

FUNCTIONALIZATION AND MODIFICATION OF CARBON NANOMATERIALS

Tatyana P. Diachkova, Alexey G. Tkachev, Nataliya V. Orlova, Andrej Yu. Orlov

Tambov State Technical University, Russia

e-mail: nanotam@yandex.ru

Abstract

Some regularities of covalent functionalization multiwalled carbon nanotubes (MWCNTs) by oxygen-containing groups were studied. The resulting materials were characterized by electron microscopy, thermogravimetric analysis, FTIR and Raman spectroscopy. The dependence of the degree of functionalization of MWCNTs from the process conditions was stated. The advantages of the gas phase to the liquid phase oxidation were shown. The effect of pristine and functionalized MWCNTs on the properties of composites with polysulfone was studied. Pristine and functionalized MWCNTs were modified with polyaniline. The effect of the method and degree of pre-functionalization of carbon nanotubes on the regularities of the oxidative polymerization of aniline and the properties of the obtained materials was shown.

Key words: multiwalled carbon nanotubes, functionalization, modification, oxidation, composites, polyaniline.

1. INTRODUCTION

Carbon nanotubes (CNTs) due to their unique properties have an increasing application in various branches of engineering and technology. They are suggested to be used as components of polymer composites [1], electrode materials [2], adsorbents [3], modifying additives for building materials [4], etc. However, the surface of carbon nanotubes is originally solvophobic and inert and this leads to their agglomeration in various matrices and prevents the formation of uniform dispersion. As a result, the practical effect of the application of CNTs, especially in the composites is lower than expected. Possible solution of this problem is modifying the surface of carbon nanotubes by non-covalent and covalent functionalization. Numerous ways of functionalization of CNT are known and the better effect of functionalized carbon nanomaterials in composites is proved [5].

Thus, the presence of [6] and carboxyl [7] functional groups on the surface of carbon nanotubes amine assists embedding CNTs into polysulfone matrix [8]. To achieve the best effect pre-oxidized carbon nanotubes are often subjected to a second functionalization. For example, in [9], the oxidized CNT were reacted with 5-isocyanato-isophthaliolchloride for joining different groups (-OOC-, -CONH-, etc.), thus yielding a composite microporous polysulfone-based material suitable for the production of ultrafiltration membranes. In [8] it was shown that treatment of carboxylated CNTs with octadecylamine improves thermal stability, strength and adsorption properties of composite membranes of polysulfone. According to some literature data pre-oxidation of CNTs promotes the reaction of oxidative polymerization of aniline on their surface. In some cases, this is explained by the fact that carboxyl groups are centers of chemisorption of aniline monomers on the surface of CNTs. The authors of [10-11] suggest that the interaction of aniline with oxidized nanotubes is not only due to the interaction of π -system of CNTs with aniline molecules, but also because of the emergence of the hydrogen bonds between the NH_2 - and COOH -groups. The influence of the method and degree of functionalization of CNTs in the above mentioned studies was not analyzed.

Also, most methods of functionalization of CNT described in the literature because of the specific conditions and reagents used may advantageously be implemented only in the laboratory. The growing need in technology of effective nanomodifiers requires the development of methods of obtaining functionalized carbon nanomaterials in large scale. In connection with it, it is necessary to study the effect of reaction conditions on the properties of the resulting materials and study the regularities of CNTs functionalization processes for its further scaling.

2. MATERIALS AND METHODS

We used carbon nanotubes "Taunit", "Taunit-M" and "Taunit-MD" (Fig. 1) produced by "NanoTechCenter" Ltd. (Tambov, Russia). Their geometric parameters and some physical properties are shown in Table. 1.

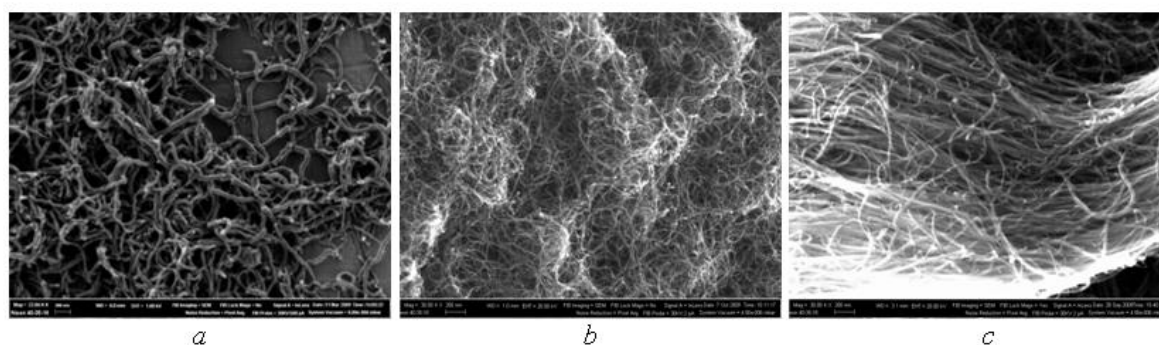


Fig.1. SEM-images of carbon nanotubes: *a* - "Taunit" *b* - "Taunit-M", *c* - "Taunit-MD"

Table 1. General characteristics of CNTs used in this work

Parameters	«Taunit»	«Taunit -MД»	«Taunit -M»
External diameter, nm	20÷70	30÷80	8÷15
Inner diameter, nm	5÷10	10÷20	4÷8
Length, μm	2 and more	20 and more	2 and more
Total impurities (%) (after treatment)	till 5 (till 1)	till 5 (till 1)	till 5 (till 1)
Bulk density, g/cm^3	0,4÷0,6	0,03÷0,05	0,03÷0,05
The specific surface area, m^2/g	120÷130 and more	180÷200	300÷320

Functionalization of the surface with oxygen-containing groups was carried out in several ways:

- 1) boiling in concentrated nitric acid;
- 2) oxidation with potassium permanganate in acidic media;

3) oxidation with nitric acid vapor.

Surface functional groups were identified by IR spectroscopy. Number of COOH groups (mmol) per unit weight of CNTs was measured titrimetrically [12].

Raman spectrum of CNTs samples were investigated on Raman amorphous polycrystalline Al_2O_3 substrate (wavelength 473 nm laser excitation). Electronic images of carbon nanotubes and their composites with polyaniline were made using scanning electron microscopic complex Neon 40, Carl Zeiss.

Modification of CNTs with polyaniline was performed by oxidative polymerization of aniline under the action of ammonium persulfate $(\text{NH}_4)_2\text{S}_2\text{O}_8$ in presence of carbon nanotubes. The weight content of polyaniline in the samples of nanocomposites obtained was calculated as the difference between the mass of dried composite and pristine carbon nanotubes, referred to the weight of a nanocomposite in %.

TG-curves of the samples were recorded with thermal analysis device STA 449 F3 Jupiter (Netzsch). During measurement, the sample chamber was purged with air at a rate of 30 ml/min, and the chamber of thermobalance was purged with inert gas (argon) at a rate of 10 ml/min. The temperature program included holding at a temperature of 30° C for 10 minutes, heating from 30 to 900°C at a rate of 10°C/min and cooling samples to room temperature at a rate of 15°C/min.

To determine the specific electrical resistivity the samples of obtained materials were placed in a glass tube and compressed using two metal pistons under pressure of 10 MPa. The electrical resistance of the material was measured and recalculated to specific resistivity ρ (Ohm-cm). The relative measurement error did not exceed 10%.

Determination of capacitance of obtained materials was made using a three-electrode cell in which a sample of PANI/CNTs composites (0.05 g) was deposited on glassy carbon disk served as the working electrode. The auxiliary electrode was a plate of graphite foil. The reference electrode was silver/silver chloride electrode. Measurements were performed in a galvanostatic mode at a current of 2-10 mA, the potential sweeps from -0.5 to 0.5, and from -0.3 to 0.3 V. The electrolyte was 0.5M Na_2SO_4 in water.

Polysulfone Ultrason 6020 ("BASF") was used as another modifiable matrix as the films with thickness of 20 and 150 microns. The specific volume resistivity of the dielectric was $>1,0 \cdot 10^{16}$ Ohm-cm. Composite films were obtained from dispersion of carbon nanotubes in a 20% solution of polysulfone in dimethylacetamide treated in an ultrasonic device (2 kW, 22 KHz, 20 min.). The film thickness was determined with a device for measuring of geometrical parameters "K5", and the electrical resistance - by teraohmmeter "E6-13A." The concentration of carbon nanotubes in the polymer was 2 wt.%.

Images of composite films were made by using metallographic microscope Axiovert 40 inverted MAT (Carl Zeiss) in reflected light using the contrast method by bright field.

3. RESULTS AND DISCUSSION

3.1. The study of oxidation of CNTs

Treatment of carbon nanotubes with potassium permanganate, according to the literature, results in appearing of oxygen-containing functional groups (hydroxyl, carboxyl) on the surface [13-16]. This oxidation process is fast.

A typical IR spectrum of carbon nanotubes "Taunit-M" oxidized by potassium permanganate is characterized by the presence of a number of absorption bands. Peaks at 2928 and 2852 cm^{-1} are caused by asymmetric and symmetric vibrations C-H (2928 and 2852 cm^{-1}) in alkyl group [17], which

is a residue of hydrocarbon molecules used in CVD-process of producing of CNT. The presence of the absorption band at 3423 cm^{-1} may be attributed to vibrations in the O-H bonds in the hydroxyl and carboxyl groups formed in the oxidation of nanotubes. According to [18], the absorption peaks at 1562 and 1637 cm^{-1} are due to the presence of the $> \text{C} = \text{O}$ group. Therefore, IR spectra prove the presence oxygen-containing functional groups on the surface of CNTs «Taunit-M» treated with potassium permanganate in acidic medium.

IR-spectra of the pristine and oxidized with nitric acid in the liquid and gas phase CNTs (Fig. 2) are characterized by the presence of absorption bands of C-H (2920 , 2850 and 1460 cm^{-1}), $> \text{C} = \text{C} <$ (1630 cm^{-1}) and O-H (3450 cm^{-1}) groups. The absorption band corresponding to the vibration of C = O bonds in the carboxyl (1740 cm^{-1}) on the IR spectrum of CNTs oxidized by boiling in nitric acid, had very low intensity. For material oxidized in nitric acid vapor, this peak becomes pronounced. Thus, the data of IR-spectroscopy indirectly indicate that treatment of carbon nanotubes with nitric acid vapor enhances their deeper oxidation and appearance more carboxyl groups than at of boiling in concentrated HNO_3 .

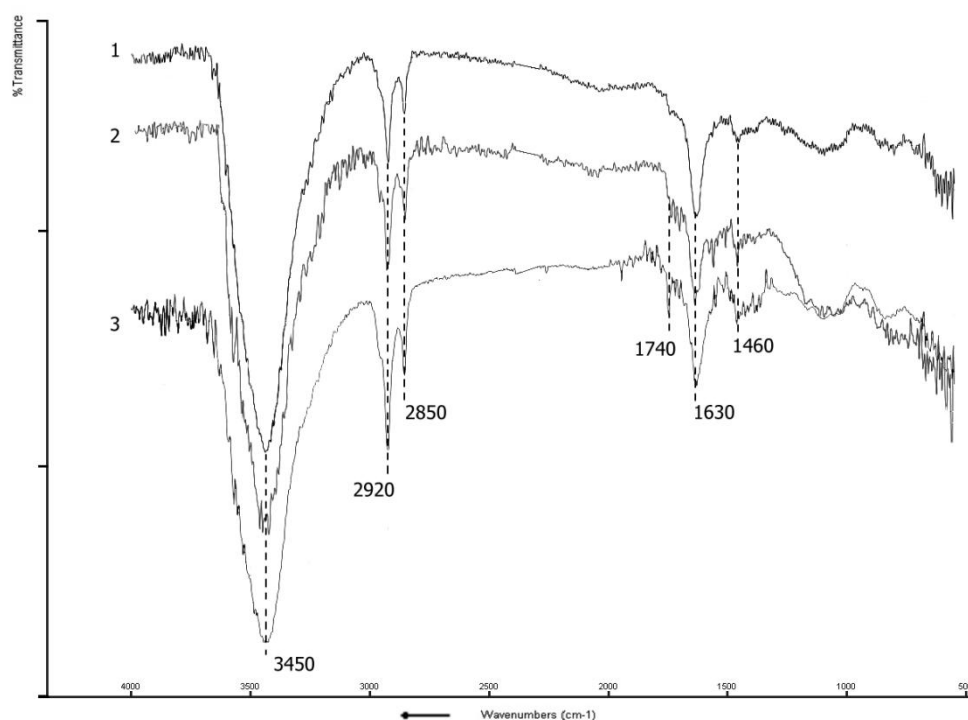


Fig. 2. IR spectra of pristine CNTs "Taunit-MD" (1), CNTs oxidized in boiling concentrated nitric acid (2) and its vapor (3).

According to the thermogravimetry data "Taunit M" is resistant to thermal decomposition in air to a temperature of about 440°C . At 495°C the 10% losses of the sample mass were observed, and the most intensive thermal and oxidative degradation of the material occurred at temperatures above 515°C (curve 1 in Fig. 3). The nature of TG and DSC curves for the samples oxidized with potassium permanganate ($\text{KMnO}_4 = 0.2$ and 1.0 g per 1 g of CNTs) is similar to analogous curves for non-functionalized material. However, with increasing of the $\text{KMnO}_4/\text{CNTs}$, ratio thermal stability of the material decreased and the thermal effect of oxidation was seen with increasing of the degree of functionalization (curves 2 and 3 in Fig. 3). Reduction of the sample weight began at 150°C .

According to [19], in similar conditions the removal of functionalized groups occurs at temperatures up to 400°C, and at higher temperatures the oxidation of CNTs themselves takes place. Thus, the temperature of the beginning of mass loss of samples of carbon nanotubes treated with potassium permanganate, showed the presence on their surface functional groups and proves the increase of degree of functionalization with changing the $\text{KMnO}_4/\text{CNTs}$ ratio.

TGA and DSC curves of the material obtained at amount of KMnO_4 equal to 3 and 4 g per 1 g of CNTs are of different character (curves 4 and 5 in Fig. 3). On the TG plot it is observed for at least 3 stages of marked reduction in weight of the samples. The first stage in the temperature range to 150°C is associated with removal of adsorbed water. Obviously, these materials have high hydrophilicity, and a longer drying of them is required. The second stage, from 150 to 320°C, according to [20], corresponds to decarboxylation of functionalized CNTs. The weight loss of materials in the temperature range from 320 to 400°C can be explained by the removal of hydroxyl groups [21]. On DSC curve of these materials, there are two distinct maxima corresponding to the removal of carboxyl functional groups and the thermal degradation of carbon.

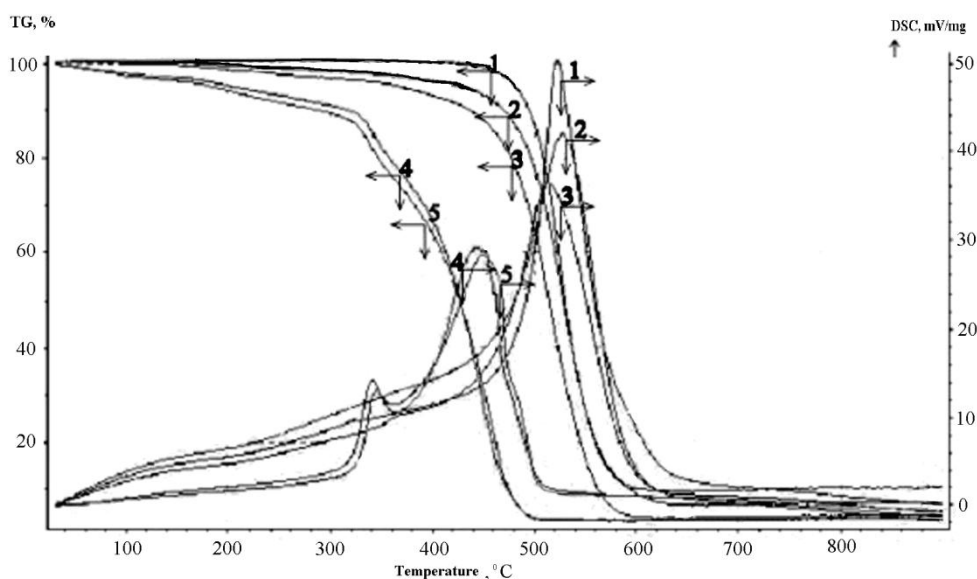


Fig. 3. TG and DSC curves (in air) of pristine (1) and oxidized with potassium permanganate CNTs "Taunit-M" at the mass ratio of $\text{KMnO}_4/\text{CNTs}$ equal to 0.2 (2) 1.0 (3), 3.0 (4), and 4.0 (5).

Carbon nanotubes oxidized with nitric acid in the liquid and gas phase have different thermal stability (Fig. 4). Pristine CNTs were the most resistant to high temperatures in oxidizing atmosphere and CNTs functionalized in nitric acid vapor were least stable to thermal oxidation in air. The mode of TG curves of functionalized materials is significantly different from the TG curve of the non-oxidized sample. The peaks in the DSC curves of the pristine and oxidized in concentrated nitric acid "Taunit-MD" are observed at 615-620°C. On a similar curve for the CNTs "Taunit-MD" treated in HNO_3 vapor, there is a slightly-manifested peak at 350°C and more pronounced - at 520°C. Each of these corresponds to a characteristic areas on the TG curve.

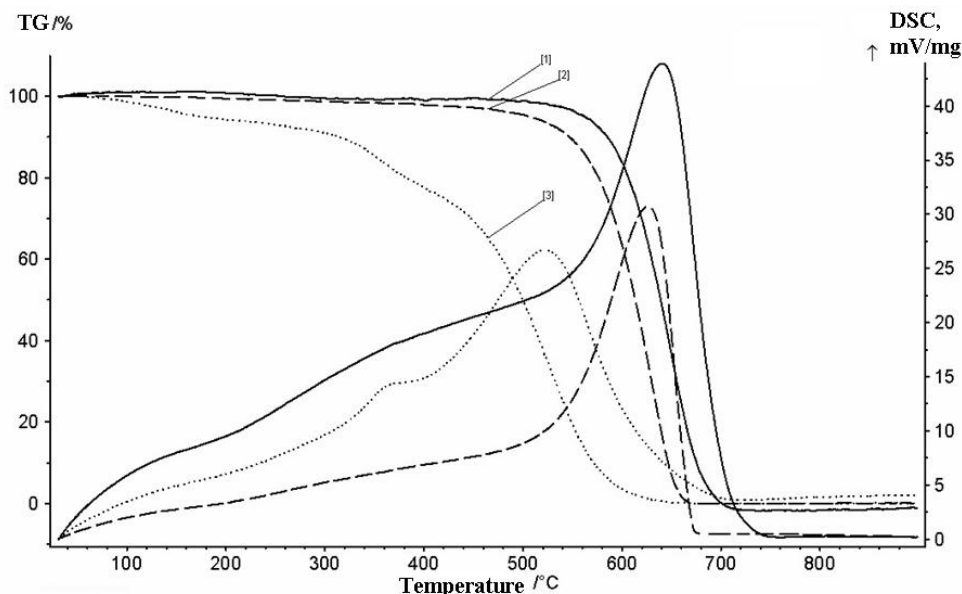


Fig. 4. TG and DSC plots of the pristine CNTs "Taunit-MD" (1), and CNTs oxidized by boiling in concentrated nitric acid (2) and in HNO₃ vapor (3).

According to titrimetry data for carbon nanotubes oxidized with potassium permanganate (Fig. 5), with increase of the oxidant amount there is a smooth increase in the degree of functionalization of "Taunit-M" by carboxylic groups (S_f). According to this dependence it is possible to obtain carboxylated carbon nanotubes with a given degree of functionalization by varying the amount of oxidant in the studied range. The advantage of this method of functionalization of CNTs in comparison with the more frequently used treatment with acids is its speed. The reaction of oxidation CNTs by potassium permanganate proceeds in 20-30 minutes while heating the reaction mass to 50-60°C, whereas during boiling in concentrated nitric acid to achieve, for example, the degree of functionalization by the carboxylic groups of 0.6 mmol/g about 10 h is required. With a small expenditure of potassium permanganate per unit mass of carbon nanotubes (up to 1-2 g/g) about 20-30% of oxidant is spent in useful oxidation of the surface of carbon nanotubes. At high expenditure of permanganate (more than 2 g per 1 g of CNTs) more than 95% of KMnO₄ is spent for side processes (oxidation CNT to CO₂, decomposition of KMnO₄). Therefore the use of KMnO₄ to oxidize the nanotube is justified only in the preparation of materials with a low degree of functionalization by the COOH-groups.

The quantity of COOH-groups on the surfaces of materials "Taunit", "Taunit-M" and "Taunit-MD", oxidized in the gas phase is higher than in the liquid phase oxidation of nitric acid at the same duration processes (Figure 6). With the increase of time the difference of the degrees of functionalization of CNTs by carboxyl groups between gas phase and liquid phase oxidation processes becomes more pronounced.

When boiling CNTs "Taunit" and "Taunit MD" in nitric acid degree of functionalization by the carboxyl groups tends to a limited value with increasing the time. The average diameter of the CNTs "Taunit-MD" and "Taunit" is nearly the same, but these nanomaterials have got different forms of graphene layers. CNTs "Taunit MD" consists of cylindrical carbon nanotubes whose surfaces are less-defective. At the same time, the surface defects, consisting of carbon atoms in the sp³-hybridization are more reactive sites for functionalization. Therefore, the "Taunit-MD" CNTs has the lowest values

of the degrees of carboxylation. The concentration of COOH groups on the surface of CNTs "Taunit" is slightly higher because its graphene layers have conical shape. The carbon atoms in sp^3 -hybridized state, which are at the ends of graphene layers of conical nanotubes are more highly susceptible to oxidation than sp^2 -hybridized carbon atoms on the surface of the cylindrical nanotubes.

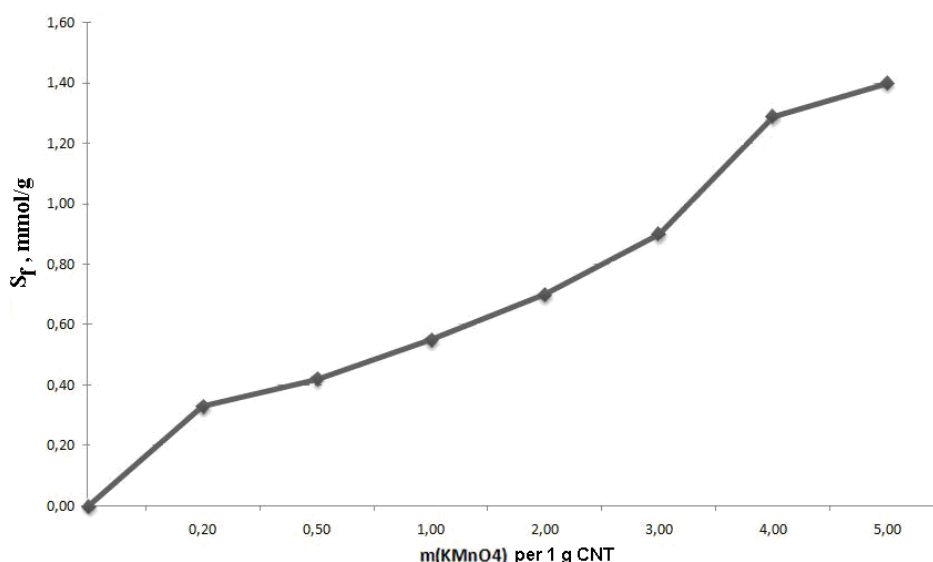


Fig. 5. The influence of expenditure $KMnO_4$ (per 1 g of CNTs) on the degree of functionalization of CNT "Taunit-M" with carboxyl groups (S_f).

The degree of functionalization of "Taunit-M", for the same duration of treatment is slightly higher than of "Taunit" and "Taunit-MD." "Taunit-M" are the cylindrical tubes, but the diameter is several times less than that of individual CNTs "Taunit-MD" and specific surface area is higher. At the same ratio of number of carboxyl groups to the total number of carbon atoms in the external layer, the degree of functionalization of CNTs "Taunit M", expressed in mmol per 1 g of the material is higher than that for "Taunit-MD", because the latter has a greater number of carbon layers. Predominantly external surface layer undergoes oxidation and inner layers remain intact. A higher degree of carboxylation of "Taunit M" in comparison with "Taunit" is explained both by smaller number of layers of carbon atoms and a higher specific surface area.

For "Taunit-M" different character of changes in the degree of functionalization with increasing time in boiling nitric acid was observed. During the first five hours dramatic increase of the concentration of carboxyl groups occurs. In the next 5 hours degree of carboxylation increases very slightly, but, having reached a certain value, begins to increase for the next 10 hours, showing no tendency to enter the limit value. Perhaps this is due to the fact that because of the specific material, the destruction of its surface layers is easier than with CNT "Taunit-MD." After saturation of the external layers of nanotubes with carboxyl groups their destruction begins, and after it the oxidation and degradation of the following subsurface occurs.

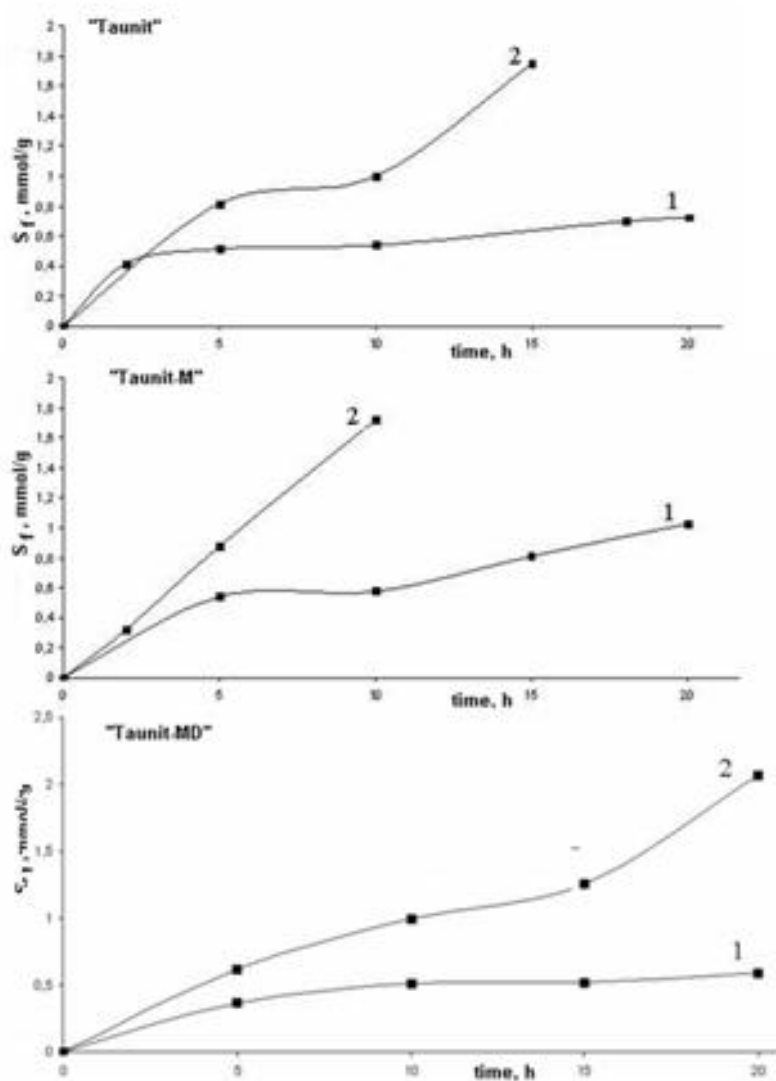


Fig. 6. Changes in the degree of functionalization (S_f) of CNT "Taunit", "Taunit-M" and "Taunit-MD" with carboxylic groups during oxidation in liquid (1) and gas phase (2) with nitric acid.

The gas-phase oxidation under equal treatment time «Taunit-M» has the greatest degree of functionalization. The concentration of surface groups was constantly growing with time, not showing any limits. Apparently, there is a rapid oxidation of the surface layer, which then begins to decay and the underlying layers are subjected to oxidation. The destruction of CNTs "Taunit-M" during the oxidation with nitric acid vapor is proved by decrease of the mass of material during the process. Therefore, for "Taunit-M" the only short-term processing with nitric acid vapor is acceptable, which allows a high degree of functionalization.

The degree of carboxylation of "Taunit-MD" treated with HNO_3 vapors is growing slower. Three areas can be distinguished in the plot: a rapid increase in the concentration of surface groups (up to 10 hours of treatment), the deceleration of the process (10-15 hours of treatment) and re-growth (after 15 hours). There are similar plots of the curve of changing of the degree of carboxylation in the gas-phase

oxidation of nitric acid vapor for "Taunit": the rapid growth observed up to 5 hours, 5 to 10 hours - the process stagnated, after 10 hours - again a sharp rise. This type of curves for the CNTs "Taunit" and "Taunit-MD", is apparently due to the greater stability of the surface layers to destruction. Retarding of increase of the degree of functionalization is observed at saturation of the surface layer, and the subsequent increase is due to its destruction. From the data obtained, the surface of the material, "Taunit-MD" is the most resistant to degradation by oxidizing gas.

We can suggest several reasons for a more efficient process of gas-phase oxidation of carbon nanotubes. On the one hand, the liquid phase process the addition of carboxylic groups occurs only at the point of initial defects of carbon nanotubes. Furthermore, in contact with liquid "Taunit-M" and "Taunit-MD" agglomerate, and because only the surface of the agglomerates contacts with the oxidant, their inner parts thereof are not exposed to functionalization. Under the gas-phase process the nanotubes are not agglomerated, and their entire surface is available for functionalization, and therefore its degree is higher. The temperature also influences the process, since the liquid phase process proceeds at about 90-110°C, and gas phase – up to 140°C. A higher degree of conversion can be achieved due to higher temperature. Finally, from CNTs obtained by CVD-technique, it is impossible to remove completely the residues of catalysts, particularly transition metals. Under the distribution of tubes in the liquid acid, transition metals pass into soluble nitrates and they are diluted in solution to low concentrations. In the gas phase process transition metal particles remain on the surface or in the interior of the nanotubes. In nitric acid vapor the nitrates can also be formed. But they immediately decompose and form non-volatile oxides under high temperature. It is even possible to establish equilibrium "nitrate of transition metal $\rightleftharpoons$ oxide of a transition metal." Thus, transition metal particles may even migrate on the surface of nanotubes. At the same time it is known that they catalyze the oxidation. Consequently, due to their presence and their migration on the surface the addition of carboxylic groups is possible not only on the points of initial defects.

For the structural characteristics of the original and functionalized CNTs Raman spectra can be used [22], in which there are two characteristic modes: G (1500-1600 cm^{-1}), corresponding to in-plane vibrations of the carbon atoms in graphene layer, and D (1250-1450 cm^{-1}), which arise due to the disturbance of symmetry of the ideal graphite layer. Therefore the ratio of the intensities of D/G can be used for characterization of the degree of ordering of the surface structure of multiwalled CNTs. Under the oxidative treatment of CNTs two opposing factors influence the D/G ratio. On the one hand, there is a removal of residual amorphous phase, which should help to reduce the degree of imperfection of the surface defined by Raman spectra [23]. On the other hand, oxidation of carbon nanotubes generates new surface defects that act as functional groups, and the ratio D/G increases [24]. According to the data of Fig. 4, oxidation by potassium permanganate initially reduces and then increases the D/G ratio. This demonstrates the predominant influence of the first factor at low expenditure of oxidant per unit mass (up to 1 g/g) of CNTs. Number of defects which arise due to the appearance of oxygen-containing groups on the surface is compensated by removing residual amorphous phase. Under high expenditure of potassium permanganate and high degrees of functionalization by the COOH-groups the second of these factors begins to dominate.

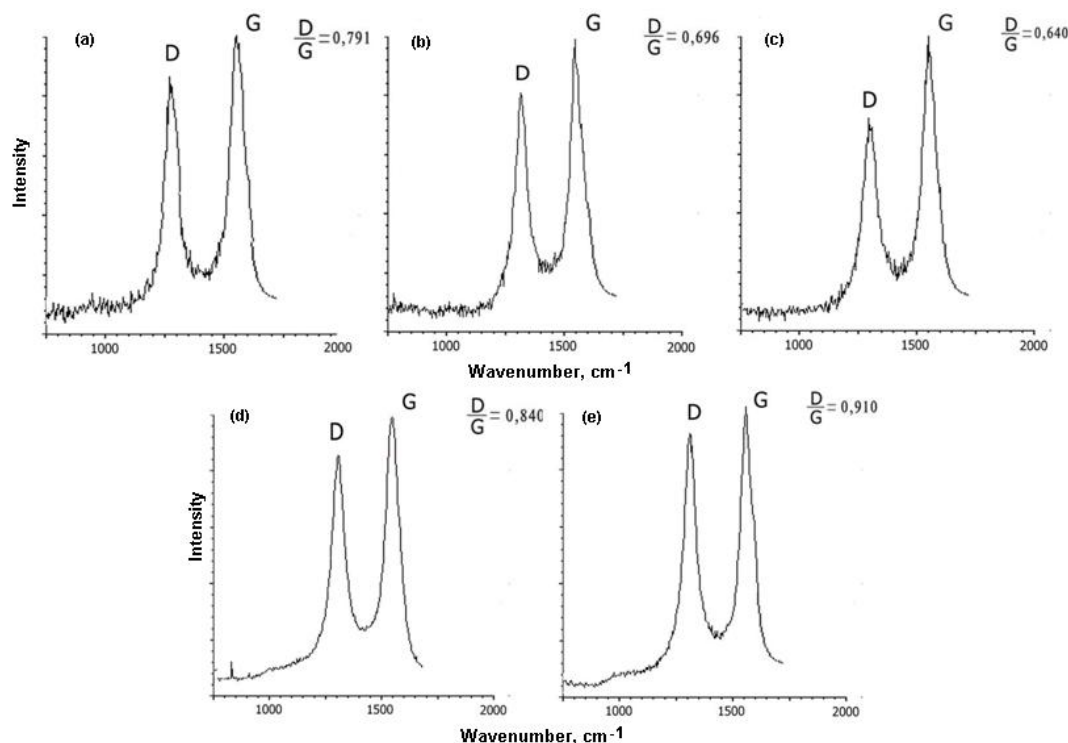


Fig. 7. Raman spectra of the pristine (a) and oxidized with potassium permanganate CNTs "Taunit M" at mass ratio $\text{KMnO}_4/\text{CNTs}$ equal to 0.2 (b) 1.0 (c) 3.0 (d) 4.0 (e).

The comparison of the degree of defectiveness of pristine and functionalized with nitric acid in the liquid and gas phase CNTs according Raman spectra (Table 2) shows that in the case of "Taunit-M" boiling in nitric acid substantially destroys the structure of the surface layers. When carrying out the process by various oxidizing agents in the gas phase the D/G ratio is even reduced that may indicate the removal in this case the residual amorphous phase. The functionalization of "Taunit-MD" by the carboxylic groups promotes the emergence of additional defects on the surface of the nanotubes, however, the gas-phase process in some cases is more gentle.

Table 2. Assessment of the defect degree of carbon nanotubes according to the Raman spectra.

Sample	Pristine «Taunit-M»	«Taunit-M» after boiling in nitric acid	«Taunit-M» after gas-phase functionalization	Pristine «Taunit-MD»	«Taunit-MD» after boiling in nitric acid	«Taunit-MD» after gas-phase functionalization
D/G ratio	0.791	0.899	0.732-0.771	0.451	0.670	0.595-0.750

Furthermore, under the processing of "Taunit-MD" by oxidizing reagents vapor the initial positions of individual tubes are stored with respect to each other in clusters in the bulk material.

Thus, for the materials "Taunit-M" and "Taunit-MD" the oxidation in nitric acid vapor is more effective. At the optimum duration of the process the structure of the surface of the graphene layers of nanotubes is also much better preserved when processing in vapor of HNO_3 . The consumption of

oxidizing agent per unit weight of the product is 10 times reduced, which solves the environmental problems. Based on these studies it can be concluded that the gas-phase oxidation of carbon nanotubes is promising for scaling to pilot production.

The oxygen-containing functional groups are responsible for the electrostatic and chemical interactions of CNTs with polar polymer matrices, so they favor the uniform distribution CNTs in matrices. However, too high degree of functionalization causes a large amount of surface defects in graphene layers. In this regard, it is necessary to choose the oxidized carbon nanotubes with an optimal degree of functionalization for efficient introduction into polymers.

3.2. Modification of CNTs with polyaniline

Analysis of the temperature profiles of oxidative polymerization of aniline in the presence and in the absence of CNTs indicates the exothermic nature of the process (Fig. 8). Some decrease in temperature in the initial sections of temperature curves is connected with the endothermic dissolution of ammonium persulfate in water. Then an induction period is observed during which the temperature remains almost unchanged. This period in the presence of carbon nanotubes is reduced from 8 to 1-2 minutes. Then a sharp rise of temperature begins. In the presence of non-functionalized CNTs temperature value at the maximum point on the temperature curve is almost the same as that of conventional synthesis of PANI. However, this maximum is reached in a shorter time. Rates of the oxidative polymerization of aniline on the surface of functionalized and pristine CNTs are about the same. However, the presence on the surface of -COOH surface groups contributes to the additional of processes accompanied by a slight evolution of heat, as evidenced by the higher values of temperature extremes points on the curves in Fig. 8.

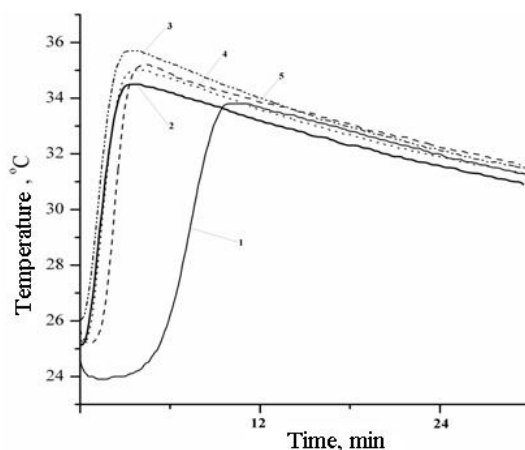


Fig. 8. Temperature profiles of oxidative polymerization of aniline without CNTs (1) and in the presence of non-functionalized (2) and pre-oxidized CNT "Taunit-M" with a degree of functionalization by carboxylic groups equal to 0.18 (3) 0.65 (4) and 1.25 mmol / g (5).

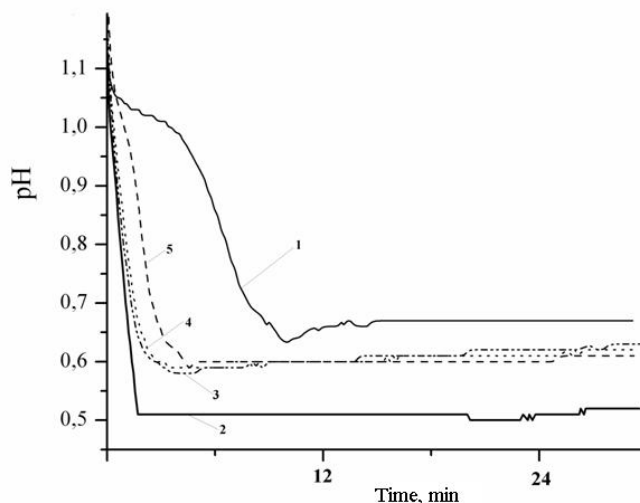


Fig. 9. The pH change during the oxidative polymerization of aniline without CNTs (1) and in presence of non-functionalized (2) and pre-oxidized CNT "Taunit-M" with a degree of functionalization by carboxylic groups equal to 0.18 (3) 0.65 (4) and 1.25 mmol / g (5).

The acidity of the medium during the oxidative polymerization increases (Fig. 9), which corresponds to the reaction scheme:

The presence of carbon nanotubes in the reaction mass favors to achievement of minimum values of pH (Fig. 9) in a shorter time. By increasing the degree of pre-functionalization with COOH-groups rate of reaching minimal pH slightly decreases, while the actual values of pH in the presence of functionalized CNTs are somewhat higher than in the presence of the pristine carbon nanotubes.

Pre-functionalization of CNTs with carboxylic groups increased the yield of polyaniline when the process was carried out at 0-2° C with gradual supply of oxidant. However, when implementing the oxidative polymerization at the initial temperature of 20-25° C and adding the required amount of oxidant at once, the degree of carboxylation CNT does not affect the yield of the reaction product.

Pre-functionalization of carbon nanotubes by carboxyl groups affects the electrical properties of the composites in different ways. The minimum electrical resistance (ρ) was observed in samples with low degree of functionalization of CNTs by COOH-groups. Pre-functionalization of CNTs with COOH-groups contributes to improving the capacity properties of composites (Table 3). Materials based on modified polyaniline with low CNTs functionalization by COOH-groups (0.33 mmol/g) show the best capacitive properties. However, the other PANI/CNTs composites were characterized by sufficiently high values of electric capacity.

Table 3. Electrical properties of of PANI/CNTs composites (80 wt.% PANI).

Material	PANI / «Taunit-M»				PANI / «Taunit-MD»			
S_i , mmol/g	0	0.3	0.5	1.3	0	0.4	0.5	1.1
Specific electrical resistivity, Ohm·cm	5.8	2.5	4.1	2.9	2.4	1.3	2.5	2.3
Specific capacitance, F/g	162	190	171	164	-	140	188	168

The analysis of SEM-images (Fig. 10) shows that the modification of the original non-functionalized nanotubes with polyaniline results in a material with a non-uniform distribution of PANI on the surface of CNTs. Polyaniline coating on some nanotubes was absent. On the surface of CNTs oxidized by boiling in concentrated nitric acid a massive layer of polyaniline was formed. The polyaniline coating of best quality and uniformity was obtained on the surface of the carbon nanotubes oxidized in nitric acid vapor.

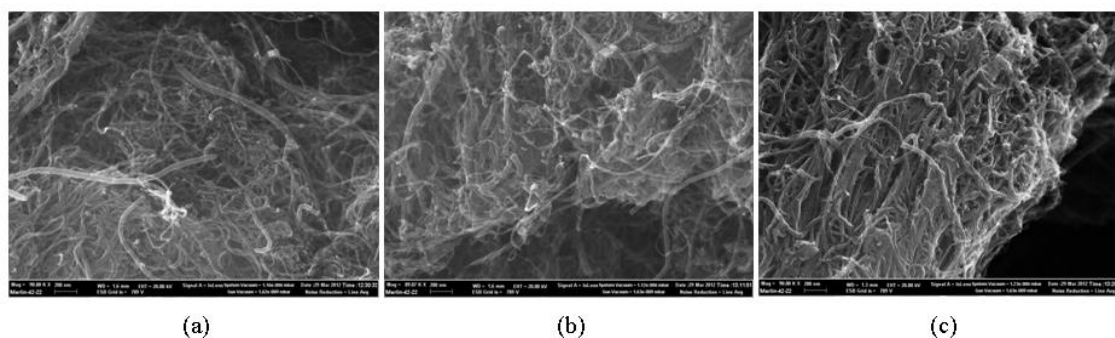


Fig. 10. SEM-images of pristine CNTs (a) and CNTs oxidized by boiling in concentrated nitric acid (b) and HNO_3 vapor (c) carbon nanotubes "Taunit-MD," modified with polyaniline at a molar ratio $n_{\text{PSA}}:n_{\text{AN}}$ under oxidative polymerization equal to 1.25:1.

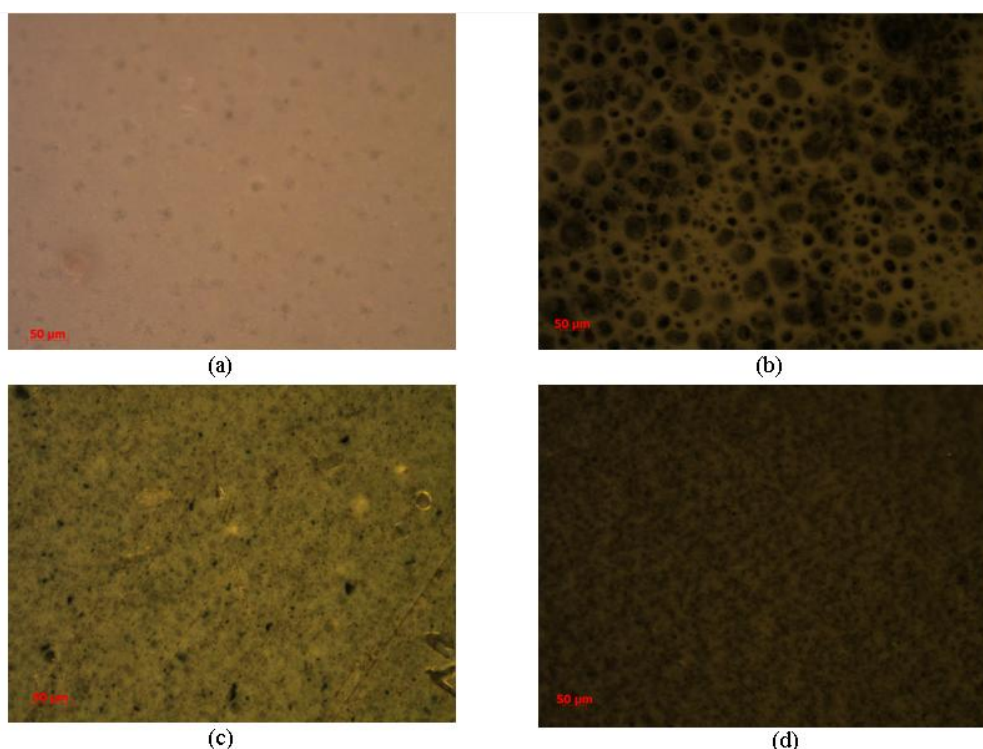


Fig. 11. Micrographs of polysulfone films (Ultrason 6020 "Basf"): non-modified (a) and modified with pristine (b) and oxidized (c and d) carbon nanotubes "Taunit-M". ($S_f = 0,33$ (c) and 0.90 (d) mmol/g).

3.3. Investigation of the properties of CNT composites with polysulfone

According to optical microscopy data unmodified polysulfone contains few pores of various sizes (Fig. 11a). With the introduction of non-functionalized CNT "Taunit-M" porosity of the polymer is significantly increased (Fig. 11b). Moreover, the pore size was substantially varying across the coating. Visually, there are large agglomerates of CNTs. When modifying polysulfone with previously oxidized CNT with low degree of functionalization by COOH-groups ($S_f = 0,33$ mmol/g, Fig. 11c) the pore volume in the composite film was much smaller and uniform in size. Agglomerates are also seen as black spots of different forms but their sizes are much smaller than in case of the polymer modified with non-functionalized carbon nanotubes.

Carbon nanotubes "Taunit M" with a high degree of functionalization with carboxylic groups ($S_f = 0,9$ mmol/g) are distributed in the matrix more uniformly than less-functionalized CNTs. The color of films becomes darker, pores practically were not visible (Fig. 11d). CNTs agglomerates become more uniform in size and they are uniformly distributed in the bulk of polymer. This is explained by the increase of lyophilic properties of nanotubes with the growth of concentration of COOH-groups on its surface. When forming films from the resulting solution the structure passes to the film volume.

Figure 12 shows the data on the surface conductivity of polysulfone films modified with pristine and oxidized CNT obtained in the present study. As it follows from Fig. 12, the resistance of both thin films and thick films filled with oxidized carbon nanotubes is higher than the resistance of films containing pristine carbon nanotubes. With increasing the degree of functionalization of carbon nanotubes, electric resistance of composite films increases (curves 1 and 2). However, in both cases, the change in R in S_f range from 0.3 to 0.9 mmol/g is negligible. Increasing the concentration of carboxylic groups above 0.9 mmol/g leads to a sharp rise in resistance in spite of a higher degree of dispersion and a more uniform distribution of nanotubes.

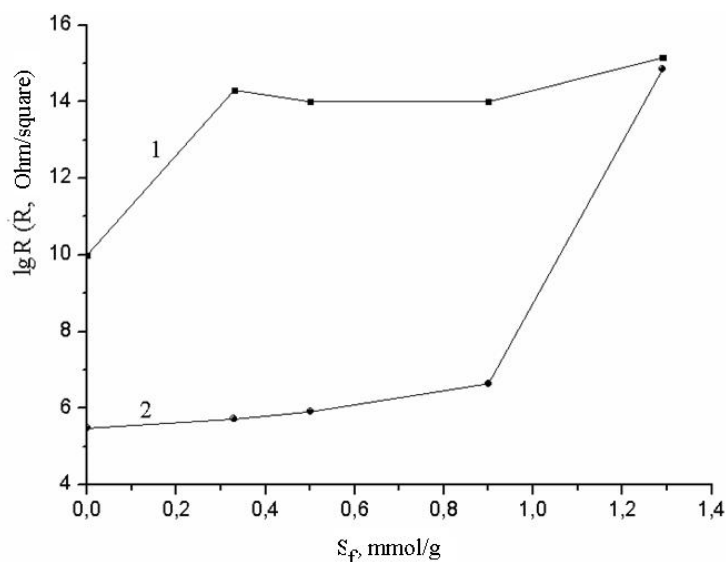


Fig. 12. Dependence of surface resistance of the polysulfone (Ultrason 6020 "BASF") films on the degree of functionalization of CNTs "Taunit M" by carboxylic groups (S_f) (film thickness 1 - 20 mm 2 - 150 microns). Mass fraction of CNTs in the composite - 2%.

Indeed, the observed in Fig.11 restructuring of matrix towards a greater homogeneity and a higher degree of dispersion of tubes would have to reduce the percolation threshold, consequently to reduce resistance. Since it does not, it can be concluded that the electrical conductivity of the films themselves depends on the nature of CNTs. However, some studies [25, 26] point to the growth of the electrical conductivity of carbon nanotubes at their oxidation treatment. Although in [27] it is shown that an increase in the degree of imperfection of the surface layers, as determined by Raman spectra by the ratio D/G, the conductive properties of CNTs are reduced. In the latter case, however, it is spoken about surface defect not related to the presence of oxygen functional groups. Therefore, the decrease in the electrical conductivity of composite polysulfone films with the degree of functionalization of the CNT-COOH groups occurs despite the supposed increase in the conductive properties of carbon nanotubes.

Therefore, it can be affirmed that at increasing the degree of functionalization of CNTs there is strengthening of their interaction with polysulfone. This reduces the interaction of CNTs with each other, so the parts of percolation circuit are isolated from each other by layers of non-conductive polymer. Consequently, to impart the composite materials the conductive properties it is necessary to choose pristine or oxidized CNT predetermined with low degree of functionalization by carboxylic groups.

4. CONCLUSIONS

1. The laws of the liquid-phase and gas phase oxidation of carbon nanotubes are studied. The possibility of obtaining materials with a given degree of functionalization with oxygen-containing groups is shown. The influence of the degree of functionalization on the surface defects of the CNTs was studied. The gas-phase oxidation methods are more efficient and can be offered to scaling for pilot production.
2. The laws of oxidative polymerization of aniline on the surface of pristine and pre-functionalized CNTs is investigated. It is shown that the presence functional groups on the surface of the CNT changes the rate and thermal effects of the processes.
3. The effect of the method and degree of pre-functionalization of carbon nanotubes on the properties of composite materials is shown. The necessity of choosing the optimal method and degree of pre-functionalization of carbon nanotubes for composite materials with superior properties is proved.

ACKNOWLEDGMENTS

This work has been supported by RFBR (grant 12-03-97555-r_center_a).

REFERENCES

1. Spitalsky Z., Tasis D., Papagelis K., Galiotis C. Carbon nanotube - polymer composites: Chemistry, processing, mechanical and electrical properties, *Progress in Polymer Science*, 2010, vol. 35, pp. 357–401.
2. Zhang Y., Feng H., Wu X., Wang L., Zhang A., Xia T., Dong H., Li X., Zhang L. Progress of electrochemical capacitor electrode materials: A review, *International journal of hydrogen energy*, 2009, vol. 34, pp. 4889–4899.

3. Ren X., Chen C., Nagatsu M., Wang X. Carbon nanotubes as adsorbents in environmental pollution management: A review, *Chemical Engineering Journal*, 2011, vol. 170, pp. 395-410.
4. Raki L., Beaudoin J., Alizadeh R., Makar J., Sato T. Cement and Concrete Nanoscience and Nanotechnology, *Materials*, 2010, No 3, pp.918-942.
5. Sahoo N.G., Rana S., Cho J.W., Li L., Chan S.H. Polymer nanocomposites based on functionalized carbon nanotubes, *Progress in Polymer Science*, 2010, vol. 35, pp. 837-867.
6. Trisca-Rusu C., Nechifor A.C., Mihai S., Parvu C., Voicu S.I., Nechifor G. Polysulfone-functionalized multiwalled carbon nanotubes composite membranes for potential sensing applications, *Semiconductor Conference*, 2009. CAS 2009. International, pp. 285-288.
7. Vatanpoura V., Madaenia S.S., Moradian R., Zinadinia S., Astinchap B. Fabrication and characterization of novel antifouling nanofiltration membrane prepared from oxidized multiwalled carbon nanotube/polyethersulfone nanocomposite, *Journal of Membrane Science*, 2010, vol. 375, pp. 284-294.
8. Qiu S., Wu L., Pan X., Zhang L., Chen H., Gao C. Preparation and properties of functionalized carbon nanotube/PSF blend ultrafiltration membranes, *Journal of Membrane Science*, 2009, vol. 342, pp. 165-172. 6.
9. Kim S., Chen L., Johnson J.K., Marand E. Polysulfone and functionalized carbon nanotube mixed matrix membranes for gas separation: Theory and experiment, *Journal of Membrane Science*, 2007, vol. 294, pp. 147-158.
10. Wu T.-M., Lin Y.-W., Liao C.-S., Preparation and characterization of polyaniline/multi-walled carbon nanotube composites, *Carbon*, 2005, vol. 43, pp. 734-740.
11. Wu T.-M., Lin Y.-W., Doped polyaniline/multi-walled carbon nanotube composites: Preparation, characterization and properties, *Polymer*, 2006, vol. 47, pp. 3576-3582.
12. Boehm H.P., Surface oxides on carbon and their analysis: a critical assessment, *Carbon*, 2002, vol. 40, pp. 145-149.
13. Zhang L., Ni Q., Fu Y., Natsuki T. One-step preparation of water-soluble single-walled carbon nanotubes, *Applied Surface Science*, 2009, vol. 255, pp. 7095-7099.
14. Hernadi K., Siska A., Then-Nga L., Forro L., Kiricsi I. Reactivity of different kinds of carbon during oxidative purification of catalytically prepared carbon nanotubes, *Solid State Ionics*, 2001, pp. 203-209.
15. Dutta D., Dubey R., Yadav J., Shami T.C., Bhasker Rao K.U. Preparation of spongy microspheres consisting of functionalized multiwalled carbon nanotubes, *New Carbon Materials*, 2011, vol.26, N2, pp. 98-102.
16. Datsyuk V., Kalyva M., Papagelis K., Parthenios J., Tasis D., Siokou A., Kallitsis I., Galiotis C. Chemical oxidation of multiwalled carbon nanotubes, *Carbon*, 2008, vol.46, pp. 833-840.
17. Daifullah A.A.M., Girgis B.S. Impact of surface characteristics of activated carbon on adsorption of BTEX, *Colloids and Surfaces A: Physicochem. Eng. Aspects*, 2003, vol. 214, pp. 181-193.
18. W.M. Davis, C.L. Erickson, C.T. Johnston. Quantitative Fourier Transform Infrared Spectroscopic Investigation of Humic Substance Functional Group Composition, *Chemosphere*, 1999, vol. 38, pp. 2913-2928.

19. Sun Y.-P., Fu K., Lin Y., Huang W. Functionalized Carbon Nanotubes: Properties and Applications, *Acc. Chem. Res.*, 2002, vol. 35, pp. 1096-1104.
20. Tang M., Dou H., Sun K. One-step synthesis of dextran based stable nanoparticles assisted by self-assembly, *Polymer*, 2006, vol.47, pp. 728-734.
21. Grandi S., Magistis A., Mustarelli P., Quartarone E., Tomasi C., Meda L. Synthesis and characterisation of SiO₂-PEG hybrid materials, *J. Noncryst. Sol.*, 2006, vol. 352, pp.273-280.
22. Keszler A. M., Nemes L., Ahmad S. R., Fang X. Characterisation of carbon nanotube materials by Raman spectroscopy and microscopy – A case study of multiwalled and singlewalled samples, *Journal of Optoelectronics and Advanced Materials*, 2004, vol. 6, N 4, pp. 1269 – 1274.
23. Osswald S., Havel M., Gogotsi Y. Monitoring oxidation of multiwalled carbon nanotubes by Raman spectroscopy, *Journal of Raman Spectroscopy*, 2007, vol. 38, pp. 728–736.
24. Irle S., Mews A., Morokuma K. Theoretical Study of Structure and Raman Spectra for Models of Carbon Nanotubes in Their Pristine and Oxidized Forms, *J. Phys. Chem. A*, 2002, vol. 106, pp. 11973-11980.
25. Lau C.H., Cervini R., Clarke S.R., Markovic M.G., Matison J.G., Hawkins S.C., Huynh C.P., Simon G.P. The effect of functionalization on structure and electrical conductivity of multi-walled carbon nanotubes, *J. Nanopart. Res.*, 2008, vol.10, pp.77–88.
26. Agrawal S., Raghuveer M., Li H., Ramanath G. Defectinduced electrical conductivity increase in individual multiwalled carbon nanotubes, *Appl. Phys. Lett.*, 2007, vol. 90, pp. 193104–193103.
27. Singjai P., Changsarn S., Thongtem S. Electrical resistivity of bulk multi-walled carbon nanotubes synthesized by an infusion chemical vapor deposition method, [*Materials Science and Engineering: A*](#), 2007, vol. 443, pp. 42–46.