Polyaniline/Carbon Nanotubes Composites:
Kinetic Laws of Synthesis, Morphology and Properties

I.V. Gutnik*, T.P. Dyachkova, A.V. Rukhov, E.A. Burakova, E.N. Tugolukov,
S.Yu. Alekseev, B.B. Kodirov, G.A. Titova

Tambov State Technical University, 106 Sovetskaya st, Tambov, 392000, Russia

*Corresponding author: Tel. +7(4752) 63 55 22. *E-mail*: anosowa_i_w@mail.ru

Abstract

The laws of oxidative aniline polymerization in the modification of multi-walled carbon nanotubes (CNT) with polyaniline (PANI) were studied. The effect of morphological features, type and method of CNT prefunctionalization on the temperature profile of the process and effective values of kinetic parameters and thermal effects was analyzed. The synthesized samples of PANI/CNT composites were studied by electron microscopy, Raman spectroscopy, thermogravimetry, and their specific surface area and electrical conductivity were determined. It was found that the maximum specific surface area S_{sp} belongs to composites that contain carboxylated CNTs. At the same time, the increase in the degree of CNT prefunctionalization by COOH-groups leads to loosening of PANI modifying layer and increasing the specific surface of the material. The samples prepared by polyaniline deposition on the CNT surface with a low degree of prefunctionalization (0.2–0.4 mmol/g) were characterized by the minimum value of electrical resistivity. Based on the results of modeling the interaction of carboxylated CNTs with intermediate and end products of oxidative aniline polymerization using molecular dynamics methods, a hypothesis was formulated about the mechanism of modification by CNT polyaniline. It was shown that the initiation centers of PANI macromolecules growth were formed on the CNT surface, while the polymer chain growth occurred in the volume of the reaction mixture.

Using the obtained experimental data, the operating parameters of PANI/CNT composite synthesis were calculated, recommendations on the choice of the main apparatus design were formulated, and a scheme of the experimental and industrial implementation of the process was proposed.

Keywords

Polyaniline; carbon nanotubes; modification; functionalization; oxidative polymerization; kinetic laws; mathematical modeling; molecular dynamics.

Introduction

Since the discovery of polyaniline to the present, there has been an increase in the number of studies devoted to the research of individual PANI synthesis and the production of composites based on it. This is evidenced by the annual increase in the number of publications on this topic. According to the information provided on the portal www.sciencedirect.com, the number of scientific articles and materials in the period from 2007 to 2017 increased from 789 to 2402 items. The interest in polyaniline is primarily associated with its electrically conductive properties. In addition, among other electrically conductive polymers, PANI is characterized by environmental stability and simple methods for synthesis and doping with proton acids [1–2].

The most common way to obtain PANI is currently the oxidative aniline polymerization which can be chemical [3], electrochemical [4], and enzymatic [5]. The literature also provides alternative methods for the synthesis of PANI: aniline polymerization under the action of X-ray irradiation in the presence of nitrate ions [6], dispersion polymerization in a weak magnetic field [7], oxidation of hydrochloride aniline with ammonium persulfate in non-aqueous media (acetone, methanol, toluene) [8]. Among these methods, chemical oxidative polymerization of aniline is distinguished by

a high yield of product from the theoretically possible (~ 90–95 %) and the possibility of obtaining a material with significant electrical conductivity (1–5 S/cm) [1]. The aniline oxidation can be started in the acidic or alkaline environment. Ammonium persulphate [9] and ferric chloride FeCl3 [10] are most frequently used as oxidizing agents in the PANI synthesis. There are also data on using compounds of transition [11–13] and noble metals [14].

The properties of PANI determine promising areas of its application – microelectronics and photoelectric elements [15], LEDs [16], absorbing radio waves [17] and electromagnetic radiation materials [18], sensors and transducers [19], electrode materials of chemical current sources and supercapacitors [20–21].

However, the large-scale use of polyaniline is limited by its instability in charge / discharge processes, accompanied by swelling, shrinkage and destruction of the polymer during the doping / dedoping processes. In addition, at relatively high potentials, PANI degradation can occur. The consequence of these facts is the low operating potential of the polyaniline electrodes. Therefore, it became necessary to develop hybrid composite materials based on PANI and a dispersed substrate, as which carbon nanotubes are most often used [22–23]. CNTs allow to increase the available surface of the material and create an electrically conductive frame. However, the characteristics of the modifying layer and the final properties of the products, depending on the conditions of production, can vary in wide ranges. In addition, it is obvious that PANI/CNT composites for different applications should differ in their most important parameters.

In this regard, the purpose of this study was to investigate the effect of the chemical composition of the CNTs surface acting as a dispersed substrate on the kinetic laws of their modification with polyaniline and the properties of the resulting composites, and to determine the conditions for the implementation of this process on the industrial scale.

Materials and methods

In order to modify polyaniline, the multi-walled carbon nanotubes Taunit-M (Fig. 1) and Taunit-MD (Fig. 2) (Tambov, NanoTechCenter), which differ in their volume morphology and geometrical parameters, were used (Table 1).

The initial and purified from the metal oxide catalyst particles CNT, as well as the nanotubes subjected to pre-gas phase and liquid phase oxidation were modified. CNT oxidation was carried out by:
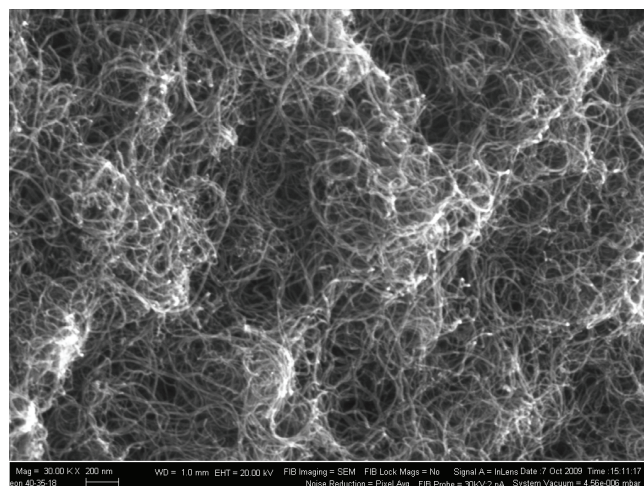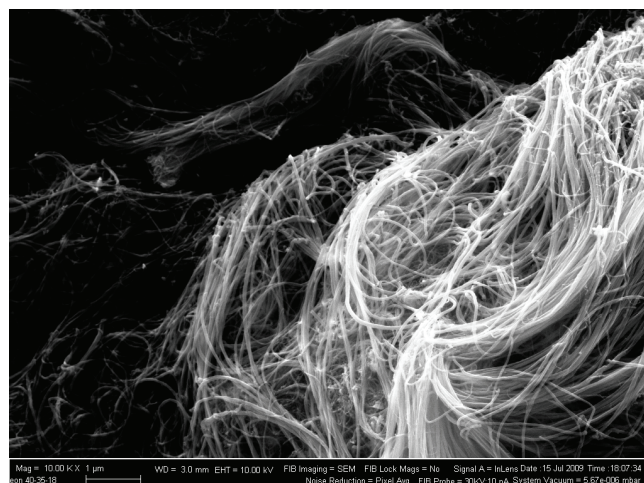

Fig. 1. SEM and TEM images of CNT Taunit-M

Рис. 2. SEM and TEM images of CNT Taunit-MD

Table 1

General characteristics of CNT Taunit-M and Taunit-MD

Parameters	Taunit-M	Taunit-MD
Outer diameter, nm	8–15	30–80
Internal diameter, nm	4–8	10–20
Length, micron	2 and more	more than 20
Specific geometric surface, m^2/g	300–320	180–200

– hydrogen peroxide vapor at 140 °C for 30 hours [24];

– Nitric acid vapor at 140 °C for 6 hours [25];

– concentrated nitric acid at 110 °C [26].

According to the total content of elemental oxygen, CNT of the presented types can be arranged in the following order: oxidized in vapors H_2O_2 < oxidized in vapors HNO_3 < oxidized in concentrated HNO_3.

PANI/CNT composites were obtained by the method of oxidative aniline polymerization in the acidic medium. Ammonium persulphate was used as an oxidizing agent. A portion of carbon nanotubes was dispersed by ultrasound in a given volume of distilled water. Then concentrated hydrochloric acid (0.1 M; 0.01 M) and aniline (0.08 M) were added to the suspension, and ammonium persulfate (0.1 M) was added and mixed for 2 hours. During the process, the pH values and temperatures were recorded.

The morphology of the obtained composites based on polyaniline modified CNTs was studied by electron microscopy using a JEM-2010 transmission electron microscope (JEOL, Japan). The specific surface of the samples was determined by the BET method by nitrogen adsorption in liquid nitrogen (77 K) using a Sorbtometer-M instrument (CATACON CJSC, Russia). Raman spectra of the samples were recorded using a DXR Raman Microscope instrument (TermoScientific, the USA) at an excitation laser wavelength of 633 nm.

To determine the electrical resistivity, the samples were placed in a glass tube with a cross section of 0.06 cm^2 and compressed by two metal punches with a diameter of 2.7 mm under the compacting pressure of 10 and 20 MPa. The determination of the specific electrical capacitance of materials was carried out using a three-electrode cell. The measurements were carried out in the galvanostatic mode at a current of 2 mA and potential sweeps from – 0.3 to 0.3 V. 0.5 M solution of Na$_2$SO$_4$ served as electrolyte.

Thermogravimetric studies of all samples were carried out in a dynamic mode, using a synchronous thermal analysis instrument STA 449 F3 Jupiter (Netzsch, Germany).

Results and discussion

The effect of medium acidity on the laws of oxidative polymerization

During PANI synthesis three characteristic regions can be distinguished on temperature profiles: 1) an induction period during which no change in the temperature of the reaction mixture is observed; 2) the area of temperature increase; 3) smooth decrease and stabilization of its value (Fig. 3, curve 1). With the introduction of CNT into the reaction mixture, the kinetic curves of the oxidative aniline polymerization change. The duration of the induction period is reduced: from 4.5 to 0.5–2 min in 0.1 M HCl and from 14 to 0.5–1 min in 0.01 M HCl (Fig. 3, curves 2 and 3). The increase in HCl concentration also contributes to the increase in temperature at the extremum points (Table 2).

To assess the effectiveness of the oxidative aniline polymerization, the yield of PANI emeraldine salt was determined from the theoretically possible. In a more acidic environment (0.1 M HCl), the presence of CNT contributes to the increase in the yield of PANI by an average of 15%. 0.01 M HCl CNT does not affect the product yield or slightly reduce it.

The effect of CNT pre-purification on the laws of oxidative polymerization

Impurities of the metal oxide catalyst, which is part of CNT obtained by the CVD method, can influence the laws of the oxidative polymerization and the properties of the resulting composites. Indeed, in the course of this study, it was shown that the use of
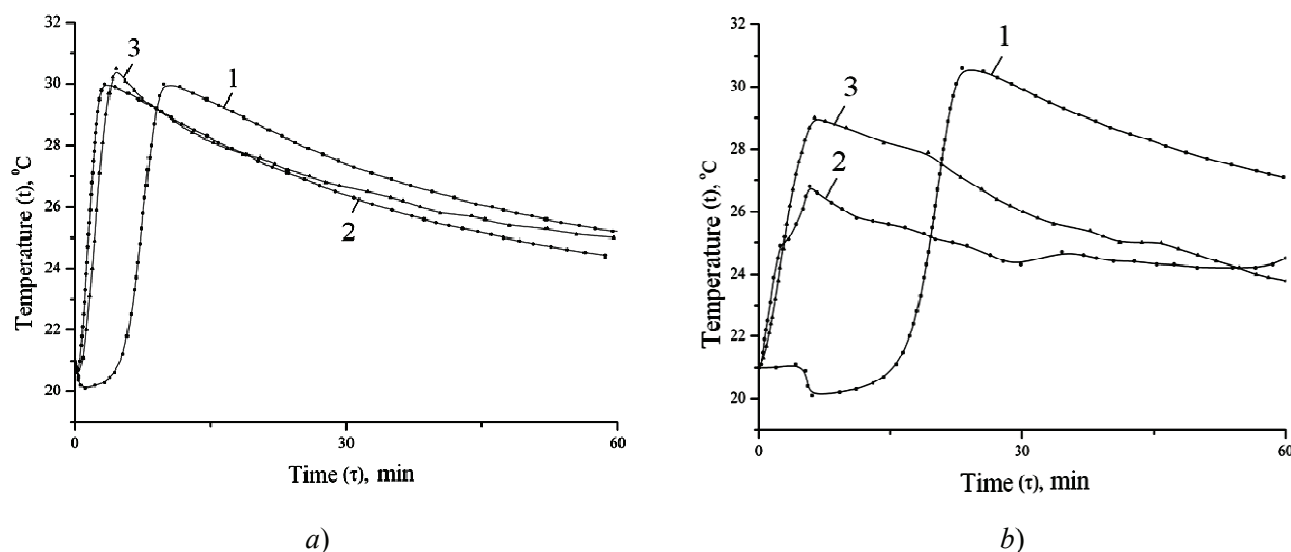

a)   *b)*

**Fig. 3. Temperature change during the oxidative aniline polymerization
in 0.1 M HCl (*a*) and in 0.01 M HCl (*b*) without CNT (*1*), in the presence of Taunit-M (*2*) and Taunit-MD (*3*)**

Table 2

The effect of CNT on the characteristics of the oxidative aniline polymerization reaction

Sample name	Concentration of HCl in the reaction mass, M	Temperature at maximum point, t_{max}, °C	Temperature change, Δt, °C	Time of reaching maximum temperature, min	PANI yield, %
PANI	0.1	30.0	9.0	9.7	79
	0.01	30.6	9.6	23.2	85
PANI/CNT Taunit-M	0.1	30.0	9.0	3.3	93
	0.01	26.8	5.8	5.7	79
PANI/CNT Taunit-MD	0.1	30.5	9.5	4.6	95
	0.01	29.0	8.0	6.3	85

Table 3

Characterization of the oxidative aniline polymerization reaction in the presence of the original and purified from the catalyst particles Taunit-M and Taunit-MD CNT

Sample name	Temperature at maximum point, t_{max}, °C	Temperature change, Δt, °C	Time of reaching maximum temperature, min	PANI yield, %
PANI/ initial Taunit-M CNT	22.6	4.1	19.3	88
PANI/ purified Taunit-M CNT	24.3	5.8	9.6	93
PANI/ initial Taunit-MD CNT	21.4	2.9	18.6	86
PANI/ purified Taunit-MD CNT	22.6	4.1	5.3	88

purified CNTs as a dispersed substrate for the deposition of PANIs contributes to a more rapid achievement of temperature extremes: for Taunit-M CNT the duration of this time interval is reduced by 2 times, for Taunit-MD CNT – by 3.5 times (Table 3). The removal of the metal oxide catalyst also contributes to the increase in temperature at the points of maximum t_{max}. The largest temperature change of the reaction mass Δt is observed when using purified Taunit-M CNT as a dispersed substrate.

This indirectly indicates that in this case the process is accompanied by the largest thermal effect. The yield of the target reaction product when used as a dispersed substrate purified Taunit-MD and Taunit-M CNT increases by 2 and 5 %, respectively, compared with the processes in the presence of the original CNT (Table 3).

By the value of Δt, it is possible to describe the structure of the forming PANI macromolecules. It is assumed that the largest temperature jump is observed when the longest macromolecules are formed during the oxidative polymerization. During the formation of oligomeric products, the temperature of the reaction mixture does not rise so much [22]. Based on experimental data, it can be concluded that the increase in the acidity of the reaction medium and the CNT pre-purification contribute to the increase in the degree of PANI polymerization.

The influence of the CNT functionalization method on the laws of oxidative polymerization and properties of PANI/CNT composites

According to many researchers [27–28], prefunctionalization can contribute to the formation of a uniform polyaniline coating on the surface of CNT and the production of composites with the best electrophysical properties. However, with different methods of nanotube oxidation, the qualitative and quantitative composition of functional groups can vary in wide ranges, which can significantly affect the laws of oxidative polymerization.

Table 4

**Characteristics of the oxidative aniline polymerization reaction in the presence
of the initial and functionalized Taunit-M CNT**

Sample name	Temperature at maximum point, t_{max}, °C	Temperature change, Δt, °C	Time of reaching maximum temperature, min	PANI yield, %
PANI/ initial CNT	21.4	2.9	6.8	93
PANI/CNT oxidized in hydrogen peroxide vapor	21.9	3.4	6.1	90
PANI/CNT oxidized in nitric acid vapor	22.1	3.6	6.4	83
PANI/CNT oxidized with concentrated nitric acid	22.5	4.0	6.6	92

Indeed, the research has shown (Table 4) that the presence of oxygen-containing groups on the surface of nanotubes contributes to the increase in the value of Δt. The maximum thermal effect is observed in the presence of CNTs oxidized with concentrated nitric acid, characterized by the highest total content of elemental oxygen. At the same time, the time of reaching the maximum temperature is practically independent of the presence of functional groups on the CNT surface.

Prefunctionalization of Taunit-M CNT has a negligible effect on the yield of the target product (Table 4). Only in the presence of CNT oxidized in nitric acid vapors, its decrease by 10% relative to the value observed during the polyaniline modification with initial CNT is noted.

The electron images of the composites (Fig. 4) allow us to conclude that there is a polyaniline coating on the CNT surface. At the same time, PANI macromolecules may not interact with the surface of the initial CNT. This is confirmed by the presence of PANI granules in the bulk of the material and the absence of coating on individual nanotubes (Fig. 4*a*). The presence of a small amount of oxygen-containing groups changes the nature of the interaction of polyaniline with the CNT surface, which results in smoothing the modifying layer (Fig. 4*b*).
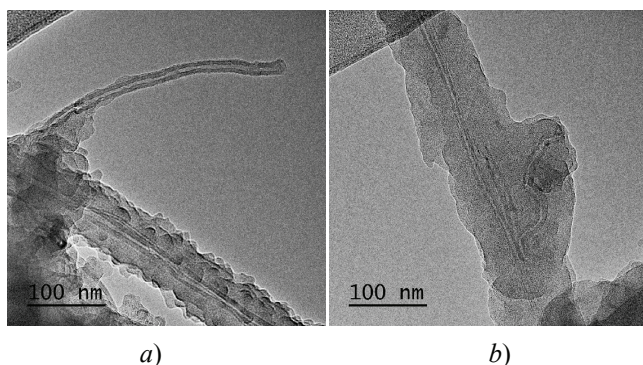

a) *b)*

Fig. 4. TEM images of polyaniline-modified initial (*a*) and oxidized with hydrogen peroxide vapor (*b*) Taunit-M CNT
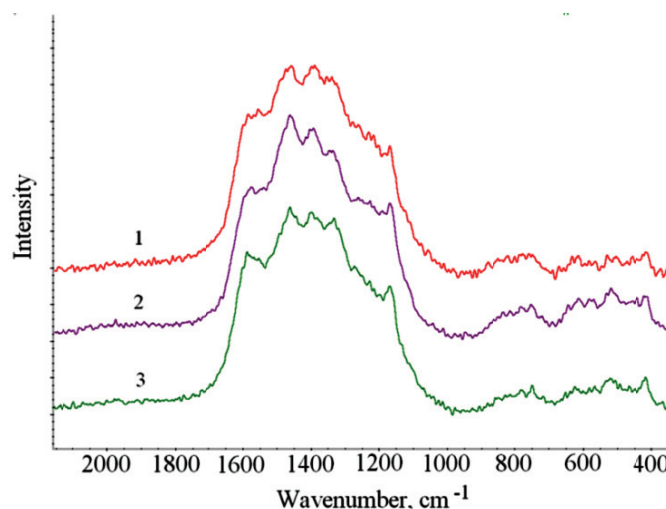

Fig. 5. Raman spectra of polyaniline-modified Taunit-M CNT samples oxidized in hydrogen peroxide vapor (*1*), in nitric acid vapor (*2*) and concentrated nitric acid (*3*)

The Raman spectra of the samples obtained by modifying CNT functionalized by various methods have peaks at 1593, 1504, 1330 and 1171 cm^{-1} (Fig. 5), characteristic of the protonated form of emeraldine polyaniline [29]. In this case, the most qualitative modifying layer is formed on the CNT surface after gas-phase and liquid-phase oxidation with nitric acid, when, according to [30], a sufficiently large number of carboxyl groups is formed.

PANI has a rather high S_{BET} (47.2 m^2/g). Its combination with the initial and functionalized CNT allows the polyaniline surface to be developed more than twofold (Table 5). The value of S_{BET} depends on the method of CNT prefunctionalization. The maximum specific surface area is shown by samples of composites with initial and oxidized by concentrated nitric acid carbon nanotubes (120.6 and 121.6 m^2/g, respectively), and the minimum – with CNT oxidized in hydrogen peroxide vapor (60.2 m^2/g).

Table 5

**Specific surface area of PANI
and PANI/CNT composites**

Sample name	S_{BET}, m²/g
PANI	47.9
PANI/initial CNT	120.6
PANI/ CNT oxidized in hydrogen peroxide vapor	60.2
PANI/CNT oxidized in nitric acid vapor	78.8
PANI/CNT oxidized with concentrated nitric acid	121.6

For composites based on functionalized CNTs, the electrical resistivity was measured (Table 6) and the decrease in its value with increasing compacting pressure was found. Composites based on carbon nanotubes oxidized in hydrogen peroxide vapors (2.8 and 1.9 ohm·cm with a compacting pressure of 10 and 20 MPa, respectively) have the best conductive properties. It can be assumed that the conductive properties of materials of this type are due to the perfect structure of the graphene CNT layers. Indeed, according to [24], CNT oxidized in hydrogen peroxide vapors have the smallest indicator of the surface defectiveness.

According to the TG curves (Fig. 6) of the PANI/CNT composites, the loss of residual moisture is observed at 150 °C. At $t \geq 370$ °C an irreversible thermal decomposition of the material begins. The position of the most pronounced peaks on DSC curves (Fig. 6) for samples based on functionalized CNTs corresponds to a temperature of 580–600 °C. And as the content of atomic oxygen on the polyaniline-modified CNT surface increases, the height of the
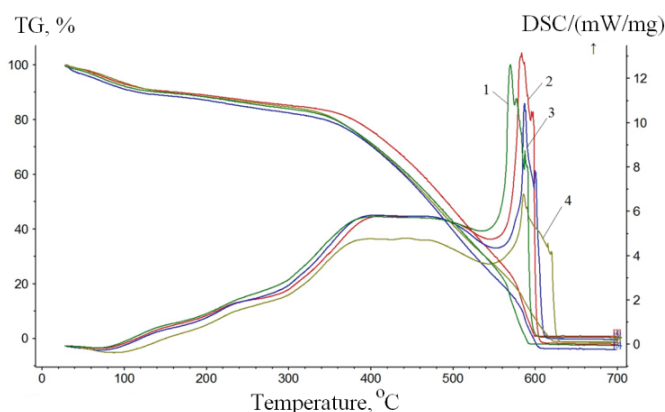
Table 6

**Electrical resistivity
of PANI/CNT Taunit-M composites**

Method of CNT oxidative functionalization	Specific electrical resistance (ohm·cm) at compact pressure	
	10 MPa	20 MPa
–	5,1	3,0
Hydrogen peroxide vapor oxidation	2,8	1,9
Nitric acid vapor oxidation	5,7	4,3
Oxidation with concentrated nitric acid	3,6	2,6

**Fig. 6. TG and DSC curves of PANI/CNT
Taunit-M composites based on:**
purified CNT (*1*); CNT oxidized in hydrogen peroxide vapors (*2*);
CNT oxidized in nitric acid vapor (*3*);
CNT oxidized with concentrated nitric acid (*4*)

peaks on the DSC curves decreases, while the width increases. For composites based on purified Taunit-M CNT (Fig. 6, curve *1*), the extremum on the DSC curve is observed at a lower temperature (540–580 ºC). Moreover, its height is only slightly lower than for a similar curve for a composite sample obtained on the basis of CNT with minimum oxygen content. The revealed patterns indicate the change in the nature of the interaction of the polyaniline coating with the surface of nanotubes in the presence of functional groups. The comparison of thermogravimetric data with the results of Raman spectroscopy suggests that a certain contribution to the nature of this interaction makes the change in the qualitative structure of PANI macromolecules in the modifying layer. The composite obtained on the basis of CNT oxidized in hydrogen peroxide vapors, characterized by the minimum number of structural defects, has the highest thermal stability.

Thus, the perfection of the CNT structure has a decisive effect on the electrical conductivity of PANI composites and their thermal stability. However, the presence of functional groups provides the most complete interaction of the modifying layer with the surface of the nanotube.

*The effect of the degree of CNT functionalization
by carboxyl groups on the laws of oxidative
polymerization and properties of PANI/CNT
composites*

The degree of functionalization of COOH groups and the morphological features of CNT show the effect on the kinetics of oxidative aniline polymerization. When modifying the carboxylated Taunit-M and Taunit-MD CNTs, the maximum temperature at the extremum points was fixed during PANI deposition on

the nanotube surface with a degree of functionalization (D_f) of 0.1 and 0.2 mmol/g, respectively (Table 7).

When PANI is deposited on the surface of Taunit-M CNT, the smallest change in the temperature of the reaction mass is observed in the presence of the initial nanotubes ($\Delta t = 2.8$ °C). The slowest reaction of oxidative polymerization occurs at $D_f = 0.4$ mmol/g, as evidenced by the longest time of reaching the maximum temperature.

For Taunit-MD CNT with the increase in the degree of functionalization, the decrease in the reaction rate is observed. The minimum thermal effect is observed at $D_f = 0.4$ mmol/g.

For Taunit-M CNT used as a dispersed substrate, the maximum yield was recorded in the presence of the initial nanotubes. The presence of COOH groups on the surface of CNT of this morphological type leads to the decrease in the PANI yield (~ 7 %). In the case of Taunit-MD CNT, with the increase in the degree of preliminary functionalization to 0.4 and 0.7 mmol/g, the increase in the yield of PANI is observed. However, in both cases, the influence of the degree of functionalization by COOH groups on the PANI yield cannot be considered significant, since the difference between the minimum and maximum values of this parameter does not exceed 8–12 %.

The different effects of functionalized Taunit-M and Taunit-MD CNTs on the laws of the process and the yield of the target product can be explained by their morphological features. Taunit-M CNTs are separate nanotubes, while Taunit-MD CNTs are in bundles, which makes it difficult to precipitate PANI macromolecules on separate tubes (Fig. 1 and 2).

The effect of carboxyl groups on the character of the modifying layer depends on D_f (Fig. 7). On the surface of carboxylated nanotubes with a low degree of functionalization (0.3 mmol/g), the polyaniline coating layer looks more dense (Fig. 7 *a*), and with a significant content of functional groups it becomes loose and uneven (Fig. 7 *b* and *c*).

Table 7

Characteristics of the oxidative aniline polymerization reaction in the presence of the initial and carboxylated Taunit-M and Taunit-MD CNT

Sample name	D_f, mmol/g	Temperature at maximum point, t_{max}, °C	Temperature change, Δt, °C	Time of reaching maximum temperature, min	PANI yield, %
Taunit-M PANI/CNT	0	21.3	2.8	6.8	94
	0.1	22.1	3.6	7.8	87
	0.4	21.4	2.9	9.9	89
	0.7	21.6	3.1	6.8	86
Taunit-MD PANI/CNT	0	21.2	2.7	5.3	86
	0.2	21.9	3.4	8.4	82
	0.4	20.7	2.2	12.8	94
	0.7	21.3	2.8	15.0	93

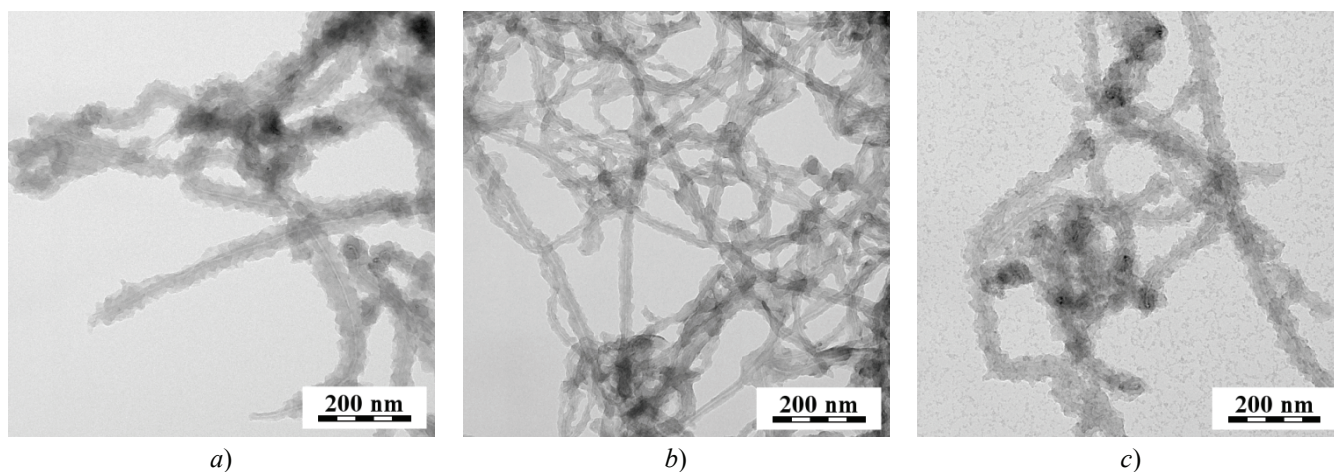*a)*   *b)*   *c)*

Fig. 7. TEM images of modified polyaniline carboxylated Taunit-M CNT. Df, mmol/g:
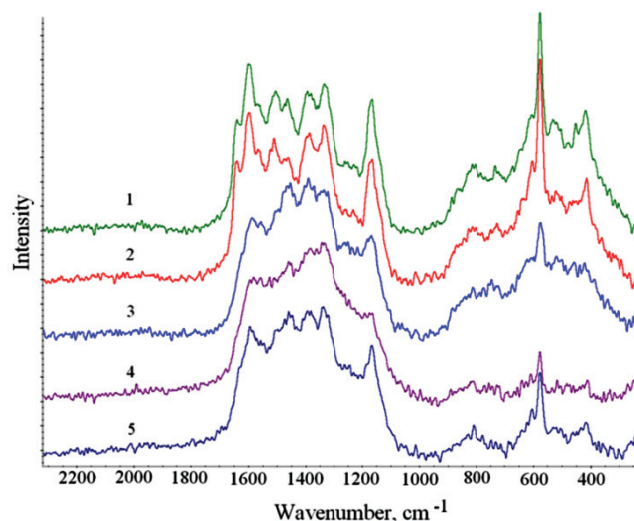*a* – 0.3; *b* – 0.5; *c* – 1.3

Table 8

Specific surface area, density of PANI and its composites with functionalized Taunit-M and Taunit-MD CNTs

Material	D_f, mmol/g	Density, g/cm^3	S_{BET}, m^2/g
PANI	–	1.341	39.2
Taunit-M PANI/CNT	0	1.400	53.5
	0.3	1.400	65.8
	0.5	1.470	103.7
	1.3	1.380	119.0
Taunit-MD PANI/CNT	0	1.390	60.6
	0.4	1.390	58.0
	0.6	1.400	95.6
	1.1	1.390	152.2

Fig. 8. Raman spectra of PANI composites with initial (*1*), purified (*2*) and carboxylated (*3, 4, 5*) Taunit-M CNT. D_f, mmol/g: *3* – 0.1; *4* – 0.4; *5* – 0.7

In the case of using Taunit-M CNT as a dispersed substrate, the specific surface of the composites is symbatically to the degree of nanotubes prefunctionalization (Table 8). The maximum specific surface area for PANI / CNT Taunit-M composites was reached at D_f = 1.3 mmol/g and amounted to 119 m^2/g. This is due to the loosening of the PANI modifying layer, which was noted in the analysis of SEM images.

When modifying Taunit-MD CNT, the influence of the degree of functionalization on the value of the specific surface of the composite is not so clear. At D_f = 0.4 mmol/g, even a small decrease in S_{BET} is observed, but then with the increase in the degree of functionalization, the specific surface area begins to grow and reaches 152.2 m^2/g at D_f = 1.1 mmol/g. This is explained by the fact that the separation of the Taunit-MD CNT bunches into individual nanotubes occurs by prolonged oxidation with nitric acid (~ 4 hours) when $D_f \geq$ 0.6 mmol/g [30]. The surface of such nanotubes becomes accessible to polyaniline modification, therefore S_{BET} grows.

The Raman spectra of the obtained composite samples contain the lines characteristic of the protonated form of the emeraldine polyaniline salt – 1630, 1590, 1510, 1460, 1390, 1330, 1160, 575, and 420 cm^{-1} (Fig. 8) [29]. The samples based on carboxylated CNTs (Fig. 8, lines *3–5*) are characterized by the absence and/or low intensity of a peak at 1630 cm^{-1}, the decrease in peak intensities at 1510 and 575 cm^{-1}, and a shift in the position of the other lines to larger or smaller wave numbers. Thus, the highest quality polyaniline coating is formed on the surface of the initial and carboxylated CNTs with a low degree of functionalization (Fig. 8).

The electrophysical properties of synthesized composites are also largely due to the degree of preliminary functionalization of the CNT. At D_f = 0.2– 0.4 mmol/g, materials with a minimum value of electrical resistivity are formed during oxidative polymerization (Table 9).

The decrease in electrical conductivity with a higher degree of functionalization (0.5–1.3 mmol/g) of the surface of carbon nanotubes by carboxyl groups can be explained in different ways. On the one hand, COOH groups enhance the interaction of the CNT with PANI. At the same time, the fragments of the percolation net turn out to be isolated from each other by layers of less conductive PANI. On the other hand,

Table 9

Electrophysical properties of polyaniline-based composites and initial and carboxylated Taunit-M and Taunit-MD CNTs

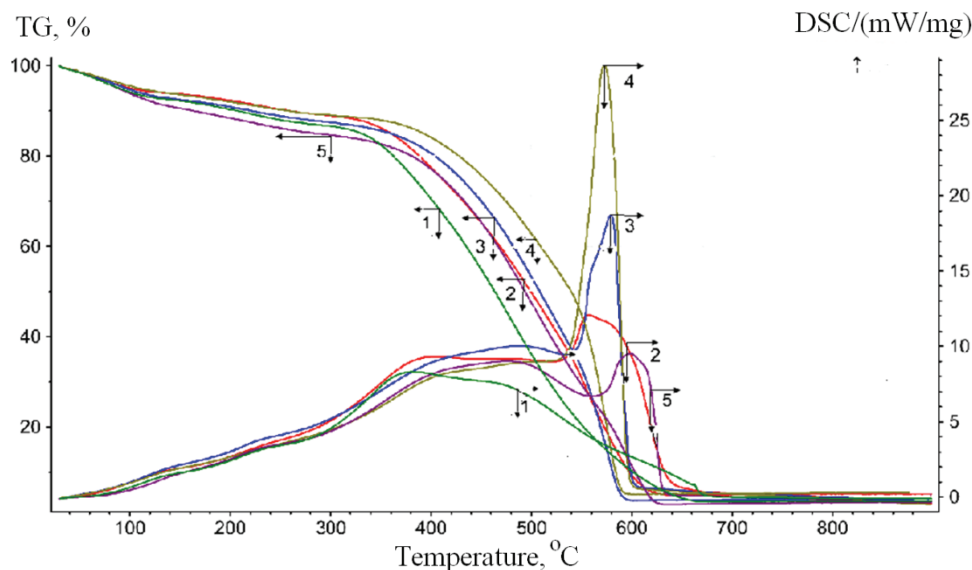| Sample name	D_f, mmol/g	Specific electrical resistivity, Ohm·cm	Specific electrical capacitance, F/g
Taunit-M PANI/CNT	0	5.8	153
	0.2	0.3	191
	0.5	4.1	171
	1.3	4.9	165
Taunit-MD PANI/CNT	0	2.4	120
	0.4	1.3	188
	0.6	2.5	141
	1.1	4.3	168

Fig. 9. TG and DSC curves of polyaniline samples (*1*) and its composites with initial (*2*) and carboxylated Taunit-M CNTs with a degree of COOH groups functionalization equal to 0.2 (*3*), 0.5 (*4*) and 1.3 mmol/g (*5*)

according to electron microscopy, the increase in D_f contributes to the loosening of the modifying PANI layer, which can also lead to the deterioration of the conductive properties.

Shallow CNT prefunctionalization with carboxyl groups also contributes to the improvement of the capacitive properties of the composites (Table 9). Materials based on polyaniline-modified CNTs with a low degree of functionalization (Taunit-M – 0.2 mmol/g; Taunit-MD – 0.4 mmol/g) show the best capacitive properties. However, the remaining PANI/CNT composites are characterized by consistently high values of electrical capacitance, which are maintained for at least 100 charge/discharge cycles.

Analysis of the TG and DSC curves (Fig. 9) shows that the thermal stability of PANI/CNT composite materials, as the degree of preliminary functionalization of CNT increases, first increases and then falls. It should be noted that the destruction of an individual PANI begins at a temperature of about 320 °C (Fig. 9, curve *1*), while the irreversible destruction of the PANI/CNT composites begins at a temperature of 380 °C.

*Investigation of the mechanisms
for the modification of polyaniline-carboxylated CNTs
by molecular dynamics methods*

To explain the revealed laws by the molecular dynamics method, the modeling of the system evolution, including carboxylated CNTs, was carried out during the oxidative aniline polymerization at pH < 2.

At the initial stage of the process, sorption of protonated aniline is observed on the outer surface of CNT (Fig. 10*a*). Then, due to thermal motion, the sorbed particles begin to converge. In some cases, this leads to the formation of chemical bonds with the formation of dimers. In this model, it was taken into account that these dimers cyclize with the formation of phenazine (Fig. 10*b*). The results of the calculation showed that the formation of dimers with their further cyclization occurs on the CNT surface, and not in the volume of the reaction mixture. Then, a protonated aniline particle is attached to phenazine, and a trimeric structure is formed – the phenazine nucleic acid, which is the center of growth initiation for the PANI macromolecule [31]. Further calculation shows that the formed trimeric structures begin to move away from the surface of the nanotubes and after 10 ps they desorb into the volume of the reaction mixture (Fig. 10*c*).

At the next stage of the process, the polymer polyaniline chain begins to grow in the form of protonated emeraldine. At an exposure time of 20 ps (Fig. 11*a*) two PANI macromolecules approach CNT, and at 54 ps PANI adsorption on the CNT surface begins (Fig. 11*b*).

At an exposure time of 54 ps the approach of the PANI macromolecules to the CNT surface begins. However, only some of the molecules are sorbed; the rest, with a further increase in exposure time (86 ps), move away to such a distance from the CNT surface that they no longer influence the value of the potential interaction energy "polyaniline – carboxylated CNT" (Fig. 11*c*).
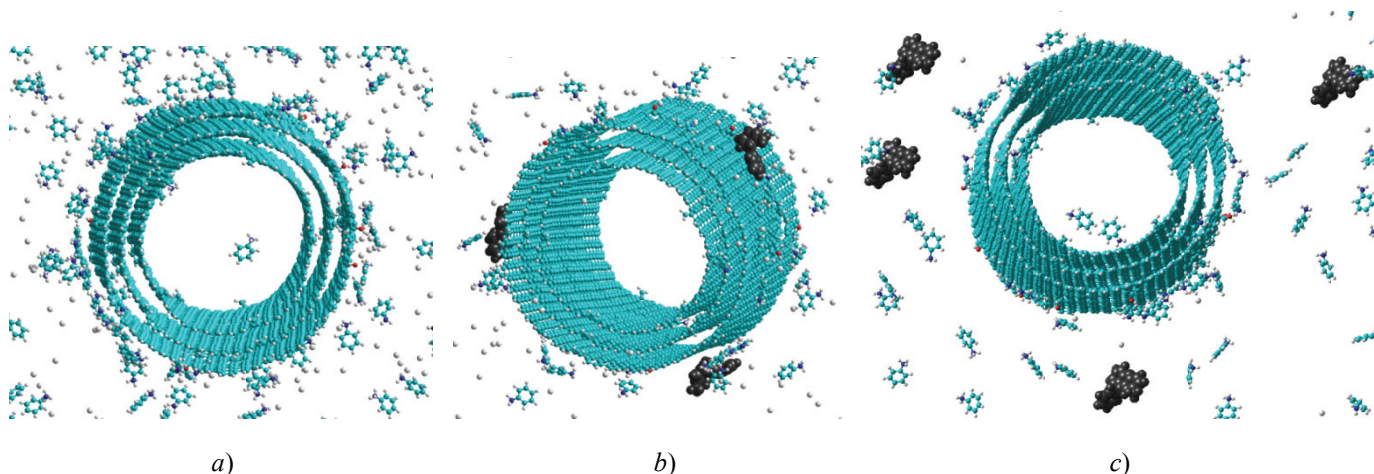
a)   *b*)   *c*)

Fig. 10. The evolution of the molecular system at the initial stages of the oxidative aniline polymerization.
Trimer structures are shown in dark color. Exposure time:
a − 2 ps; *b* − 6 ps; *c* − 10 ps

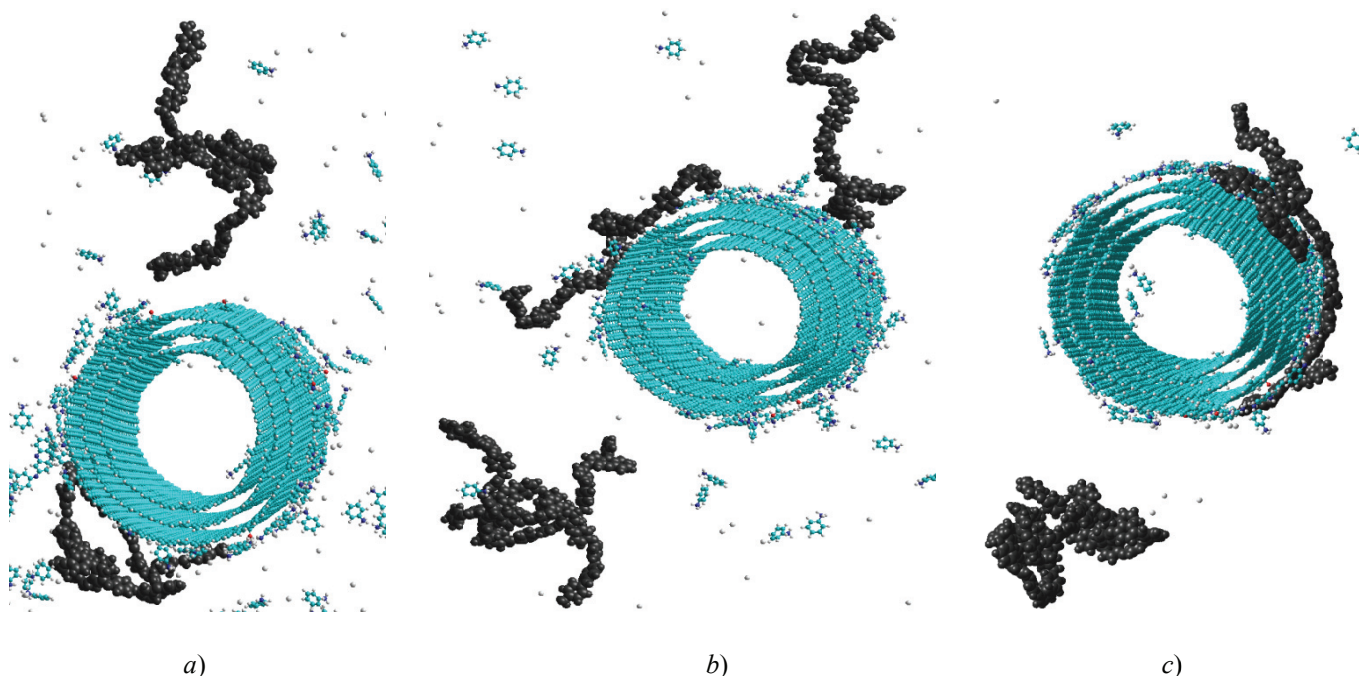*a*)   *b*)   *c*)

Fig. 11. The evolution of the molecular system "polyaniline - carboxylated carbon nanotube".
The dark color shows the synthesized PANI macromolecules. Exposure time:
a – 20 ps; *b* – 54 ps; *c* – 86 ps

According to the obtained results, it can be concluded that hydrogen bonds are not formed when modifying polyaniline-carboxylated CNTs. Polyaniline rests on the surface of CNT due to the forces of electrostatic interaction and van der Waals. At the same time, settling on the CNT surface, the PANI macromolecule tends to move away from the COOH groups (Fig. 12).

The information obtained in the course of mathematical modeling allowed us to propose a hypothesis explaining the dependence of the electrophysical properties of PANI/CNT composites on the degree of functionalization of the surface of the carbon material by COOH groups.

Around the carboxyl groups, protruding above the CNT surface, there is an energy layer, getting into which the polyaniline macromolecule begins to be attracted to the CNT surface. This process takes place until the atom participating in the interaction approaches the surface of the nanotube at a distance r_1, at which the potential energy of this interaction is minimal (Fig. 13). With a further approach of CNT with the PANI macromolecule, the interacting atoms begin to repel each other. At the same time, the CNT
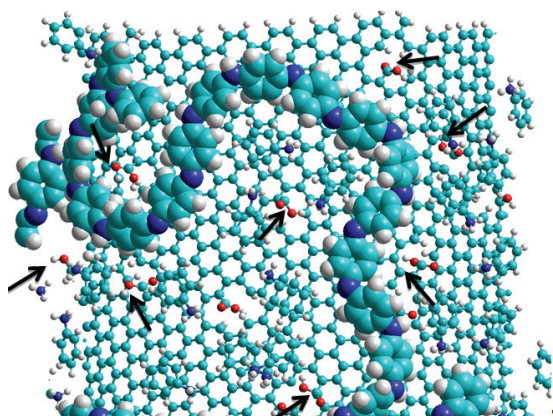
Fig. 12. Fragment of the surface of a carbon nanotube and polyaniline macromolecule. COOH groups are marked with arrows

molecule falls in the field of attraction forces to the surface of the nanotube free from functional groups. As a result, the polymer chain begins to shift relative to the COOH group, remaining from it at a distance of r_1, and at the same time approaching the CNT surface at a distance of r_2 corresponding to the maximum effect of attraction forces. Consequently, the PANI macromolecule reaches the minimum state of the potential energy of interaction with both the carboxyl groups and the surface of the nanotube, being located at a distance of r_1 and r_2 from them, respectively.

In the case when the distance between adjacent carboxyl groups on the CNT surface does not exceed $2r_1$, the PANI molecule is not able to approach the CNT surface by the distance r_2. This leads to the decrease in the total energy of polyaniline retention and the instability of the modifying layer. As a result, PANI macromolecules will be located at a large distance from the CNT surface, forming a loose layer or inclusion of individual polyaniline. This composite structure does not provide contact between the CNT surface and the

modifying layer, which contributes to the decrease in the conductive and capacitive properties.

Based on the mentioned hypothesis, an equation was proposed for calculating the degree of CNT prefunctionalization with COOH groups (φ), which will ensure the formation of the most stable modifying layer provided that these groups are evenly distributed on the surface of the nanotube.

$$\varphi = \frac{D}{N\, r_1^2\, \rho\left(D^2 - d^2\right)},$$

where ρ – graphite density, kg/m^3; D, d – CNT outer and inner diameter, respectively, m; N – Avogadro number.

Evaluation of the kinetic parameters of the modification process of carbon nanotubes surface with polyaniline

The method of studying the kinetics of the oxidative aniline polymerization process in the presence of CNT is based on solving an inverse problem of mathematical modeling of the non-stationary heat exchange process. The differential equation describing the change in temperature of the reaction mixture in a laboratory reactor is:

$$\frac{dt_1(\tau)}{d\tau} + \frac{kF}{m_c c_c} t_1(\tau) = \frac{jM}{m_c c_c}, \tag{1}$$

$$t_1(\tau) = t(\tau) - t_{oc}, \tag{2}$$

Initial conditions:

$$t_1(0) = t_0 - t_{oc}, \tag{3}$$

where k – heat transfer coefficient, W/(m^2·K); F – heat exchange surface with the environment, m^2; m_c – mass
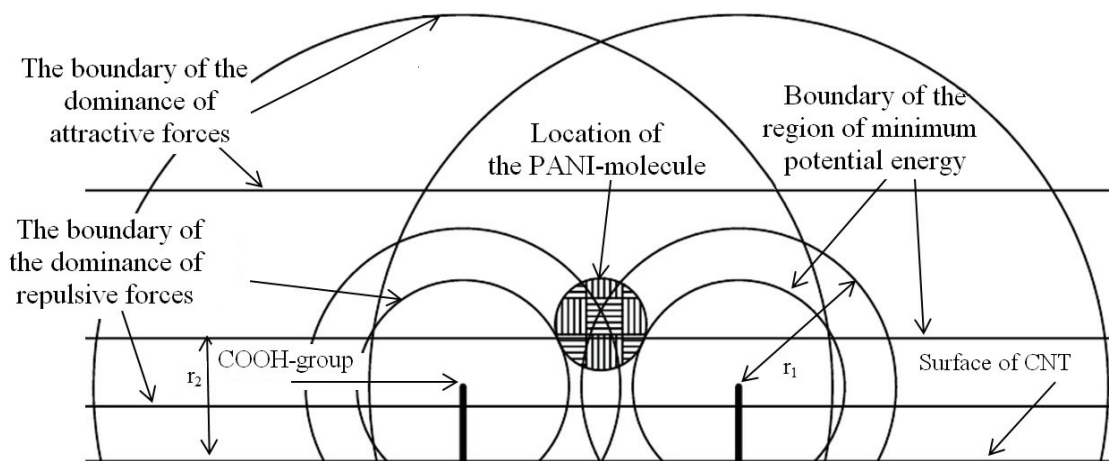

Fig. 13. Diagram of carboxylated CNT and polyaniline molecule interaction

of the reaction mixture, kg; c_c – specific heat capacity of the reaction mixture, J/(kg·K); j – specific thermal effect of the chemical reaction, J/kg; M – mass productivity of the chemical reaction by product, kg/s; $t(\tau)$ –temperature of the reaction mixture, °C; t_0 – initial temperature of the reaction mixture, °C; t_{oc} – environment temperature, °C.

Analytical solution of equation (1) under the condition of a constant value of the mass productivity of the chemical reaction by product in a short period of time has the following form:

$$t_1(\tau) = \frac{jM}{kF} + \left(t_0 - t_{oc} - \frac{jM}{kF} \right) \exp\left(-\frac{kF}{m_c c_c}\tau \right). \qquad (4)$$

The developed technique allowed to study the change in the aniline concentration and the polyaniline mass during its deposition on the CNT surface (Fig. 14). The duration of the section corresponding to the induction period of the reaction, in which the concentration of aniline remains practically unchanged, is very small. After it, the growth of PANI macromolecules begins. Calculations are performed using the Mathcad application.

The information on the kinetics of the modification process of the CNT surface with polyaniline makes it possible to estimate the values of the kinetic coefficients – the pre-exponential factor of the Arrhenius equation k_0 and the activation energy E_A. The E_A value is determined as a result of linear approximation, and k_0 – according to the dependence obtained from the equation of formal chemical kinetics.

The highest specific thermal effect of the process j is observed when using CNTs of both morphological types with a minimal degree of functionalization (Table 10). It is noteworthy that with the increase in the degree of Taunit-M CNT functionalization to 0.7, the value of j decreases. In the presence of Taunit-MD CNT it is not observed. The activation energy of the process in the presence of Taunit-M CNT is much higher than in the presence of Taunit-MD CNT.

Certain constants of kinetic equations were used in the interrelated calculation of the kinetics of modifying carbon nanotubes with polyaniline.
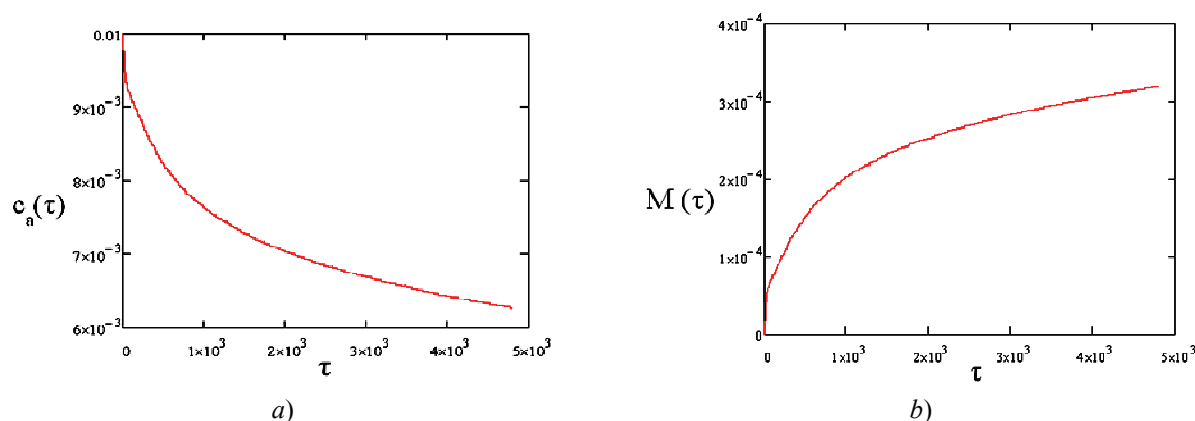

a)   *b)*

Fig. 14. The change in the aniline concentration (*a*) and the polyaniline mass (*b*)
during the process of modifying Taunit-M CNT. D_f = 0.2 mmol/g

Table 10

Calculated data for the process of oxidative aniline polymerization on the surface of carboxylated CNTs

Sample name	D_f, mmol/g	Thermal effect, j		Activation energy, E_A, J/mol	Pre-exponential factor, lg k_0
		J/kg	J/mol		
Taunit-M PANI/CNT	0	$1.49 \cdot 10^6$	$1.93 \cdot 10^5$	$3.58 \cdot 10^5$	61.14
	0.1	$2.45 \cdot 10^7$	$2.27 \cdot 10^6$	$1.73 \cdot 10^6$	302.37
	0.4	$9.24 \cdot 10^6$	$8.59 \cdot 10^5$	$1.07 \cdot 10^6$	186.82
	0.7	$4.98 \cdot 10^6$	$4.63 \cdot 10^5$	$1.56 \cdot 10^6$	274.86
Taunit-MD PANI/CNT	0	$7.00 \cdot 10^6$	$6.52 \cdot 10^5$	$7.12 \cdot 10^6$	–
	0.2	$7.72 \cdot 10^6$	$7.19 \cdot 10^5$	$8.59 \cdot 10^5$	149.73
	0.4	$3.64 \cdot 10^6$	$3.39 \cdot 10^5$	$9.44 \cdot 10^5$	165.58
	0.7	$5.27 \cdot 10^6$	$4.91 \cdot 10^5$	$2.01 \cdot 10^5$	33.60

Mathematical modeling of the kinetics of modifying carbon nanotubes with polyaniline

The development of industrial technology for producing modified polyaniline CNTs is inextricably linked with the calculation of the determining dimensions of the reaction equipment and operating parameters of the process. It is commonly known that chemical processes cannot be directly scaled from a laboratory setup to an industrial reactor. To solve this problem, methods of mathematical modeling are used. The analysis of the experimental data showed a high value of the temperature coefficient of the chemical reaction rate, which requires taking into account changes in the temperature of the reaction mass in the reactor during kinetic calculations. A number of assumptions were made (the laboratory reactor operates in perfect mixing mode; the process of modifying CNTs with polyaniline takes place under kinetic control; the oxidative aniline polymerization proceeds in one stage, and the thermal effect of the reaction has a constant value; the heat from the operation of the mixing device can be neglected), considering which the kinetics of the CNT modifying process with polyaniline can be described using a system of differential equations.

The change in PANI mass in the process of modifying CNTs:

$$\frac{dm(\tau)}{d\tau} = k_0 \exp\left(\frac{-E_a}{R(273{,}15 + t(\tau))}\right) c_a m_c, \qquad (5)$$

Initial conditions:

$$m(0) = 0, \qquad (6)$$

where c_a – aniline concentration, kg/kg.

The temperature change in the reaction mass in the process of modifying carbon nanotubes with polyaniline:

$$\frac{dt(\tau)}{d\tau} + At(\tau) = B. \qquad (7)$$

Initial conditions:

$$t(0) = t_s, \qquad (8)$$

where

$$A = \frac{kF}{m_c c_c}; \quad B = \frac{j_Q M}{m_c c_c} - \frac{kF}{m_c c_c} t_{oc} - W. \qquad (9)$$

As a result of the analytical solution of differential equations, the system (5) – (9) was reduced to the system of algebraic equations, the roots of which were determined by the numerical method. The findings which make it possible to determine the allowable operating parameters are presented in Fig. 15.
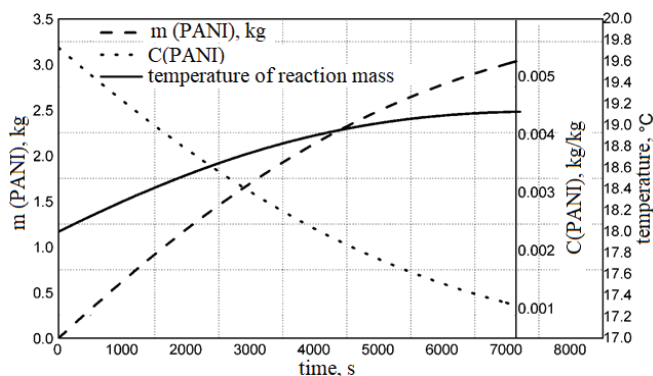

Fig. 15. The calculation results of the kinetics of the CNT modification processes with polyaniline

During the process (2 hours), the mass of the obtained polyaniline was 3.048 kg, the aniline concentration decreased from $5.50 \cdot 10^{-3}$ to $1.05 \cdot 10^{-3}$ kg/kg. The temperature of the reaction mass increased by no more than 1 °C, which is explained by the high heat capacity of the reaction mixture and the low aniline concentration. The technological mode obtained as a result of the calculations is recommended as the main one in industrial production, the data on the temperature change made it possible to recommend the use of a reactor without a heat exchange device.

Conclusion

The laws governing the oxidative aniline polymerization in the presence of carbon nanotubes with different morphology and chemical composition of the surface were investigated. The values of the exothermic thermal effect of the processes, which were 416–2270 kJ/mol, were determined. It was shown that the presence of carbon nanotubes in the reaction mass contributes to the increase in the reaction rate and the reduction in the duration of the induction period. As the content of oxygen-containing groups on the CNT surface increases, the thermal effect of the process increases, and the rate of reaching the extremum of temperatures on the dependence $t = f(\tau)$ is maximum in the presence of oxidized CNTs with the lowest content of functional groups.

The relationship between the characteristics of carbon nanotubes and the properties of synthesized composites with PANI was shown. It was established that both the CNT morphology and the chemical composition of the surface (the degree of prefunctionalization) affects the electrical conductivity and electrical intensity of the synthesized materials. Composites based on carboxylated CNTs with a low degree of functionalization (D_f = 0.2–0.4 mmol/g) have the best electrophysical indicators. There is a tendency

to increase the specific surface of the composites with increasing D_f. Materials based on CNTs with a high degree of functionalization (1.3 mmol/g) have lower thermal stability (intense mass loss occurs when heated to 320 °C) compared to CNT-based composites with an average (0.3–0.6 mmol/g) value of the functionalization degree (mass loss begins at a temperature of > 380 °C).

A hypothesis about the mechanism of modifying carboxylated CNTs with polyaniline was formulated, according to which phenazine nucleotides during oxidative aniline polymerization form on the CNT surface, desorb into the volume of the reaction mixture, where the PANI macromolecules grow.

A mathematical model of the non-stationary temperature field of the reaction mass in the process of oxidative aniline polymerization in the presence of CNTs was developed, which allowed the kinetic and thermodynamic characteristics of the chemical process (rate constant and thermal effect of the reaction) occurring in the non-stationary temperature mode to be determined.

It has been shown that the use of the kinetic equation of a first-order chemical reaction for describing the kinetics of the CNT polyaniline-modifying process due to high values of the temperature coefficient of the chemical reaction is possible only together with solving the problem of non-stationary heat exchange.

The mathematical model of the combined process of modifying the CNT surface with polyaniline, describing its kinetics in the non-stationary temperature field of the reaction area of the apparatus, was developed. The model was used to determine a number of design and operating parameters of the reactor (initial aniline concentration – 0.0055 kg/kg, process time – 2 hours, no need for a heat exchanging device was confirmed).

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