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Oxidation and reduction of multiwalled carbon nanotubes — preparation and characterization

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ABSTRACT

This work presents the use of a modified titration (Boehm's) process which is a simple and efficient method to quantify functional groups formed on the surface of oxidized multiwalled carbon nanotubes (MWCNTs). The MWCNTs were synthesized via chemical vapor deposition (CVD) and were purified through a hydrochloric acid treatment. Purified material was oxidized in a mixture of nitric and sulfuric acids. A part of oxidized sample was reduced with sodium borohydrate ($NaBH_4$). Boehm's titration is a complimentary method to Fourier Transform Infrared spectroscopy (FT-IR) with which to investigate the changes to the surface of oxidized MWCNTs after the reduction process. The reduction process led to threefold increase in the hydroxyl group content. In addition, the pristine, oxidized and reduced samples were investigated by thermogravimetry analysis (TGA) and Raman spectroscopy.

1. Introduction

The commonly noticed existence of carbon nanotubes e.g. in 1991 [1] opened new advancement paths of the interdisciplinary sciences. The chemical and thermal stability, electronic properties, high tensile strength and ultra-light weight are the main features of multiwalled carbon nanotubes (MWCNTs). These materials offer a plethora of application potential in many different branches of science [2–5]. The egzohedral functionalization of MWCNTs surface can be achieved by many different processes and is one of the most important fields of the current research due to the broadening of the potential applications of the carbon nanotubes [6–9].

The refluxing process involving acid treatment is a widely used oxidation technique of MWCNTs which leads to an increase in the concentration of carboxyl and carbonyl functional groups [10,11]. However, in many potential applications such as a polymer nanocomposite technologies, the most important groups are hydroxyls, which act as binding sites in the silanization process [5,12]. Especially in field of nanobiotechnology, carbon nanotube surface areas containing carboxyl and hydroxyl groups are widely used as active sites for further functionalization which improves the solubility and biocompatibility of the material [13–16]. In this case there is a strong need for the controlled modification of other functional groups i.e. lactone, lactol, carbonyl, quinone, and phenolic hydroxyl which are useless for certain applications such as polymer nanocomposites.

In order to achieve carbon nanotubes enriched in both carboxyl and hydroxyl functional groups, the hydroxyl groups content has to be increased by the reduction of the existing groups but the carboxyl groups content should be preserved. Luqi et. al. converted amide groups into hydroxyl groups on functionalized MWCNTs surfaces through a $LiAlH_4$ treatment. In their work, qualitative and quantitative estimates of the functional group content were obtained by Fourier Transform

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Infrared (FT-IR) spectroscopy and X-ray photoelectron spectroscopy (XPS), respectively [9].

In the current work, the conversion of carbonyl and lactone groups into desirable hydroxyl groups has been achieved via a sodium tetrahydroborate ($NaBH_4$) treatment. This reducing agent is widely used for reduction of aldehydes and ketones. The reduction of esters via $NaBH_4$ is a relatively uncommon process which needs additives to enhance its activity [17]. However, in this work the reduction of ester like groups has been observed.

A quantitative estimation of the functional group content has been performed by an adaptation of the titration route proposed by Boehm [18], which is often used to determine the functional groups on the surface of carbon materials [19,20]. Along with the FT-IR spectroscopy, the modified Boehm's titration method allowed the investigation of the reduction process.

In order to comprehend the influence of the oxidation and reduction processes on the nanotubes graphitic wall structure, the MWCNT samples were additionally investigated by the Raman spectroscopy and thermogravimetric analysis.

2. Experimental

Sodium borohydrate ≥98.5% was purchased from Sigma-Aldrich. Anhydrous ethanol 99.8% p.a. was obtained from [Eurochem BGD]. Hydrochloric acid 35%–38% p.a., nitric acid 65% p.a., and acetone 99.5% p.a were obtained from Chempur. Sulfuric acid 96% p.a. was purchased from Cheman. Multiwalled carbon nanotubes were synthesized by a chemical vapor deposition (CVD) method [21]. Shortly, the catalyst mix with molar ratio of catalysts to substrate (here MgO):Fe:Co:MgO = 1:1:100 was placed to the horizontal oven and first evacuated (~10^{-3} mbar) then heated. After reaching the desired temperature the Ar was passed through the boiling ethanol with a flow rate of 600 ml min^{-1}. The temperature and time of the synthesis process were 850 °C and 30 min, respectively.

The MWCNTs were purified by a hydrochloric acid treatment in an ultra-sonication bath (300 W, 40 kHz) for 3 h. Next the sample was subjected to multiple filtration in order to remove impurities such as metal particles and the residual catalyst. Then MWCNTs were dried under vacuum at 180 °C for 1 h.

The pristine MWCNTs were mixed with 80 ml mixture of 2.6 M HNO_3/H_2SO_4 (v/v = 1:3). Then the sample was sonicated for 10 min and refluxed for 18 h at 175 °C. After this treatment, the mixture was neutralized with RO H_2O (type II water obtained in reversed osmosis process with conductance: 0.056 μS cm^{-1}) and filtrated through the polycarbonate filter (Whatman pore size 0.2 μm). Subsequently, the sample was rinsed thoroughly with RO H_2O and acetone. Then the oxidated MWCNTs were dried under vacuum at 180 °C for 1 h to degass adsorbed CO_2 and hydrogen.

The oxidized MWCNTs were mixed with 200 ml of 99.8% anhydrous ethanol and sonicated in the ultra-sonication bath until dispersed. Then the sodium borohydrate powder (w/w = 5:1 $NaBH_4$/MWCNTs) has been gently added into the solution and the mixture was placed onto magnetic stirrer for 18 h at 4 °C. Subsequently, the mixture was filtrated through the polycarbonate filter and the sample was rinsed thoroughly with RO H_2O and acetone. Then the reduced MWCNTs were dried under vacuum at 180 °C for 1 h to degass adsorbed CO_2 and H_2O.

For investigations by FT-IR spectroscopy [Nicolet 6700 FT-IR Spectrometer], the pristine, oxidized and reduced MWCNT samples were prepared onto KBr crystals by drag and drop method. The MWCNT sample was dispersed in an acetone solution ultra-sonication bath, then MWCNT solution was dragged out using the pasteur pipette and dropped onto crystal surface. Subsequently, the acetone from KBr surface was evaporated at hot plate at 80 °C and a thin film of the investigated sample was obtained.

The titration method proposed by Boehm was used to estimate the number of oxygenated surface groups. The MWCNT samples, each weighing 5 mg of the material were immersed in 5 ml of the following solutions: 0.05 M $NaHCO_3$, 0.05 M Na_2CO_3, 0.05 M NaOH and 0.05 M HCl. All solutions were based on RO H_2O and all compounds were p.a. grade. Each sample was placed into the test tube (Falcon — 50 ml), which was connected to the vacuum pump. Then each MWCNT sample was dispersed under vacuum at ultra-sonication bath for 2.5 min, in order to degass CO_2 from the solution. Subsequently, the existing vacuum was gently removed from the test tubes, which was rapidly closed. Three reference samples of 5 ml of each solution were prepared and treated in the same way as the analysed samples. Closed test tubes containing reference and analysed samples were placed on a rotary shaker at room temperature with continuous stirring (200 rpm) for 72 h. After the equilibration process, the analysed samples were filtered through the polycarbonate filter. A volume of 1 ml of the solutions obtained by the filtration process of the analysed samples and the reference solutions collected from reference samples, were transferred into the test tubes for further analysis. A drop (50 μl) of the 0.1% indicator (v/v = 3:2 bromocresol green/methyl red) was added to each of the test tubes which were subsequently stirred at the vortex. Then the all prepared solutions were used to the acid–base titration by 0.05 M NaOH and 0.05 M HCl. The reproducibility of the results was verified via multiple analysis of the titration process performed for each sample. Raman analysis was carried out using a micro Raman Renishaw spectrometer (λ = 785 nm). Thermogravimetric analysis was performed on 5 mg samples on DTA-Q600 SDT TA Instruments apparatus with the heating rate of 10 °C/min from room temperature to 900 °C at an air.

3. Results and Discussion

FT-IR spectroscopy is a well used qualitative technique for the evaluation of the chemical structure or characterization of chemically modified carbon nanotubes. The results in Fig. 1 summarize the behavior of the functional groups observed via FT-IR spectroscopy of the pristine, oxidized and reduced MWCNT samples. In the pristine MWCNT spectrum, asymmetric methyl stretching band at 2960 cm^{-1} and asymmetric / symmetric methylene stretching bands at 2920 cm^{-1} and 2850 cm^{-1} are observed, respectively. It is usually assumed that these groups are located at defect sites on the sidewall surface. Also, the pristine sample contains a band at 1180 cm^{-1} which is the C–O stretch mode and asymmetric stretching

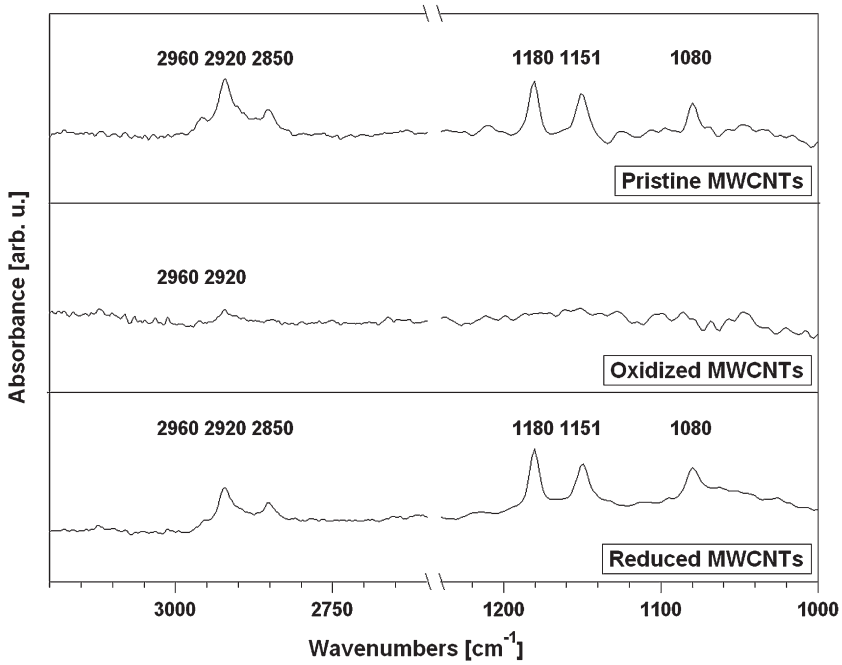

Fig. 1 – FT-IR spectra of the pristine, oxidized and reduced MWCNT samples.

bands at 1151 cm^{-1} and 1080 cm^{-1} which are associated with ether type groups. However, the details of the mechanisms behind the introduction of these oxygen containing functionalities during the synthesis of the multiwalled carbon nanotubes are still unknown.

In the oxidized sample spectrum the $\upsilon_s CH_2$ band disappeared and $\upsilon_{as} CH_3$ and $\upsilon_{as} CH_2$ bands were significantly decreased. The disappearance and reduction of the bands which can be correlated to functional groups existing at defect sites suggests that during the oxidation process other functional groups are created through the mechanism of defect-consuming and defect-generation steps proposed by Zhang et al. [22]. A simultaneous disappearance of the bands at 1180 cm^{-1}, 1151 cm^{-1} and 1080 cm^{-1} could be caused by the cleavage of the C–O bond of the C–O–C fragment in the ether type functional groups by the nitric and sulfuric acid mixture which was used in the refluxing process [23]. A spectrum of the reduced sample featured the reappearance of the bands at 1180 cm^{-1}, 1151 cm^{-1} and 1080 cm^{-1}. It has been assumed that after the reduction process of oxidized MWCNTs via sodium borohydrate treatment, lactone groups convert to the hydroxyl groups and the latter connected to the ether type group which was created during the reduction process. Subsequently, branching at the carbon atom adjacent to an oxygen atom of the ether group can lead to the spontaneous cleavage of C–O–C bond [24]. It has been proposed that the reappearance of the methylene band at 2850 cm^{-1}, highly growth of the methylene band at 2920 cm^{-1} and slightly growth of the methyl band at 2960 cm^{-1} were a result of the spontaneous cleavage of the ether bonds and further bonding between carbon atoms with reactive hydrogen atoms during the reduction process.

Chemical titration methods present several drawbacks such as very long equilibrium times, low reproducibility when dealing with small amounts of the sample and low (about 50%) detectability of the total oxygen content. However, FT-IR spectroscopy and the titration methods support each other very effectively [11,25]. In this adaptation of the titration proposed by Boehm [18], sensitive measurements and highly reproducible results were obtained through the use of the automated pipettes instead of standard burettes. The most critical element during the sample preparation for the titration analysis was degassing of CO_2. This was accomplished by drying the sample and further degassing of the reference and sample solutions by ultra-sonication at the vacuum conditions. It has been found in several experiments that the amount of CO_2 adsorbed on the MWCNT surface and dissolved in the solution results in complete disturbance of the whole titration analysis. From several available acid–base pH indicators, the mixture of 0.1% bromocresol green solution and 0.1% methyl red solution at the ratio of 3:2 (v/v) was the most accurate indicator in the estimation of the end point of the titration process. The main feature of that indicator was the property of color changing exactly at pH 5.1 from red to green or green to red in the acidic or alkali solutions, respectively. The reduction process of the oxidized MWCNTs was carried out in aqueous and ethanol solutions. It has been observed that the proceeding reaction in the aqueous solution led to an unwanted reduction of 25% of the carboxyl groups (data not shown). However, 100% of the carboxyl groups were preserved when the reduction process was conducted in ethanol solution. In both reactions, the amount of phenolic hydroxyl group was constant. The sodium borohydrate treatment of the MWCNTs converted 100% of the estimated lactone group content into the hydroxyl groups. As a result, the hydroxyl group content became almost threefold higher than before the $NaBH_4$ treatment. It is suggested that carbonyl functional groups could also undergo the reduction

process but this could not be confirmed. The concentrations of the surface functional groups were estimated by the following equation:

$$\%w/w = \frac{\text{Functional Groups} \times \frac{M \times C \times R}{10}}{\text{Sample Weight}}$$

where:

M Molecular weight of the titrated species (g mol^{-1})
C Molar concentration of the titrant (mol ml^{-1} 10^{-3})
R Reaction ratio of the titrant/titrated species
Functional Groups Reference Titer — Sample Titer (ml)*
Sample Weight Amount of material used for the titration analysis (g)

*The amount of the acidic functional groups was estimated under assumption that $NaHCO_3$ neutralizes only carboxyl groups; Na_2CO_3 neutralizes only carboxyl and phenolic hydroxyl groups; NaOH neutralizes carboxyl, phenolic hydroxyl and lactone groups. The amount of the hydroxyl groups was estimated from the amount of HCl that reacted with the MWCNTs.

The concentrations of the estimated functional groups for the MWCNT samples after the oxidation and reduction processes are summarized in Table 1.

The Raman spectra of the pristine, oxidized and reduced MWNTs are shown in Fig. 2. The Raman spectra exhibit the D and G bands typical of MWCNT. The D mode is observed in sp^2 carbons containing impurities or other symmetry-breaking defects. The G mode is related to the vibrations in all sp^2 carbon materials [26]. Raman spectroscopy can be used to determine the quality of the sample which was estimated via the I_G/I_D ratio [8,26]. The I_G/I_D ratio of the pristine MWCNT sample was 0.75. This indicated a high quantity of structural defects in the MWCNT graphitic structure which provided a lot of active sites for further functionalization. From the results presented in Fig. 2 one can observe that the vibrational properties of the oxidized MWCNTs modified the I_G/I_D ratio to 0.70. The change of the I_G/I_D ratio in the oxidized material could be due to the introduction of new defects as well as changes in the MWCNT geometry caused by the binding of new functional groups [27] or an electrophilic addition at hexatomic–hexatomic boundaries [22]. A careful examination of the pristine and oxidized MWCNT spectra revealed an upshift of the oxidized sample in the D-band region (3.7 cm^{-1}) at 1310–1314 cm^{-1} and G-band region (4.6 cm^{-1}) at 1597–1603 cm^{-1}, respectively. This shift of the Raman response of the oxidized sample could be caused by doping effects (electron doping) upon acid treatment [28,29]. This indicates that the oxidation process via acid treatment has a significant impact on the egzohedral graphitic wall structure [30] of the carbon nanotubes. From Fig. 2 it can be observed that reduction process of the oxidized MWCNT sample via sodium borohydrate treatment did not have any significant impact on the I_G/I_D ratio of the reduced sample which was 0.69. However, the vibrational properties of the reduced MWCNT sample were restored to the state of the pristine sample which was observed as a recovery of the D-band and G-band regions in the spectrum of the oxidized MWCNTs sample. The recovery of the Raman modes positions of the reduced sample [Fig. 2] could be due to the dedoping effects which had occurred during the reduction process [29].

Table 1 – The functional groups content of the oxidized and reduced MWCNT samples estimated by the Boehm titrations.

Functional groups content	Oxidized MWCNTs (%) ($\times 10^{-3}$)	Reduced MWCNTs (%) ($\times 10^{-3}$)
Carboxyl	0.50	0.50
Lactone	1.48	0.00
Phenolic hydroxyl	0.20	0.20
Hydroxyl	0.22	0.62

The thermogravimetric analysis of the pristine [Fig. 3], oxidized [Fig. 4] and reduced [Fig. 5] samples present the thermal stability of each sample fractions by monitoring the change of weight during the heating process. In each figure, the bold, dash and dot lines correspond to the TG, DTG and Voigt fitting of DTG curve, respectively. From the TG curves of the Figs. 3–5 it can be observed that the initial burning temperature of the pristine, oxidized and reduced MWCNT samples are about 350 °C, 300 °C and 250 °C, respectively. It suggests that the consecutive decrease of the initial burning temperature of the oxidized sample is closely related to the introduction of the defects and functional groups upon acids treatment. However, a decrease of the initial burning temperature of the reduced sample is an effect of the $NaBH_4$ treatment which converted previously introduced functional groups with the high decomposition temperature into the groups with a lower temperature of decomposition. The DTG curve of the pristine sample [Fig. 3] featured four stepwise weight-losses which correspond to the oxidation temperatures (T_o) for each sample fraction. The quantitative analysis of each fraction corresponding to its peak areas was performed via Voigt fitting of the DTG curve [31]. The oxidation temperature of the fraction I corresponds to the oxidation temperature of the amorphous carbon. The oxidation temperatures of the remaining fractions of the pristine sample correspond to the MWCNTs. It has been assumed that the presence of the three fractions of the carbon nanotubes which T_o difference in range of 50 °C is related to the fact that purified MWCNTs contain different amounts of initial defects in their egzohedral structure. It has been shown that the purification process of the MWCNTs via HCl treatment allowed one to achieve a sample with very low content of the catalysts, an insignificant amount of the amorphous carbon and high yield of the carbon nanotubes. From the DTG curve of the oxidized sample [Fig. 4] it has been assumed that three stepwise weight-losses correspond to the oxidation temperatures of the MWCNT fractions with different functionalization/defects degree. It has been proposed that the decrease of the oxidation temperature of the different MWCNT fractions was an effect of the defect introduction to the MWCNTs egzohedral structure and the subsequent introduction of the functional groups at newly created active sites. However, an oxidation temperature of the most MWCNTs was only 3 °C lower than the T_o of the comparable pristine MWCNTs fraction. Additionally, it has been assumed that an absence of the characteristic peak which corresponds to the amorphous carbon content was due to its removal during the refluxing process in a mixture of nitric and sulfuric acid. Finally, the DTG curve of the reduced

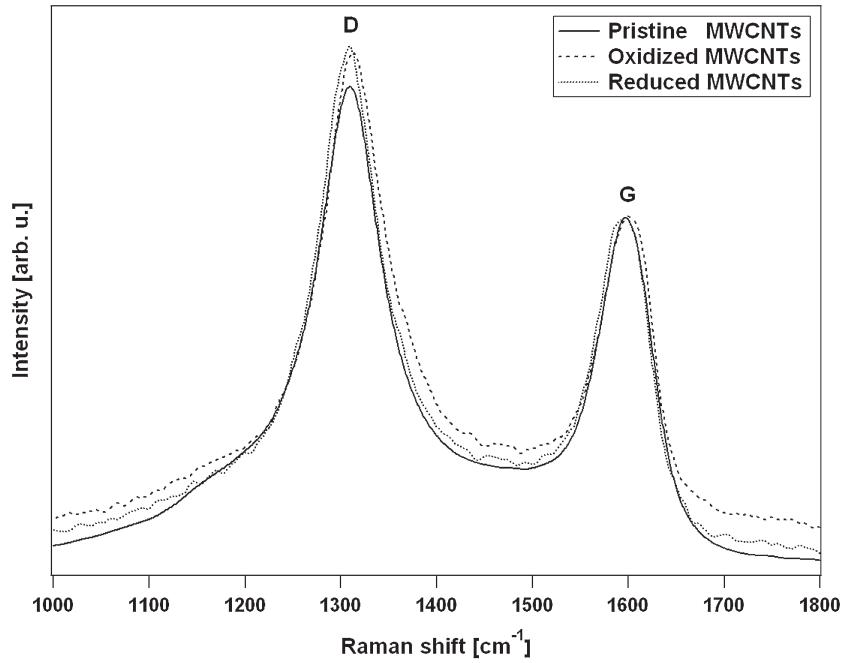

Fig. 2 – Raman spectra of the pristine, oxidized and reduced MWCNT samples.

sample [Fig. 5] exhibited four stepwise weight-losses which correspond to the oxidation temperatures (T_o) of the oxidized MWCNT fractions after the reduction of the carbonyl and lactone functional groups via sodium borohydrate treatment. According to the fraction peak areas of the oxidized and reduced MWCNT samples it has been suggested that fractions I and II of the reduced sample were originated from most defected fraction I of the oxidized sample. Similarly, fractions III and IV of the reduced sample could correspond to the fractions II and III of the oxidized sample before the reduction process. It has been assumed that the high decrease of the oxidation temperatures of the reduced sample in comparison to the oxidized sample could be due to an appreciable degree of the functionality formation on the MWCNTs egzohedral surface. Moreover, comparing the results from the various experiments one can notice that an insignificant difference between I_G/I_D ratio of the oxidized and reduced samples shown by the Raman spectroscopy proves that the following high decrease of the oxidation temperatures in the fractions of the reduced sample in comparison to the fractions of the

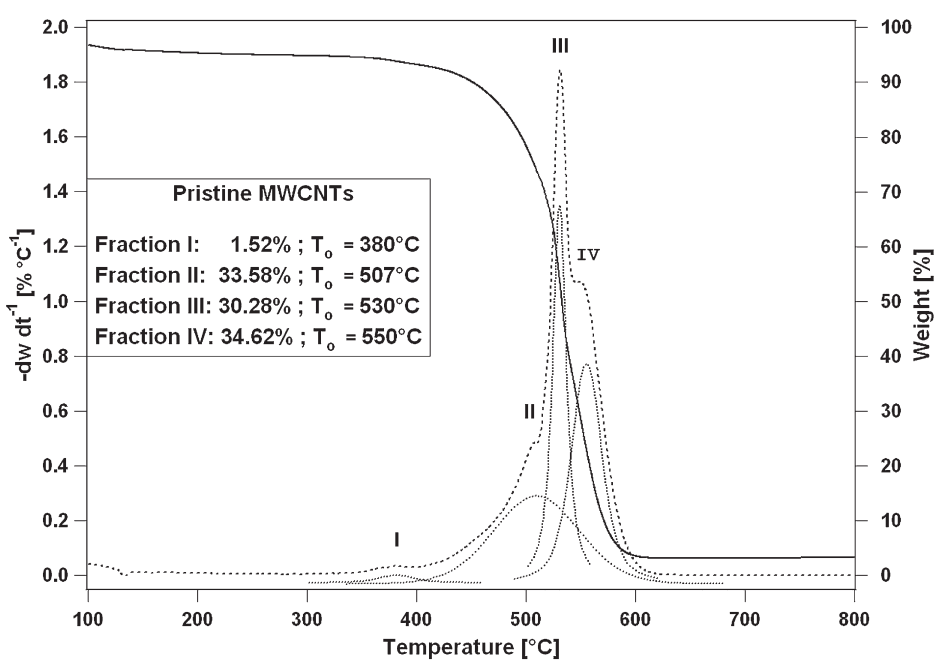

Fig. 3 – TGA curves of the pristine MWCNT sample.

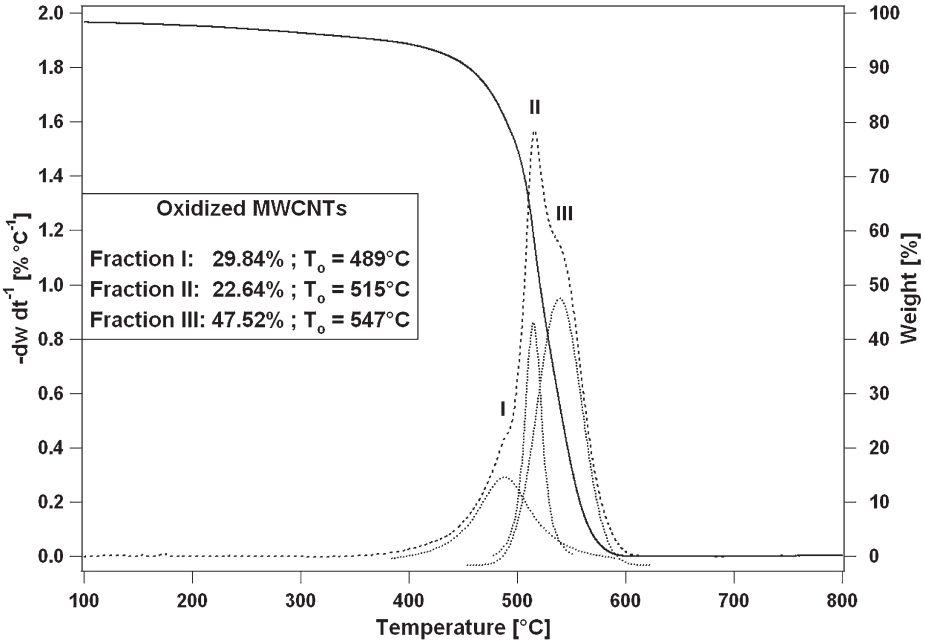

Fig. 4 – TGA curves of the oxidized MWCNT sample.

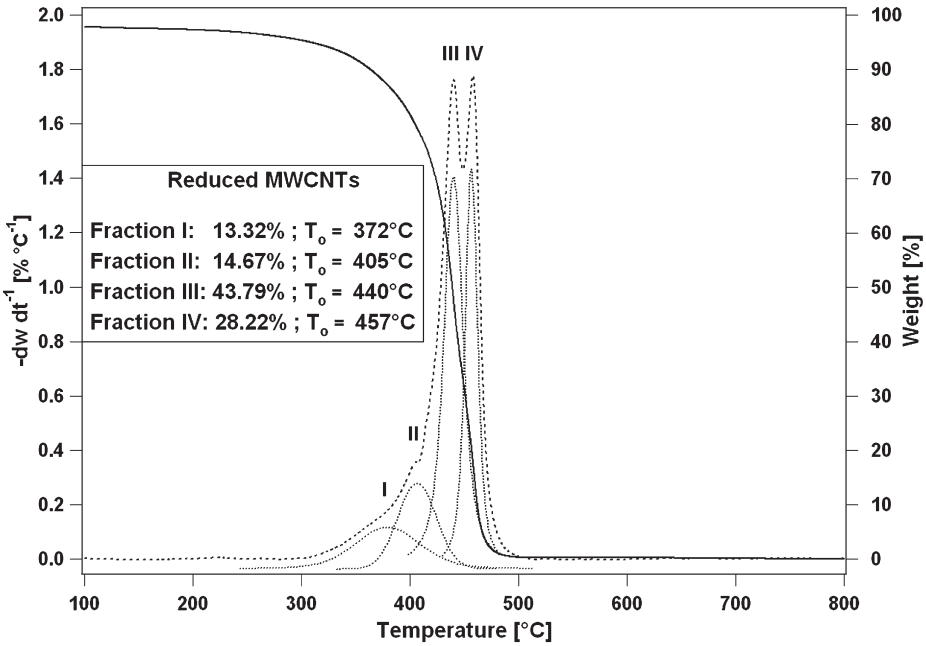

Fig. 5 – TGA curves of the reduced MWCNT sample.

oxidized sample was strictly induced by the factual increase of the hydroxyl group content which was confirmed by the Boehm's titration method.

4. Conclusions

The modified procedure of the Boehm's titration demonstrated in this paper is shown to be a reliable method for the evaluation of the general trends in the surface acidity of carbon nanotubes. It is particularly useful for the quantitative estimation of oxygen containing functional groups. It has been shown that the reduction via $NaBH_4$ is an efficient and easy modification technique for oxidized multiwalled carbon nanotubes for the preparation of MWCNTs with high hydroxyl group content. The presence and concentration of the carboxyl and hydroxyl groups on carbon nanotube surface are essential features, which are attractive for many branches of science such as nanomedicine, biosensors or polymer nanocomposites.

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