SOME ASPECTS OF FUNCTIONALIZATION AND MODIFICATION OF CARBON NANOMATERIALS

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Some regularities of covalent functionalization of multi-walled carbon nanotubes (MWCNTs) with oxygen-containing moieties were investigated. The materials obtained were studied by electron microscopy, thermogravimetry, FT-IR and Raman spectroscopy. The dependence of the degree of MWCNTs functionalization on the process conditions was studied. The advantages of the gas phase to liquid phase oxidation of MWCNTs were shown. The effects of pristine and functionalized MWCNTs on the properties of composites with polysulfone were investigated. Both pristine and functionalized MWCNTs were modified with polyaniline. The effects of the method and the degree of pre-functionalization of the MWCNTs on the oxidative polymerization of aniline and the properties of the materials obtained were elucidated.

Keywords: multiwalled carbon nanotubes, functionalization, modification, oxidation, composites, polyaniline.

1. Introduction

Carbon nanotubes (CNTs), due to their unique properties, are finding increasing application in various branches of engineering and technology. They are suggested for use as components of polymer composites [1], electrode materials [2], sorbents [3], modifying additives in building materials [4], etc. However, the surface of carbon nanotubes is originally inert and solvophobic, thus favoring their agglomeration in various matrices and preventing their uniform dispersion. As a result, the practical effect of the application of CNTs, especially in composites, is lower than expected. A possible solution to this problem is to modify the surface of carbon nanotubes by covalent or non-covalent functionalization. Numerous methods for attaching different functional groups to the surface of CNTs have been described and the best effect of the use of composites with functionalized carbon nanomaterials was proved [5].

Thus, the presence of amine [6] and carboxyl [7] functional groups on the surface of CNTs facilitates their embedding into a polysulfone matrix [8]. Often, to achieve the best effect, pre-oxidized CNTs were subjected to a secondary functionalization. For example, the oxidized CNTs were reacted with 5-isocyanato-isophthaloylchloride in order to attach different groups (-OOC-,-CONH-, etc.) [9]. With use of these CNTs, a composite microporous material with polysulfone matrix was obtained which was suitable for the production of ultrafiltration membranes. The treatment of carboxylated nanotubes with octadecylamine was shown to improve the thermal stability, strength and sorption properties of the CNTs/polysulfone composite membranes [8]. According to some literature data, preliminary attachment of -COOH groups to CNTs promotes the oxidative polymerization of aniline on the CNTs surface. This fact can be explained by the chemisorption of aniline monomer and soluble oligomers by carboxyl groups on the surface of CNTs. The interaction of CNTs with aniline molecules, but also because of emergence of hydrogen bonds between the $-NH_2$ - and -COOH groups [10, 11]. The works

| Parameter\CNTs | "Taunit" | "Taunit-M" | "Taunit-MD" | |
|--|------------|-------------|-------------|--|
| External diameter, nm | 20÷70 | 30÷80 | 8÷15 | |
| Internal diameter, nm | 5÷10 | 10÷20 | 4÷8 | |
| Length, μm | 2 and more | 20 and more | 2 and more | |
| Contents of mineral impurities, wt. % | ≤ 5 | ≤ 5 | ≤ 5 | |
| (after acid purification) | (≤1) | (≤1) | (≤1) | |
| Bulk density, g/cm ³ | 0,4÷0,6 | 0,03÷0,05 | 0,03÷0,05 | |
| Specific surface area, m ² /g | 120÷130 | 180÷200 | 300÷320 | |

TABLE 1. General characteristics of CNTs used in this work

cited above did not analyze the influence of the method used and the degree of functionalization of the CNTs.

Most methods of CNTs functionalization described in literature are very expensive and can be performed only at a laboratory scale because they require the use of large amounts of expensive reagents. The growing application of carbon nanomaterials to different technologies necessitates the development of methods for obtaining functionalized carbon nanomaterials in large quantities at acceptable costs. In this regard, it is necessary to study the standard conditions for CNTs functionalization processes and the effect of reaction conditions on the properties of the resulting materials with a view to further increasing the scale of synthesis.

2. Matherials and methods

"Taunit", "Taunit-M" and "Taunit-MD" CNTs produced by "NanotechCenter" (Tambov, Russia) were used in this work. Their geometric parameters and some physical properties are shown in Table 1, while SEM images are shown in Fig. 1.



FIG. 1. SEM images of CNTs used: a - "Taunit", b - "Taunit-M", c - "Taunit-MD"

The functionalization of CNTs surfaces with oxygen-containing groups was carried out by several methods: 1) by treatment with concentrated nitric acid, 2) oxidation by potassium permanganate in acidic medium, 3) oxidation by nitric acid vapor.

Surface functional groups were identified by IR spectroscopy. The amount of COOH groups (mmol) per unit weight of CNTs was determined titrimetrically according to known methods [12].

In order to obtain Raman spectra, the CNTs samples were placed on a Raman amorphous polycrystalline Al_2O_3 substrate, and Raman spectra were recorded with use of an Integra Spectra spectrometer, NT MDT (wavelength of laser excitation 473 nm). SEM images of carbon

nanotubes and their composites with polyaniline were obtained using a two beam scanning electron microscopic complex Neon 40, Carl Zeiss.

Modification of carbon nanotubes with polyaniline was performed during oxidative polymerization of aniline under the action of ammonium persulfate $(NH_4)_2S_2O_8$ in an acidic solution in the presence of CNTs. The weight content (%) of polyaniline in the nanocomposites obtained was calculated as the difference between the mass of dry composite and the starting CNTs, referred to as the weight of the nanocomposite.

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

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

Capacitance of the obtained materials was determined by using a three-electrode cell in which a sample of the polyaniline-modified CNTs (0.05 g) was deposited on glassy carbon disk which served as the working electrode. The auxiliary electrode was made from an expanded graphite foil. Saturated silver chloride electrode was used as a reference electrode. Measurements were performed in a galvanostatic mode at a current of 2-10 mA, the potential swept from -0.5 to 0.5, and from -0.3 to 0.3 V. An aqueous solution of 0.5 M Na₂SO₄ was used as electrolyte.

Polysulfone Ultrason 6020 ("Basf") in the form of films with thickness of 20 and 150 microns was used as the polymer matrix. The volume resistivity of this dielectric is $> 1.0 \cdot 10^{16}$ Ohm·cm. Composite films were obtained from the dispersion of CNTs in a 20% solution of polysulfone in dimethylacetamide (DMA), which was then subjected to ultrasonic treatment in an IL-10 (2 kW, 22 KHz, 20 min). The film thickness was determined by a "Constant K5" device for measurement of geometrical parameters, and electrical resistance – by a teraohmmeter "E6-13A." The concentration of carbon nanotubes in the polymer was 2 wt.%.

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

3. Results and discussion

3.1. The study of CNTs oxidation processes

Treatment of CNTs with potassium permanganate, according to the literature, gives rise to oxygen-containing functional groups (hydroxyl, carboxyl) on the CNT surface [13–16]. These oxidation processes proceed quickly. A typical IR spectrum of "Taunit-M" CNTs oxidized with 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 C–H vibrations of alkyl group [17] which are a residue of hydrocarbon molecules used for growing the CNTs in the CVD process. The band at 3423 cm⁻¹ can be attributed to vibrations of O–H bonds in hydroxyl and carboxyl groups formed upon the oxidation of the nanotubes. According to [18], the absorption peaks at 1562 and 1637 cm⁻¹ can be attributed to >C=O groups. Therefore, IR spectra prove the presence of oxygen-containing functional groups on the surface of "Taunit M" CNTs treated with potassium permanganate in acidic medium.

IR-spectra of the initial CNTs and those oxidized with nitric acid in liquid and gas phase (Fig. 2) are characterized by the presence of absorption bands corresponding to C–H (2920, 2850, and 1460 cm⁻¹), >C=C< 1630 cm⁻¹), and O–H (3450 cm⁻¹) bonds. The absorption band corresponding to the C=O bond vibration in the carboxyl (1740 cm⁻¹) in the IR spectrum of the boiling nitric acid-oxidized CNTs, has a very low intensity. This peak was more pronounced for the material oxidized with nitric acid vapor. Thus, the IR-spectroscopy data indirectly indicated that treatment of the CNTs with nitric acid vapor resulted in much more deep oxidation and thus, the appearance more carboxyl groups than obtained with boiling in concentrated nitric acid.



FIG. 2. IR-spectra: 1 – initial CNTs "Taunit-MD"; 2 – the CNTs oxidized by boiling in concentrated nitric acid; 3 – the CNTs oxidized in vapor of nitric acid

According to the TG data obtained, the initial "Taunit M" CNTs are stable to thermal oxidation in air up to 440 °C. At 495 °C, a 10% loss of the sample mass occurs, and the most intensive thermal oxidation of the material occurs at temperatures above 515 °C (plot 1 in Fig. 3). The character of TG and DSC curves for CNTs samples oxidized with potassium permanganate at a rate of 0.2 and 1.0 g KMnO₄ per 1 g of CNTs does not differ from the analogous plots for non-functionalized material. However, increasing the mass ratio of (KMnO₄)/(CNTs) leads to an increase in the degree of functionalization, however, the thermal stability of the material, as well as the heat effect of the thermal oxidation, decreases (plots 2 and 3 in Fig. 3). Loss of sample mass for oxidized CNTs begins at a temperature of 150 °C. According to [19], in similar TG conditions, loss of surface functional groups on CNTs occurs at temperatures up to 400 °C, and at higher temperatures, the thermal oxidation of CNTs themselves proceeds. Thus, the low temperature mass loss of CNTS treated with potassium permanganate proves the presence of

functional groups on their surface and accordingly, the degree of functionalization was increased with a higher $(KMnO_4)/(CNTs)$ mass ratio.



FIG. 3. TG and DSC plots (in air) for original (1) and oxidized with potassium permanganate CNTs "Taunit-M" at the mass ratio $(KMnO_4)/(CNTs)$ equal to 0.2 (2), 1.0 (3), 3.0 (4), and 4.0 (5)

TG and DSC plots for material obtained after treatment with KMnO₄, at levels equal to 3 and 4 g per 1 g of CNTs have different character (plots 4 and 5 in Fig. 3). At least 3 sections of marked weight reduction were observed on the TG curve. The first, in the temperature range near 150 °C, is associated with removal of adsorbed water. Obviously, these materials have increased hydrophilicity, and thus, require longer drying times. The second section, from 150 to 320 °C, according to the literature [20] corresponds to the decarboxylation of functionalized CNTs. The weight loss of materials in the temperature range from 320 to 400 °C can be explained by the cleavage of hydroxyl groups [21]. DSC plots of these materials have two distinct maxima corresponding to the cleavage of carboxyl functional groups and the carbon thermal oxidation.

Carbon nanotubes oxidized with liquid or gas phase nitric acid have different thermal stabilities (Fig. 4). The original CNTs are most resistant to high temperatures in an oxidizing atmosphere, while those treated with nitric acid vapor are the least stable. The nature of TG plots for functionalized materials is significantly different from the TG plot for starting CNTs. The peaks in the DSC plots for the original and concentrated nitric acid-oxidized "Taunita-MD" CNTs were observed at 615–620 °C. On a similar plot for the "Taunita-MD" CNTs treated with HNO₃ vapor, there is an ill-defined extremum at 350 °C and a more pronounced one at 520 °C. Each of these corresponds to characteristic areas on the TG plot.

According to titrimetric data, increasing the potassium permanganate amount taken for CNTs oxidation results in a smooth increase in the degree of functionalization for "Taunita-M" CNTs with carboxyl groups (D_f) (Fig. 5). Based on the data obtained, it is possible to synthesize carboxylated CNTs with a given degree of functionalization by varying amount of oxidant used . The advantage of this CNTs functionalization method over the more frequently used acidic treatment is the shortness of reaction times. The KMnO₄-mediated oxidation of CNTs at 50–60°C is typically complete in 20–30 minutes, whereas in refluxing concentrated



FIG. 4. TGA and DSC plots: 1 - original CNTs "Taunit-MD"; 2 - CNTs "Taunit-MD" oxidized by refluxing in concentrated nitric acid; 3 - CNTs "Taunit-MD" oxidized in HNO₃ vapor

nitric acid, to achieve a CNTs functionalization of 0.6 mmol/g requires about 10 h. At smaller loadings of potassium permanganate per unit mass of CNTs (up to 1.2 g/g) about 20–30% of the oxidizer is spent for useful oxidation of the CNTs surface. At higher loadings of potassium permanganate (2 g per 1 g of CNTs and more), more than 95% of the KMnO₄ was consumed in unwanted side reactions (oxidation of CNTs to CO_2 , decomposition of KMnO₄). Therefore, the use of KMnO₄ for CNTs oxidation is justified only for the preparation of materials with a low degree of COOH functionalization.

The amount of COOH groups on the surfaces of "Taunit", "Taunit-M" and "Taunit-MD" CNTs oxidized in the gas phase, is higher compared to those performed with boiling nitric acid at the same duration (Fig. 6). With an increase in the treatment time, the difference in the degree of CNTs carboxylation between the liquid- and gas-phase processes becomes even more pronounced.

With extended treatment of "Taunit" and "Taunit-MD" CNTs in refluxing nitric acid, the degree of carboxyl group functionalization tends to approach some limiting value. The average external diameters of the "Taunit-MD" and "Taunit" CNTs are similar, but these nanomaterials differ in the structure of their graphene layers. "Taunit-MD" consists of cylindrical carbon nanotubes whose graphene layers are highly ordered. At the same time, surface defects, consisting of protruding carbon atoms in the sp³-hybridization state, are the most reactive sites for functionalization. Therefore, from the materials in question "Taunit-MD" CNTs have the lowest degree of carboxylation upon treatment with oxidizing agents. The concentration of COOH groups on the surface of oxidized "Taunit" CNTs is higher because its graphene layers have a conical shape. The carbon atoms in the sp³-hybridization state, which are located at the edges of the conical graphene layers, are much more susceptible to oxidation than the sp²-hybridized carbon atoms on the surface of the cylindrical nanotubes.

The degree of functionalization for "Taunit-M", is somewhat higher than that of "Taunit" and "Taunit-MD" at the same duration of treatment. "Taunit-M" consists of cylindrical



FIG. 5. The influence of KMnO₄ charge (per 1 g of CNTs) on the degree of functionalization (D_f) of CNTs "Taunit-M" with carboxyl groups

nanotubes like "Taunit-MD", but the diameter of "Taunit-M" is several times less, and thus, its specific surface area is higher. At the same ratio of carboxyl groups to the total carbon atoms of the outer layer of the CNTs, the degree of functionalization of "Taunit M" CNTs, expressed in mmol per 1 g of the material is higher compared to "Taunit-MD" CNTs, because the latter has a greater number of carbon atom layers. Oxidation predominantly affects the outer layer, while the inner layers remain intact. After saturation of the outer carbon layer with carboxyl groups, its destruction begins, whereupon the oxidation and degradation of the following subsurface layers occurs. A higher degree of carboxylation of "Taunit M" in comparison with "Taunit" is explained as a result of its smaller number of carbon atom layers and higher specific surface area.

"Taunit-M" CNTs also shows changes in the character and degree of functionalization with increased reaction time in boiling nitric acid. During the first five hours, a dramatic increase in the concentration of carboxyl groups occurs. In the next five hours, the degree of carboxylation increases insignificantly, but, after having reached a certain value, begins to increase over the next 10 hours, showing no tendency to reach a limiting value. Perhaps this is due to the fact that the original "Taunit-M" CNTs are more defective and have a smaller diameter than "Taunit-MD" CNTs. Then, the combustion of surface layers leads to a considerable reduction in the CNTs diameter, and the fraction of surface atoms increases, as well as the maximum concentration of functional groups.

In gas-phase oxidation process "Taunit-M" CNTs showed the greatest degree of functionalization at equal treatment times. The concentration of surface groups for this material grows with treatment time and does not show any limit. Obviously, again, the rapid oxidation of the surface layer occurs, and then it begins to decay and the underlying layers become available for oxidation. The destruction of the "Taunit-M" CNTs under nitric acid vapor oxidation is proved by the decrease in the mass of material for long reaction times. Consequently, in the case of "Taunit-M" CNTs, only the short-term processing in nitric acid vapor is acceptable, which, nevertheless, still allows a high degree of functionalization.



FIG. 6. Changes of the degree of functionalization (D_f) of CNTs "Taunit-MD", "Taunit-M", and "Taunit" with carboxyl groups in time during liquid phase (1) and gas phase (2) oxidation with nitric acid

The degree of carboxylation of "Taunit-MD" when using HNO_3 vapor progresses more slowly with treatment time. Three areas can easily be distinguished in the corresponding plot: rapid increase of the surface group concentration (up to 10 hours), deceleration of the process (10–15 hours), and subsequent renewal of reaction (after 15 hours). Similar sequences were observed for the nitric acid vapor-oxidation of "Taunit" CNTs: rapid carboxylation was observed up to 5 hours, at 5 to 10 hours-a slowing down of the process, and after 10 hours - again a sharp rise in the oxidation. The characteristics shown by the "Taunit" and "Taunit-MD" plots probably appear due to the greater resistance of the CNTs surface layers to destruction. The stunting in the time dependence of the degree of functionalizationis most likely caused by saturation of the surface layer with functional groups, and the subsequent increase in reaction is due to its destruction. As follows from the data obtained, among the CNTs studied, the surface of "Taunit-MD" is the most resistant to gas-phase oxidative degradation.

We can suggest several reasons for higher efficiency of gas-phase oxidation of CNTs compared to liquid-phase. First, in the liquid phase process, the attachment of carboxyl groups occurs only at the points of initial defects on the CNTs surface. It is also likely that a higher degree of functionalization in the gas phase can be achieved due to the higher temperature, because the liquid-phase HNO₃ oxidation of CNTs proceeds at 90-110 °C, while the gas-phase oxidation occurs at 140 °C. Finally, it is impossible to completely remove catalyst residues, particularly transition metals, from CNTs obtained by the CVD technique. When boiling in liquid nitric acid, transition metals are transformed into soluble nitrates, which are in solution in low concentration. However, in the gas phase process, the transition metals or their compounds remain on the surface or inside of the nanotubes. In the nitric acid vapor method, metals and metal oxides can be converted into nitrates, which at the process temperatures immediately decompose to form non-volatile metal oxides or basic nitrates. It is even possible to establish a dynamic equilibrium "transition metal nitrate \Leftrightarrow basic nitrate \Leftrightarrow metal oxide". Due to these processes, the transition metal compounds can migrate to the surface of the nanotubes. At the same time, it is known that transition metal compounds can catalyze oxidation reactions. Consequently, due to the presence of the transition metal compounds in the surface layer, and the migration of these compounds to the surface of CNTs, the attachment of carboxyl groups can occur not only in the points of initial defects of carbon layers.



FIG. 7. Raman spectra of initial (a) and oxidized by potassium permanganate CNTs "Taunit-M" at the mass ratio $(KMnO_4)/(CNTs)$ equal to 0.2 (b), 1.0 (c), 3.0 (d), and 4.0 (e)

"Taunit-M" "Taunit-MD" Initial "Taunit-M" Initial "Taunit-MD" after gas-phase after gas-phase "Taunit-Substance "Taunitafter boiling after boiling functionalifunctionali-M" in HNO₃ MD" in HNO₃ zation zation 0.899 0.732-0.771 0.670 0.595-0.750 D/G ratio 0.791 0.451

TABLE 2. Estimation of the structure defects of carbon nanotubes according to Raman spectra

For the structural characteristics of the original and functionalized CNTs, Raman spectroscopy [22] can be applied, in which there are two characteristic modes: G (1500–1600 cm⁻¹), due to the in-plane vibrations of carbon atoms in the graphene layer, and D ($1250-1450 \text{ cm}^{-1}$), caused by the disturbance of the symmetry of an ideal graphene layer. Therefore, the ratio of D/G intensities can be used to characterize the degree of order in the surface structure of a multi-walled CNTs. The oxidative treatment of CNTs influences the value of the D/G ratio in two opposing ways. First, there is the removal of low ordered carbon structures, which should reduce the degree of disorder as determined by Raman spectra [23]. Conversely, intensive oxidation of the CNTs surfaces generates new defects that act as functional groups, and this increases D/G ratio [24]. According to the data obtained (Fig. 4), potassium permanganate oxidation initially leads to a decrease, and then an increase in the D/G index. This demonstrates the predominant influence of the first factor at low loading of the oxidant per unit mass of CNTs (up to 1 g/g). In this case, the number of defects which arise due to the appearance of oxygen-containing groups on the surface is compensated for by the removal of amorphous carbon. When the loading of potassium permanganate and degree of COOH functionalization are higher, the second of the mentioned factors begins to predominate.

Comparison of the structural defects of initial, liquid- and vapor-phase nitric acidfunctionalizedCNTs according to Raman spectra shows that in the case of "Taunit-M" CNTs, boiling in nitric acid substantially destroys the structure of the surface layers (Table 2). When carrying out the oxidation process in gas phase by various oxidizing agents, the D/G ratio is reduced, which may indicate the removal of amorphous carbon in this case. Functionalization of "Taunit-MD" CNTs with carboxyl groups promotes the emergence of additional defects on the surface of the nanotubes, however, in some cases, gas phase reactions can be milder.

Thus, oxidation of the "Taunit-M" and "Taunit-MD" materials in nitric acid vapor is more efficient in terms of degree of functionalization. At the optimum duration of the gas-phase oxidation process, the structure of graphene layers of nanotubes is also preserved much better compared to boiling in HNO₃. Additionally, consumption of the oxidizing agent per unit weight of the product is reduced , which lessens the required neutralization of acidic by-products. Based on these studies, it can be concluded that the gas-phase technology is suitable for scaling to pilot plant scale and thus, industrial production of functionalized CNTs.

It should also be noted that a significant part of the individual nanotubes in assynthesized "Taunit-MD" materials are in the form of parallel-packed nanotube bundles. Treatment of "Taunit-MD" CNTs with oxidizing agent vapors preserves the original arrangement of individual tubes in the bundles, whereas the liquid-phase process results in destruction of the bundles and entanglement of the nanotubes.

Oxygen-containing functional groups are responsible for the electrostatic and chemical interactions of CNTs with polar polymer matrices, which favors the uniform distribution of CNTs in a polymer matrix. However, too high a degree of functionalization causes a large

amount of surface defects in the graphene layers. In this regard, for introduction into polymers, it is necessary to choose oxidized CNTs with an optimal degree of functionalization.

3.2. Modification of nanotubes with polyaniline

Considering the promising applications of polyaniline (PANI)/CNTs nanocomposites as electrode materials in electrochemical cells, adsorbents and other areas, we investigated the process of oxidative aniline polymerization in the presence of CNTs. Analysis of the temperature profiles of oxidative aniline polymerization in the presence and in the absence of CNTs indicates the exothermic nature of the processes (Fig. 8). An initial decrease in the temperature plots is caused by the endothermic dissolution of ammonium persulfate in water. This is followed by an induction period, during which the temperature remains almost unchanged. In the presence of CNTs, this period is reduced from 8 to 1–2 minutes. This is followed by a sharp rise in the temperature. In the presence of non-functionalized CNTs the temperature at the maximum point on the temperature plot is almost the same as in the normal synthesis of polyaniline without the addition of CNTs. However, this maximum is reached in a shorter time. Judging by the pictures, the rate of oxidative aniline polymerization on the surface of functionalized and initial CNTs is about the same. However, the presence of –COOH groups on the surface of CNTs contributes to some additional processes accompanied by a slight evolution of heat, as evidenced by the higher values of temperature at extrema points on the plots in Fig. 8.

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

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

When CNTs were introduced into the reaction medium, the minimum pH value was achieved in a shorter time (Fig. 9). Increasing the degree of CNTs pre-functionalization with COOH groups somewhat decreases the velocity of reaching minimal pH, while the actual pH values in the presence of functionalized CNTs are somewhat higher than in the presence of the starting CNTs.

FIG. 9. Change of pH during the oxidative polymerization of aniline without CNTs (1), in presence of non-functionalized CNTs (2), and in presence of preoxidized CNTs "Taunit-M" with degree of functionalization with carboxyl groups equal to 0.18 (3), 0.65 (4), and 1.25 mmol/g (5)

As was indicated in [25], pre-functionalization of CNTs with carboxyl groups increases the yield of polyaniline when the process is carried out at 0-2 °C and the oxidant is supplied gradually. However, when implementing the oxidative polymerization process at 20-25 °C and adding all the required amount of oxidant at the beginning, the degree of CNTs carboxylation does not affect the yield of the desired reaction product.

Pre-functionalization of carbon nanotubes by carboxyl groups affects the electrical properties of the PANI/CNTs composites in an ambiguous way. The minimum electrical resistance

616

| Material | PANI/"Taunit-M" | | | | PANI/"Taunit-MD" | | | |
|--|-----------------|-----|-----|-----|------------------|-----|-----|-----|
| D_f , mmol/g | 0 | 0.3 | 0.5 | 1.3 | 0 | 0.4 | 0.5 | 1.1 |
| Specific electrical resistance, Ohm·cm | 5.8 | 2.5 | 4.1 | 2.9 | 2.4 | 1.3 | 2.5 | 2.3 |
| Specific electrical capacity, F/g | 162 | 190 | 171 | 164 | _ | 140 | 188 | 168 |

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

was observed at low values for the degree of COOH functionalization of CNTs (Table 3). The low degree pre-functionalization of CNTs with –COOH groups improves the capacitance properties of the composites (Table 3). Materials based on CNTs with a low degree of functionalization (0.33 mmol of COOH groups/g), modified with PANI, show the best capacitive properties. However, other PANI/CNTs composites are also characterized by consistently high capacitance values.

Analysis of SEM-images (Fig. 10) shows that the modification of the original nonfunctionalized nanotubes with polyaniline resulted in a material with nonuniform distribution of PANI on the surface of CNTs. In fact, on some nanotubes, the polyaniline coating was practically absent. In the case of boiling nitric acid-oxidized CNTs, a more uniform layer of polyaniline was formed on the CNTs surface. The best quality and uniformity of the polyaniline coating was observed on the surface of CNTs oxidized with nitric acid vapor.

FIG. 10. SEM images of carbon nanotubes "Taunit-MD" modified with PANI: non-functionalized CNTs (a); oxidized by boiling in concentrated nitric acid (b); oxidized in HNO3 vapor (c)

3.3. Investigation of the CNT/polysulfone composites

According to optical microscopy, unmodified polysulfone contains few pores of various sizes (Fig. 11a). Introduction of non-functionalized "Taunit-M" CNTs significantly increased the porosity of the polymer (Fig. 11b), and the pore sizes became significantly different. Visually, large agglomerates of CNTs were observed. When pre-oxidized CNTs with low degrees of COOH functionalization ($D_f = 0.33 \text{ mmol/g}$, Fig. 11c) were introduced into a polysulfone matrix, the pores in the composite film became much smaller and uniform in size. CNTs agglomerates were visible as black spots of different shapes, but their sizes were much smaller than in the case of polysulfone containing non-functionalized CNTs.

"Taunit-M" CNTs with higher degrees of COOH functionalization ($D_f = 0.9 \text{ mmol/g}$) were distributed in the matrix more uniformly than low-functionalization CNTs. The color of films became darker, pores in them were practically non-existent (Fig. 11d). CNTs agglomerates became more uniform in size and were uniformly distributed in the bulk of polymer. This can be

explained by increasing the lyophilic properties of CNTs with increasing concentration of surface carboxylic groups and increasing their interaction with polar solvent, and possibly with dissolved polysulfone. When forming films from solution, the structure of the CNTs agglomerates formed is retained in CNTs containing films.

FIG. 11. Optical microscope images of polysulfone films (Ultrason 6020 "Basf"): (a) polysulfone film without CNTs;(b) filled with raw (non-oxidized) CNTs "Taunit-M";(c, d) filled with oxidized carbon nanotubes "Taunit-M", $D_f = 0.33$ (c) and 0.90 (d) mmol/g

Fig. 12 shows the data on the surface conductivity of polysulfone films filled with raw and oxidized "Taunit-M" CNTs, obtained using conditions of the present study.

As seen in Fig. 12, the electrical resistance (R) of the films of varying thickness filled with oxidized nanotubes was higher than that of the films filled with initial (non-oxidized) CNTs. It appears from plots 1 and 2 that the electrical resistance of composite films increased with an increased degree of CNTs functionalization. Accordingly, the change of R in the range of D_f from 0.3 to 0.9 mmol/g is negligible. Increasing the carboxyl group content above 0.9 mmol/g leads to a sharp rise in the resistance, in spite of the higher degree of dispersion and more uniform CNTs distribution in the polymer matrix.

The restructuring of the nanocomposite to greater uniformity and higher degree of CNTs dispersion, as observed in Figure 11, should result in a decrease of the percolation threshold, and consequently, a decrease in the electrical resistance. Since it does not, it can be concluded that the electrical conductivity of the composite films is also affected by the nature of CNTs. However, in some studies [26, 27], it was observed that the electrical conductivity of CNTs

FIG. 12. Dependence of surface electrical resistance of the polysulfone films (Ultrason 6020 "Basf") on the degree of functionalization of CNTs "Taunit-M" with carboxyl group (D_f) at film thickness 20 microns (1) and 150 microns (2). Mass content of CNTs in the composite was 2%

increased with their oxidative treatment. Increasing the degree of disorder of CNTs surface layers, as determined by D/G ratio in Raman spectra, was shown to reduce the conductive properties of CNTs [28]. However, in this case, the surface defects considered were not caused by oxygenated functional groups. Therefore, the decrease in electrical conductivity for CNTs/polysulfone composite films with increased degree of COOH functionalization on the CNTs is despite the anticipated increase of conductivity of the CNTs themselves.

It can be assumed that increasing the degree of CNTs functionalization results in a strengthening of their interaction with polysulfone, but reduces interaction of CNTs with each other. So, fragments of percolation network become isolated from each other by layers of a non-conductive polymer. Consequently, for obtaining composite materials with maximal conductivity one should take CNTs with low degrees of COOH functionalization or non-oxidized CNTs.

4. Conclusions

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

method and degree of pre-functionalization of CNTs for composite materials with superior properties was proven.

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620

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