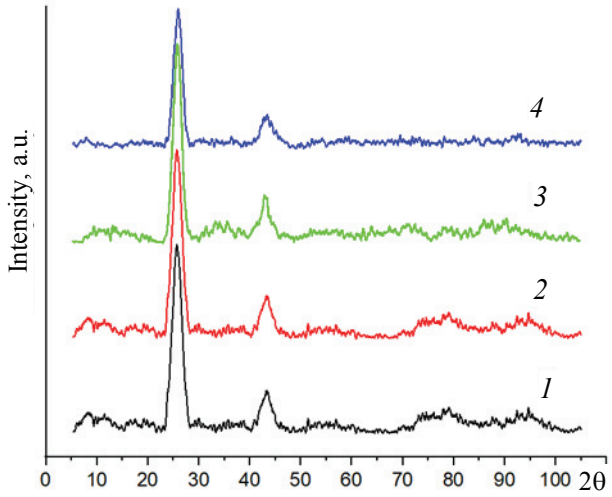

Fig. 2. X-ray diffraction patterns of native (*1*) and iodine-modified (*2 – 4*) MWCNTs. The concentration of iodine in the initial mixture with MWCNTs (wt. %): *2* – 5; *3* – 10; *4* – 15

Table 4. Peak characteristics of X-ray diffraction patterns of original and iodine-modified MWCNTs

Concentration of iodine in the initial mixture, wt. %	Peakposition 002, deg.	Interplanar distance (d_{002}), Å
0	25.7	3.46
5	25.5	3.49
10	26	3.43
15	26	3.42

Raman spectroscopy data (Fig. 3 and Table 5) allow a more detailed analysis of the nature of the change in the MWCNTs structure upon treatment with iodine. All MWCNTs-I samples are characterized by destructive changes compared to the original nanotubes, as indicated by an increased value of the intensity ratio of characteristic D/G peaks for them.

The destruction of graphene layers and amorphization of the material are indicated by the position shift of the 2D peak towards short-wavelength values. In this case, according to the calculated values of the intensity ratio 2D/G, the sample obtained from a mixture containing 15 wt. % iodine consists of nanotubes with a smaller number of layers.

A sample of MWCNTs-I obtained from a 10 % mixture is characterized by a lower defectiveness from modified materials.

Due to the volatility of iodine, its content in finished MWCNTs-I is noticeably lower than in the initial mixtures. According to energy dispersive analysis from mixtures containing 5, 10 and 15 wt. % I_2, MWCNTs-I containing 0.576, 0.990 and 0.911 wt. % of this element, respectively, were obtained.

To prepare composites with UHMWPE, MWCNTs-I with the maximum iodine content were selected according to the data of energy dispersive analysis. These are samples obtained from a mixture containing 10 wt. % iodine. According to the data of Raman spectroscopy, they are also characterized by minimal destructive changes compared to the original nanotubes, as a result of which they should have the best conducting properties.

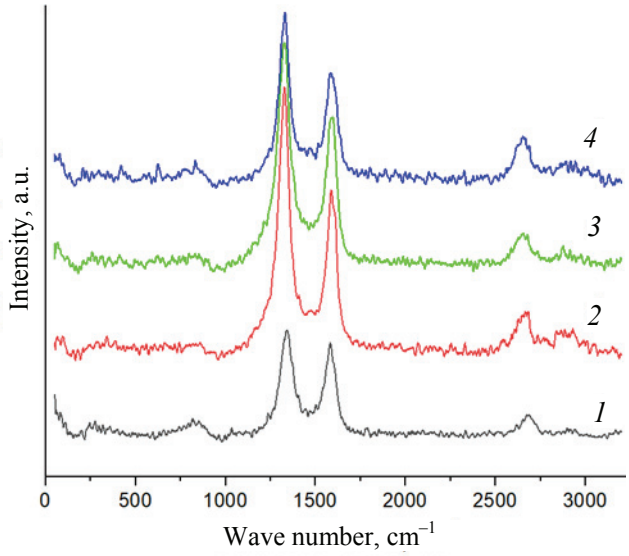

Fig. 3. Raman spectra of native (*1*) and iodine-modified (*2 – 4*) MWCNTs. The concentration of iodine in the initial mixture with MWCNTs (wt. %): *2* – 5; *3* – 10; *4* – 15

Table 5. Raman spectroscopy data of MWCNTs samples

Iodine concentration in the initial mixture, wt. %	Peak 2D position, cm^{-1}	Peak intensity ratio	
		D/G	2D/G
0	2687	1.21	0.21
5	2667	1.62	0.23
10	2646	1.52	0.19
15	2653	1.63	0.38

3.2. Electrical conductivity of UHMWPE nanocomposites containing a hybrid filler

Dependences of the electrical conductivity of composites based on UHMWPE modified with mixtures of GNPs and MWCNTs in various variations are shown in Fig. 4. They are similar in nature and consist of 3 pronounced sections. On the first one, the material demonstrates the properties of a dielectric; on the second one, the electrical conductivity increases significantly; on the third one, it has a maximum value and ceases to depend on the nanomodifier concentration. The electrical conductivity value in the last section for different samples is within the same order of magnitude and is $3.4–5.4\times10^{-4}$ S·cm^{-1}.

Differences in curves *1–4* in Fig. 4 lie in the length of these sections, and, consequently, in the values of concentrations that characterize the formation of a percolation cluster. An increase in the GNPs content in the composite composition promotes a more efficient increase in electrical conductivity upon the introduction of MWCNTs. The sample with 1 wt. % GNPs has the best conductive properties with the addition of 0.5 wt. % MWCNTs-I. To achieve the same electrical conductivity values, a twofold higher concentration of the initial MWCNTs is required.

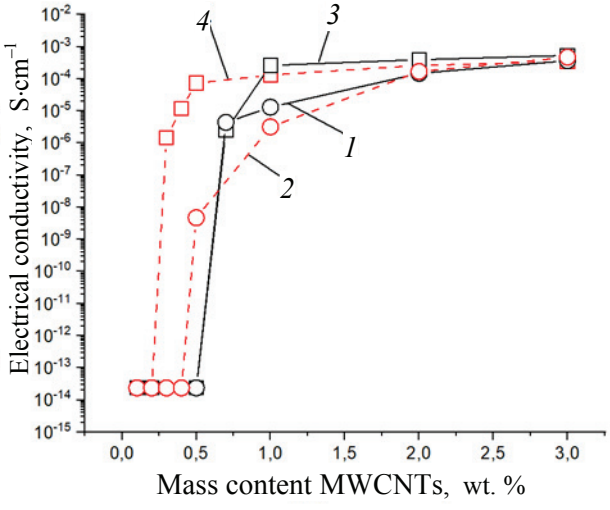

Fig. 4. Electrical conductivity of composites based on UHMWPE containing 0.5 (*1*, *2*) and 1 (*3*, *4*) wt. % GNPs, initial (*1*, *3*) and iodine-modified (*2*, *4*) MWCNTs

The dependences shown in Fig. 4 can be applied to the classical equation of percolation theory 1 [37]:

$$\sigma = \sigma_f (\varphi - \varphi_c)^t, \quad (1)$$

where φ_c is the filler volume fraction corresponding to the percolation threshold (it was recalculated based on the values of the mass concentration of the filler in the composite, taking into account the data on the densities of the matrix and filler (Table 6)), t is the critical electrical conductivity index, σ_f is the electrical conductivity of the filler. Bulkdensity UHMWPE is 0.45 g·cm^{-3}, MWCNTs is 0.025 g·cm^{-3}.

For the convenience of approximating the experimental dependences of electrical conductivity, the logarithm of both parts of equation (1) is taken and as a result the following is obtained:

$$\log\sigma = \log\sigma_f + t\log(\varphi - \varphi_c). \quad (2)$$

The values of MWCNTs volume fractions at the percolation threshold φ_c and the critical values of electrical conductivity t were determined using linear regression of the dependence $\log\sigma$ on $\log(\varphi - \varphi_c)$ (Fig. 5).

Table 6. Calculated values of the MWCNTs volume concentrations in the composite

Mass content of MWCNTs in the composite, wt. %	Volume content of MWCNTs in the composite, vol. %
0.1	0.033
0.2	0.061
0.3	0.088
0.4	0.114
0.5	0.138
1	0.243
2	0.392
3	0.494

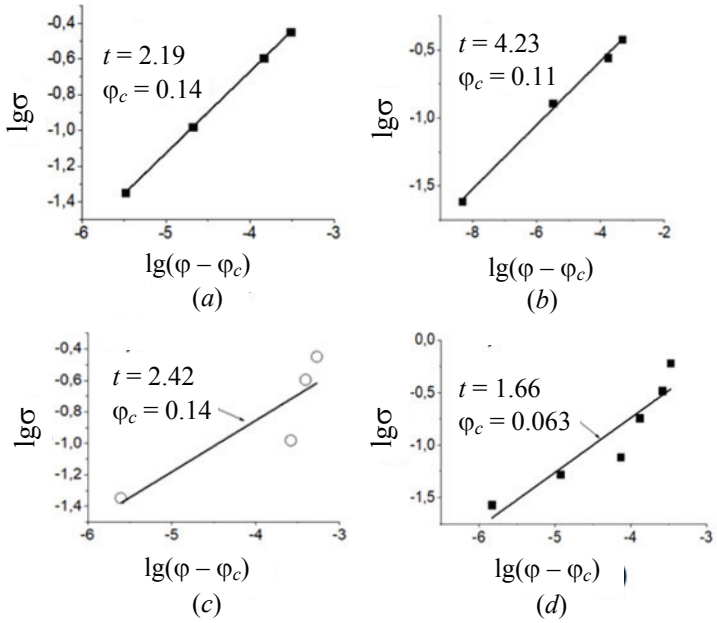

Fig. 5. Dependence plots in the coordinates of equation (2) for composites based on UHMWPE containing 0.5 (*a*, *b*) and 1 (*c*, *d*) wt. % GNP, initial (*a*, *c*) and iodine-modified (*b*, *d*) MWCNTs

For sample series 1 (containing 0.5 wt. % GNPs and MWCNTs of various concentrations), φ_c and t were 0.14 and 2.19, respectively (Fig. 5*a*), while the convergence coefficient R^2 was equal to 1.

The use of MWCNTs-I instead of the initial nanotubes (sample series 2) led to a decrease in φ_c and an increase in t, these indicators became equal to 0.11 and 4.23, respectively (Fig. 5*b*), the convergence coefficient was 0.99667.

Series 3 nanocomposites (containing 1 wt. % GNPs and initial MWCNTs) are characterized by approximately the same values of φ_c and t as for the sample series 1 (Fig. 5*c*). In this case, the convergence coefficient took a minimum value of 0.79075.

The use of MWCNTs-I (samples series 4) leads to a change in these indicators. The parameter φ_c decreases to 0.063 and t decreases to 1.66 (Fig. 5*d*), $R^2 = 0.86238$.

The values of t obtained as a result of approximating the experimental data by equation (2) range from 1.3 to 4 and are indicative of a satisfactory agreement between the experimental results and the estimated values of the percolation theory for composites with a three-dimensional conductive network of MWCNTs in the matrix [38, 39].

4. Conclusion

Modification of carbon nanotubes with iodine and their use as a modifying filler leads to earlier formation of a percolation cluster in composites based on ultrahigh molecular weight polyethylene compared to control samples. An increase in the concentration of graphene nanoplates contributes to a twofold decrease in the percolation threshold. The maximum electrical conductivity of 5.4×10^{-4} S·cm^{-1} was achieved in nanocomposites containing 3 wt. % iodinated MWCNTs and 1 wt. % graphene nanoplates. X-ray phase analysis demonstrates the absence of iodine in the interlayer space of graphene sheets, while a change in the surface is observed. According to the results of Raman spectroscopy, an insignificant destructive effect of iodine on the surface of the nanomaterial is noticeable. The results obtained in the work make it possible to expand the range of practical application of these materials, for example, as functional antistatic coatings.

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7. Conflict of interests

The authors declare no conflicts of interest.

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