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MULTIWALLED CARBON NANOTUBES MODIFIED WITH BIOCOMPATIBLE COMPOUNDS

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Oxidized with solution of hydrogen peroxide multiwalled carbon nanotubes (MWCNTs) were modified with 2-hydroxyethylmethacrylate (HEMA) or chitosan (CTS). Morphology and surface properties of the pristine and modified MWCNTs have been investigated. The zeta-potential behaviour of MWCNTs was studied as a function of pH and suspension concentration. After oxidation, the divided nanotubes are found to have uncapped ports decorated with hydroxyl groups mostly. Surface oxygen-containing groups specify the negative zeta-potential in all pH range studied (pH=3-11). The values of zeta-potential display an inverse dependence on the dispersion concentration in acidic and basic solutions. After modification of oxidized MWCNTs with HEMA their isoelectric point is shifted from pH=2 to pH=10. Repeated surface treatment with HEMA (MWCNTs-HEMA-HEMA), along with change of the nature of terminal groups, provides stable surface charge increasing with nanotubes concentration in the pH range of 3-9. The isoelectric point of MWCNTs modified with CTS occurs at pH=4.5. At relatively small zeta-potential values, which become more negative with a decrease in the nanotubes concentration, such suspensions are the most stable.

INTRODUCTION

Due to the numerous potential applications carbon nanotubes (CNTs) have attracted researchers' interest. Considerable attention has focused on chemical modification of nanotubes because it opens new possibilities in fabrication of new polymeric materials with improved characteristics, in particular for biomedical applications (sensors, drug delivery systems etc.). Use of such materials demands the strict functionality of the components and their biocompatibility [1, 2].

Possessing unique mechanical, electrical, optical properties, carbon nanotubes are severely limited in processability because they practically insoluble and infusible, chemically inert, have poor dispersion capacity in liquid media, as well as weak interfacial interaction [3]. Grafting the necessary functional groups to the nanotubes surface allows one to obtain the best dispersion ability, better stability of suspensions and can regulate interaction with the dispersion medium. Especially it is very important for the polymeric composites in biomedical applications.

The functionalization of surface with biopolymers promises to be one of the most successful methods to improve the CNTs hydrophilicity. Some biocompatible polymers (or monomers), in particular chitosan (CTS) or 2-hydroxyethylmethacrylate (HEMA), can introduce into surface layer groups which are capable to form covalent, ionic and donor-acceptor bonds with bioactive molecules. Formation of modifying layer on the nanotubes surface can be realized in several routes. In the work [4] the nanotubes functionalization was carried out by adsorption coating with chitosan and following crosslinking of the modifying layer with glutaraldehyde. Such modification imparted biphilic properties to the MWCNTs surface. Obtained modifying layer was stable and did not affect the original structure of the nanotubes. Another way of noncovalent modification consists in precipitation of chitosan from acidic solution at pH increasing [5]. At this modification methodology the determining factor is a deacetylation degree of chitosan.

Covalent attachment of modifiers is commonly realised through chemically active anchor

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groups generated on the nanotubes surface and ports [6]. Such approach was used for MWCNTs modification with chitosan in [7]. Covalent bonding was achieved by interaction of chitosan with acyl chloride (-COCl) groups obtained on surface during suspending of oxidized MWCNTs in solution of thionyl chloride. The same approach was applied in [8] to polyHEMA grafting to walls of MWCNTs. But it is possible to achieve modifier covalent attachment by direct interaction of the polymer (monomer) with the functional groups of oxidized nanotubes in the presence of a catalyst [9]. This approach reduces the number of stages of nanotubes modification.

Because of a recent increase in interest in preparation and application of aqueous dispersions of carbon nanotubes, investigations of MWCNTs surface charge behaviour at different pH and suspension concentration were intensified. As known, the particles are stabilized in the liquid media by electrostatic repulsion [6] as dependent on zeta potential value which is determined by a variety of factors including dispersion concentration. The influence of the solid phase concentration on the zeta potential remains ambiguous. Thus, for polystyrene latex, a zeta potential does not depend on the content of particles in dispersion [10]. But a tendency to disperse phase coagulation makes the concentration one of the defining parameters in the formation of double electrical layer (DEL). Therefore, for the stable dispersion obtaining, it is important to know not only the surface characteristics of modified nanotubes but also dependence of a zeta potential value on the suspension concentration.

In this work we have studied the oxidized MWCNTs modified with 2-hydroxyethylmethacrylate and chitosan which were obtained via interaction of the modifying reagents directly with the oxygen-containing groups on the MWCNTs surface. The samples obtained were investigated by scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDX), FTIR spectroscopy and low temperature N_2 adsorption/desorption. The zeta-potential behaviour of MWCNTs was studied in KCl solution as a function of pH and suspension concentration.

EXPERIMENTAL

Materials. MWCNTs were synthesized by pyrolysis of propylene on ferric catalyst and purified by mixture of HCl and HF for removing the residual catalyst and amorphous carbon with the following washing from acids by water [11]. 2-hydroxyethylmethacrylate (HEMA), 2,2'-azo-isobutyronitrile (AIBN), glutaraldehyde (GA) were purchased from Fluka. Laboratory preparation of chitosan was obtained from shrimp shells. All other chemicals were of analytical grade and used without additional processing.

MWCNTs functionalization

Oxidation. Purified MWCNTs were dispersed in water, and then hydrogen peroxide was added to suspension. Mixture was heated at 80°C under stirring for 47 h. The concentration of H_2O_2 was 30%. The obtained oxidized nanotubes were filtered under vacuum and dried at 150°C [12].

Modification with HEMA. Oxidized MWCNTs (0.2 g) were dispersed in 50 ml toluene, then 2 ml HEMA was added to suspension with stirring. This mixture was heated to 80°C and 0.03 ml H_2SO_4 was added as a catalyst. Process of modification was carried out for 8 h at 80°C under reflux. Then sample was filtrated and washed several times with ethanol, water and again ethanol. Sample was dried at 60°C until the solvent was removed. HEMA-functionalized MWCNTs represented as MWCNTs-HEMA. In this case the modifying functional layer contains methacrylic groups that are able to the following reaction via radical polymerization process [12]. This opportunity was used at the next stage of modification. So, the monomer HEMA (2 ml) was added to toluene dispersion (50 ml) of MWCNTs-HEMA (0.2 g) in the AIBN presence. Such type repeated modification results in change of functionality of the modifying layer. The process was conducted under the same conditions. This sample is represented as MWCNTs-HEMA-HEMA.

Modification with chitosan. Oxidized MWCNTs (0.6 g) were ultrasonicated for 30 min in the chitosan (0.2 g) solution in acetic acid (2%). The dispersion was slowly stirring during one hour for chitosan adsorption on nanotubes. Then the ammonium solution drop-by-drop was added to dispersion until pH became 8. After this procedure the mixture was heated to 60°C and glutaraldehyde (0.2 g) was added. In this way chitosan adsorbed on oxidized nanotubes was cross-linked by glutaraldehyde. Obtained nanotubes were washed several times in acid and water in order to remove unreacted polymer followed by drying at 60°C to yield the final product. Obtained sample is represented as MWCNTs-CTS.

Characterizations of MWCNTs. The surface morphological image and elemental composition of MWCNTs were obtained using scanning electron microscope (SEM) and energy dispersive X-ray (EDX) analysis (JEOL JSM-5500LV, Japan) after gold plating at an accelerating voltage of 25 kV. Before plating the samples were dispersed and maintained on copper grids with double-sided adhesive black carbon tape. Quantachrome NOVA® Surface Area Analyzer was used to determine the MWCNTs structural characteristics by N_2 adsorption/desorption at 77 K. Specific surface area values and a pore size distribution were obtained by the Barrett, Joyner and Halenda (BJH) equation using the desorption isotherm.

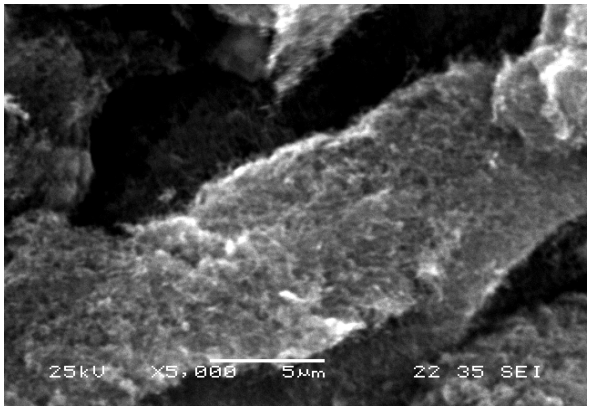
The surface functional groups of nanotubes were detected by a Fourier transform infrared (FTIR) spectrometer (Nicolet NEXUS FTIR) in the frequency range of 4000–400 cm^{-1} with the resolution of 8.0 cm^{-1}, the average number of scans was 50. Samples were mixed with KBr before taking measurements.

The zeta-potential values of pure and functionalized carbon nanotubes were determined at the different concentrations of nanotubes dispersion in sodium chloride aqueous solution (0.01 M) using a Zeta-analyzer (Zetaplus, Brookhaven, USA). Samples were ultrasonicated (22 kHz, 90% power and mood sweep) for 30 min before taking measurements. The pH of the MWCNTs dispersion was adjusted from 3 to 11 by adding 1 M potassium hydroxide or hydrochloric acid. Electrophoretic mobility of dispersions was measured to determine the zeta-potential using the Smoluchowski equation.

RESULTS AND DISCUSSION

Morphology study. SEM images of purified MWCNTs at the different magnifications are shown in Fig. 1. As is easy to see, after sonication in toluene MWCNTs adhere to one another in plate-like particles due to intermolecular interactions. As could be expected, nanotubes in such particles are ramified and entangled (Fig. 1*b*), however, individual nanotubes are also visible.

Treatment of nanotubes with hydrogen peroxide is an alternative to the use of mineral acids for oxidation. The hydrogen peroxide could behave as reducing or oxidizing agent with predominance of the oxidizing properties [13]. The side benefit of such approach is the absence of pollutants at an input of the oxidizer solution.



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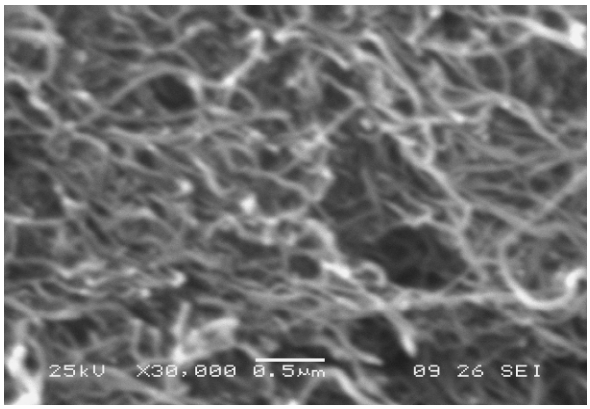
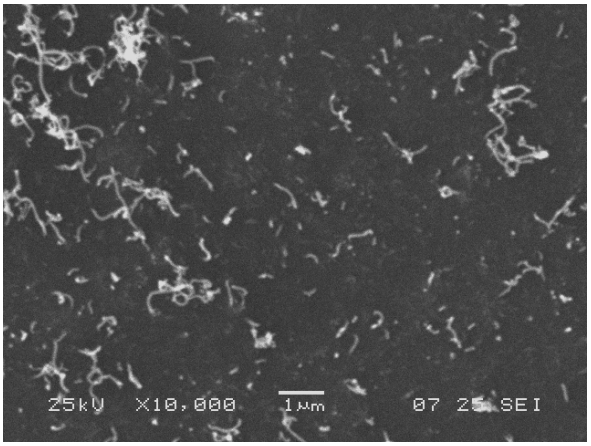


b

Fig. 1. SEM images of purified MWCNTs at the different magnifications (×500 – *a*, ×30000 – *b*)

Decrease in debundling and break of nanotubes were marked after MWCNTs oxidation (Fig. 2*a*,*b*). SEM images of the oxidized MWCNTs display the long (near 1.5 μm) as well as shorter (0.5 μm) nanotubes with the average diameter about 0.1 μm. The absence of big bundles and relatively narrow length distribution allows one to consider the sample as uniform.

Fig. 3 shows the N_2 adsorption/desorption isotherms (*a*, *b*) and the pore size distributions (*c*) obtained for purified (*a*) and oxidized MWCNTs (*b*). As will readily be observed, the adsorption isotherms exhibit a type II shape [14]. The reversible type II isotherm is typical of the nonporous or macroporous adsorbent. But observed shoulder at the very low p/p_0 (about 0.01) testifies to the presence of micropores or pores with diameter near low bounder of the mesoporous scale. At $p/p_0 = 0.9$ the isotherms display a sharp increment showing mesoporous nature of the samples. A small closed adsorption/desorption hysteresis loop is also observed at p/p_0 above 0.2. Hysteresis is closest to the H3 type (according to the IUPAC classification) which is usually associated with the slit-like pores.



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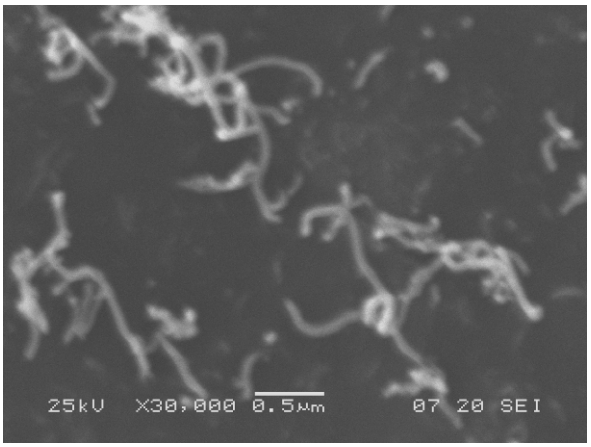
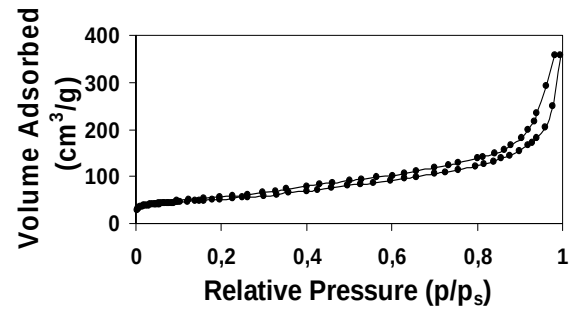


b

Fig. 2. SEM images of oxidized MWCNTs at the different magnifications (×10000 – *a*, ×30000 – *b*)

The nanotubes surface characteristics obtained from N_2 adsorption/desorption isotherms (Fig. 3*a*, *b*) indicate the change of the specific surface area (*S*) of purified MWCNTs from 150 to 240 m^2/g after oxidation. Pore size distribution curve (Fig. 3*c*, curve *1*) for the purified MWCNTs has two major peaks at 3.4 and 33 nm but the latter pores have a low volume. Narrow pore size distribution testified about the nanotubes structure uniformity. Small total pore volume V_Σ (0.55 cm^3/g) and relatively high specific surface area suggest that the mentioned pores are constitute the inner cavities on the nanotubes ports [15] which are formed during catalyst removal.

Specific surface area of oxidized nanotubes had increased insignificantly (about 60%). Analogous results were found by other authors [16] for MWCNTs oxidized with acids and were explained as an effect of interparticle repulsions of nanotubes resulting in smaller-sized "globs" of nanotubes. But in our case after oxidation the nanotubes are splintered (Fig. 2) and the pores



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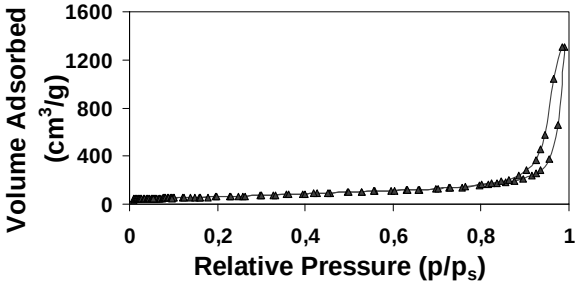

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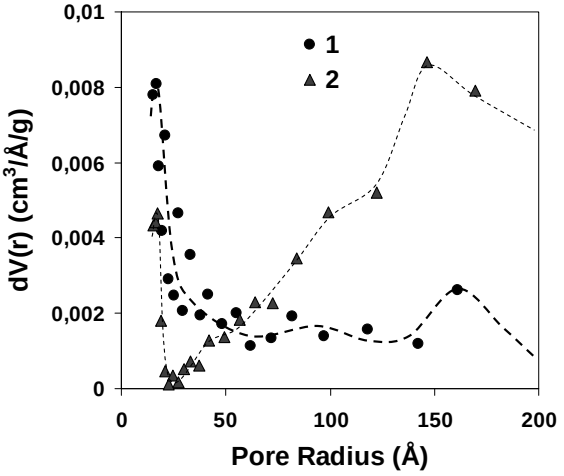


c

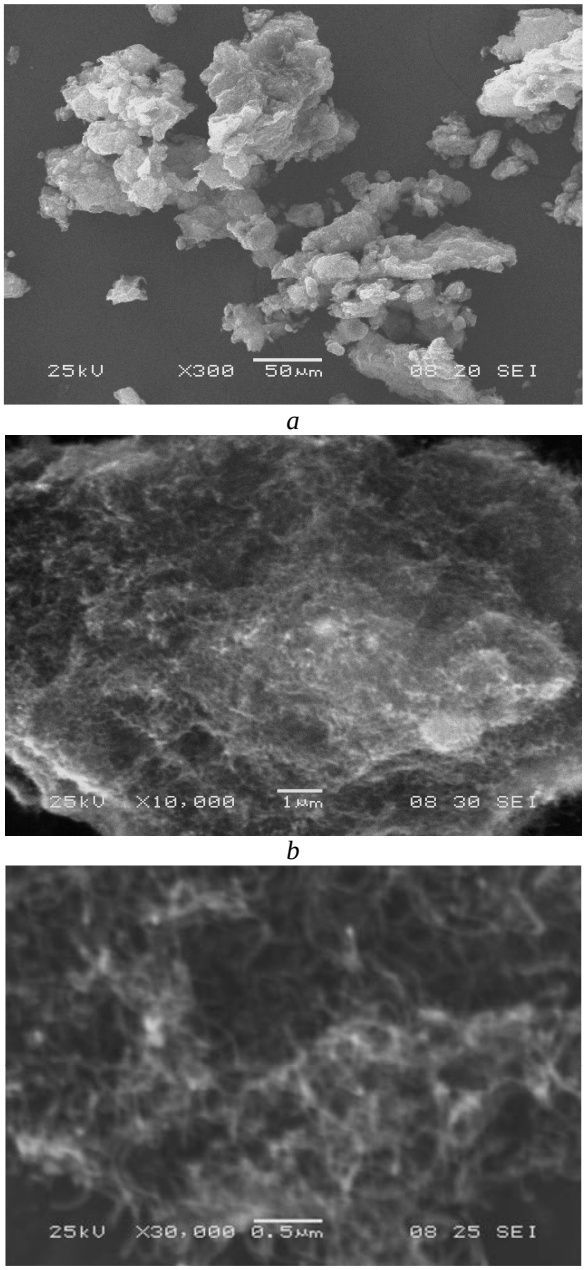
Fig. 3. The nitrogen adsorption–desorption isotherms of purified (*a*) and oxidized (*b*) MWCNTs and pore size distribution (*c*) for purified (*1*) and oxidized (*2*) nanotubes

volume and pores diameter are increased in nearly 4 times. After oxidation the average pore diameter is 29.4 nm (Fig. 3*c*, curve *2*) and V_Σ=2.03 cm^3/g (BJH). Nitrogen isotherm for oxidized sample (Fig. 3*b*) indicated the adsorption hysteresis in the p/p_0 range of 0.6 to 0.99. So, the sample is mainly mesoporous. The increase in both pore volume and diameter could testify about caps opening in nanotubes oxidized at the ends. This assertion is confirmed by XPS data presented below (Table).

Table. Elemental composition of MWCNTs using XPS data

Sample	Content, %			
	E= 284.3 eV C–C	*E*= 285.0 eV C=C	*E*= 286.0–286.5 eV C–OH, C–O–C	*E*= 90.1–290.4 eV C=O, O–C=O
MWCNTs purified	48.7	3.95	8.04	39.3
MWCNTs oxidized	38.13	15.39	33.15	13.33

SEM images of nanotubes modified with HEMA display the aggregates with layered structure (Fig. 4). Perhaps agglomeration of oxidized nanotubes during modification with the HEMA was caused by bound monomers or oligomers interaction which can envelop nanotubes and entangle to one-another. MWCNTs coated with chitosan are shown in Fig. 5.



a

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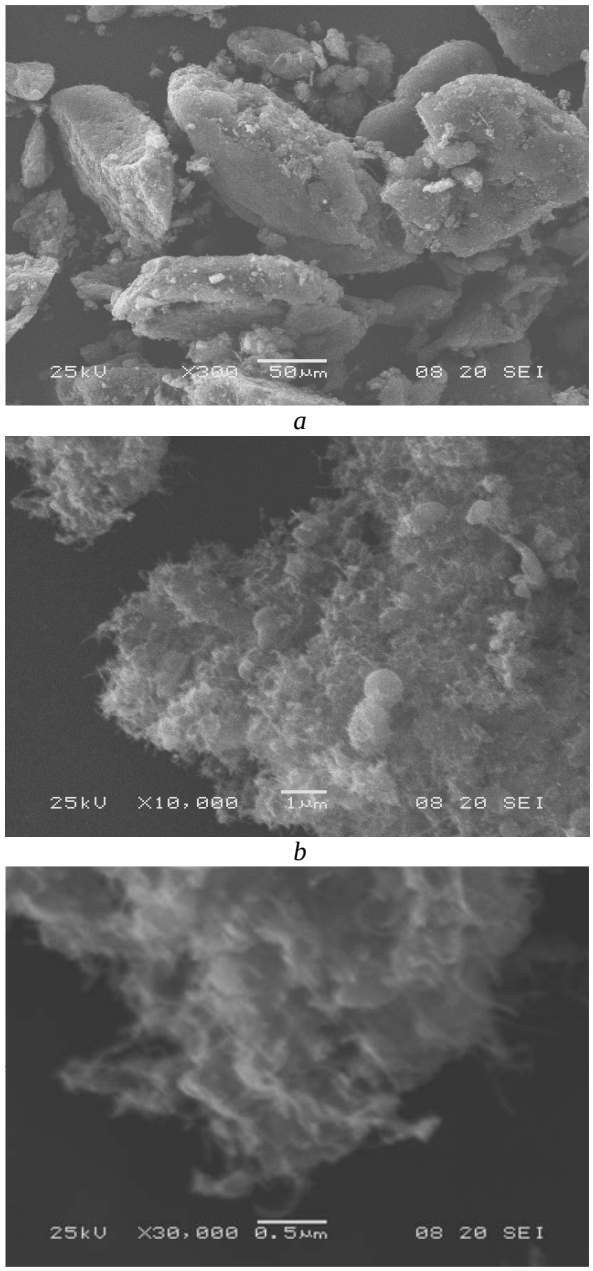
Fig. 4. SEM images of MWCNTs modified with HEMA (MWCNTs-HEMA) at the different magnifications (×300 – *a*, ×10000 - *b*, ×30000 – *c*)



a

b

c

Fig. 5. SEM images of MWCNTs modified with chitosan (MWCNTs-CTS) at the different magnifications (×300 – *a*, ×10000 – *b*, ×30000 – *c*)

The composite obtained is the pellet with diameter of 50–150 μm. At the chosen synthesis conditions the nanotubes are introduced into polymer domains, and polymer beams with d=1 μm surrounded by linear chains are observed.

Surface chemistry of modified MWCNTs. The SEM/EDX technique was applied for obtain information about the elemental composition of surfaces (within an information depth of around 8 nm). Obtained results testified that samples contained residual quantity of S and Cl (0.17 and 0.93 at %) which were introduced with solutions during purification and washing. Low content of Fe on the MWCNTs surface (0.49 at %) permits to assert that the sample was enough purified from catalyst.

XPS results (Table) testify domination of C=O and C–O=C groups on purified MWCNTs. In FTIR spectra (Fig. 6, spectrum *1*) the band with the absorption maxima at 1639 cm^{-1} attributed to the benzene derivatives and the band at 1465 cm^{-1} pointed on the presence of O–C=O groups. The weak band at 1270 cm^{-1} and broad one at 1122 cm^{-1} are attributed to vibrations of C–O–C groups.

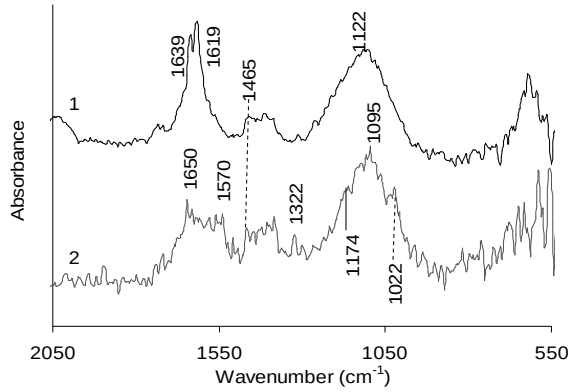


Fig. 6. FTIR spectra of the purified (*1*) and oxidized MWCNTs (*2*)

After oxidation, splitted nanotubes without caps should have the ports fringed with oxygen-containing groups. XPS data obtained (Table) testify that during nanotubes treatment with hydrogen peroxide the nanotubes ports were mostly oxidized [12]. In the sample C–OH and C–O–C groups predominated over C=O ones in accordance with the literature data [17, 18], and percentage of the phenolic groups is increased in comparison with untreated nanotubes.

The FTIR spectrum of the oxidized MWCNTs (Fig. 6, spectrum *2*) shows the band at 1650 cm^{-1} attributed to the benzene derivatives stretching and the band at 1570 cm^{-1}. The adsorption bands localized at 1450 cm^{-1} (C–H) attributed to bending vibrations of benzene ring and band at 1022 cm^{-1} corresponded to tangential C–H bending vibrations in mono-substituted benzene. The band at 1465 cm^{-1} points on the presence O–C=O groups and the bands at 1174 cm^{-1}(C–O) and 1095 cm^{-1} (C–O–C) are associated with the ring vibrations in *ortho*-disubstituted benzene with attached hydroxyl and lactone groups [19, 20].

It is conceivable that the monomer HEMA is preferentially attached to the relatively reactive tube ends or defect sites of nanotubes such as ether, carbonyl (lactone) or hydroxyl groups. IR spectra of MWCNTs functionalized with HEMA show the absorption at 1630 cm^{-1} (C=C) and 1604 cm^{-1} (COO) assigned to bound –O–C(O)–C(CH_3)=CH_2 groups (Fig. 7).

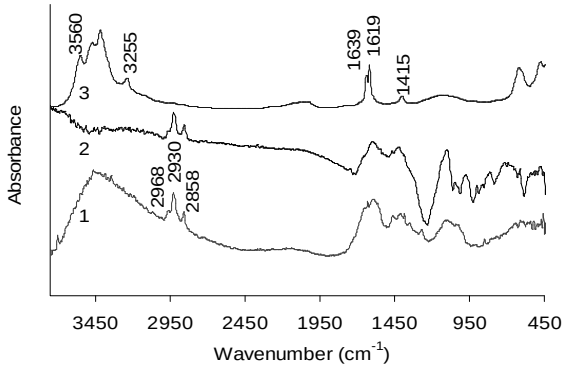


Fig. 7. FTIR spectra of MWCNTs-HEMA (*1*), MWCNTs-HEMA-HEMA (*2*) and MWCNTs-CTS (*3*)

The band at 1385 cm^{-1} corresponding to the bending vibrations of C–H bonds in –CH_3 groups confirms the presence of methacrylic groups in the modifying layer. Narrow band with an intermediate intensity at 1465 cm^{-1} is attributed to O–C=O groups. Availability of C–O–C bonds and –OH groups attached to benzene rings is confirmed by the bands at 1095 and 1022 cm^{-1}. The absorption band with maximum at 1369 cm^{-1} attributed to vibrations of C–H bonds in –CH_2–OH groups and bands at 1570 and 1480 cm^{-1} corresponding to C–H bonds vibrations in substituted benzene indicated HEMA attachment to nanotubes [8, 21]. Hence, the modifying layer of the MWCNTs-HEMA includes both methacrylate and ester groups as well as phenolic and hydroxyl groups. The absence in the IR spectrum the bands corresponding to polymer (Fig. 7, spec-

trum *1*) allows one to assume that the modifying layer consists of molecules of the monomer or oligomers.

After repeated MWCNTs-HEMA modification with HEMA in the presence of the initiator of radical polymerization there are the bands at 1730 and 1060 cm^{-1} attributed to the C=O and C–O–C groups in the modifying reagent molecules An increase of the relative intensity of the bands of $–CH_2–$ groups and an appearance of the band near 894 cm^{-1} testify about the modifier grafting by interaction with vinyl groups of the preliminarily immobilized molecules. The presence of bands at 894 and 786 cm^{-1} indicates the formation of polymer chains.

After MWCNTs modification with chitosan FTIR spectra (Fig. 7, spectrum *3*) clearly show new absorption at 3552–3417 cm^{-1} that is typical of N–H vibrations in –NHCO. Appearance in spectrum of MWCNTs-CTS several peaks at 3600–3300 cm^{-1} indicates the formation of intermolecular hydrogen bonds. Strong peaks 1639, 1619, 1415 and 624 cm^{-1} were also observed. Weak broad absorbance at 1137 cm^{-1} and sharp band at 624 cm^{-1}, attributed to C–O–C and O–C–O vibrations, indicates the esters presence. The results confirm the MWCNTs capsulation by chitosan.

Surface charge of modified MWCNTs. The measurement of zeta-potential of the nanotubes in water is complicated by low stability of the dispersion, but these data give useful information about surface charge properties. As known, zeta-potential depends on the type and concentration of the electrolyte [22, 23], nanotubes concentration in suspension. Fig. 8 depicts zeta potential of purified MWCNTs taken at the different concentrations of the suspension in KCl solution (pH=7.1). Each point is average zeta potential value from 10 measurements (within a measuring time of 7 min). With an increase of the suspension concentration up to 0.7 mg/ml the zeta potential changes slightly, but the relative error of measurements is significantly augmenting and at $C = 0.8$ mg/ml a sign of the surface charge is reversed. Fluctuations in the values of zeta potential during measuring, detected also by authors [16, 24], may be caused by the nanotubes tendency to coagulation. It can be assumed that the various values of zeta-potentials are related to nanotube agglomerates of different sizes.

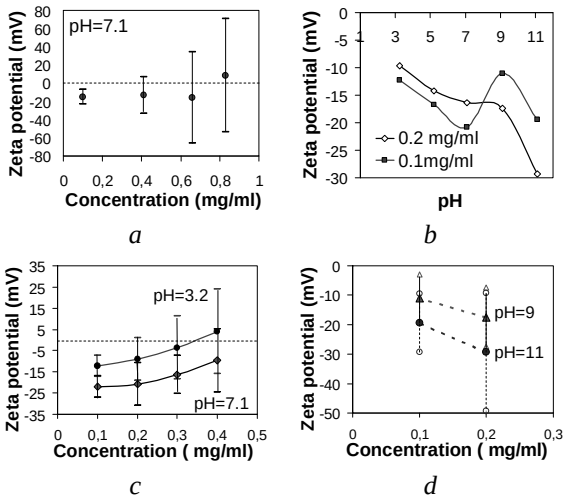


Fig. 8. Dependences of zeta potential of purified (*a*) and oxidized (*b*–*d*) MWCNTs on suspension concentration in 0.01 mol/l KCl solution (*a*, *c*, *d*) and on medium pH (*b*)

According to the literature data [25], as-produced carbon nanotubes have the isoelectric point (IEP) in the pH range of 5–8 and with increasing of pH the zeta potential becomes more negative, probably because of adsorption of hydroxide ions on the MWCNTs surface. Usually, after purification the presence of acidic groups shifts IEP to the lowest pH values [25]. As was shown in [26], purified nanotubes have small and positive zeta-potential in the acidic medium with IEP in the pH range of 2–3. For tested herein purified MWCNTs IEP was about pH=3. After oxidation, the presence of oxygen-containing groups shifts the isoelectric point to values often below pH=2 what is close to the value presented in [27]. The oxidized MWCNTs exhibit negative charge in the whole pH range investigated and till pH=7 the zeta potential values are increased with pH growth what correlate with the literature data. It can be explained by dissociation of the hydroxyl groups. It will impart the negative charge to the nanotubes surface. The character of the curve (Fig. 8*b*) in pH range of 3–7 is similar to those of the plots obtained in [16, 26, 28, 29] for oxidized nanotubes. The low potential values (in the range from -10 to -25 mV) demonstrate that the MWCNTs are less sensitive to protons (H^+) and hydroxide anions (OH^-) [30]. It is usual when the functional groups are primary ketones, aldehydes, alcohols or esters [31, 32], because these groups are electrically neutral and do not dissociate in the pH range of 2–12. The dependences of the zeta potential for nanotubes under study testify

that oxidized nanotubes contain mainly alcohol and ester groups.

As known, zeta potential values of colloidal particles are increased with the suspension concentration decrease [22]. The results obtained for oxidized MWCNTs correlate with this observation in the acidic media: when suspension concentration increases zeta potential becomes more positive (Fig. 8*c*) and the IEP shifts to higher pH. IEP for the suspension with concentration of 0.4 mg/ml was near pH=4. Positive zeta potential (Fig. 8*c*, pH 3.2) is characteristic of nanotubes with the low content of oxygen-containing groups, and it is defined by an increase in the agglomerates size with enhancement of the suspension concentration. Diffusion of counterions inside agglomerates is complicated and the degree of the functional groups dissociation is reduced. Under such conditions, the DEL is formed in boundary layer of the aggregates and neutralization of the surface charge is realized at the lower concentration of the counter-ions. With decrease in the nanotubes concentration, the surface accessibility is increased and for the DEL formation more counter-ions are required.

Above pH=7 an effect of the suspension concentration on zeta-potential (Fig. 8*d*) is higher: potential becomes more positive with a decrease in the concentration. Nanotubes suspensions was found to be more stable in the alkaline media in comparison with those in the acidic media, and at the concentrations above 0.2 mg/ml the zeta potential measurements became impossible because of low transparency of the suspensions.

Hence, the nanotubes oxidation improved the MWCNTs stability in aqueous suspension, but this stability strongly depends on the nanotubes ability to coagulation and the nature of the surface functional groups. It should be marked that largest values of zeta-potential (-29.34 mV) corresponding the best stability of dispersion have reached at pH=11.

Zeta potential of MWCNTs-HEMA (Fig. 9*a*) was positive until pH=9 with IEP close to pH=10. Similarity of the obtained pH-dependence with such dependence for nanotubes suspensions with the Disperbyk-2150 dispersant in the ethanol solution [21] is paid an attention. Positive surface charge was also achieved by the use of non-ionic surfactant Pluronic 123 or cationic surfactant CTAB (SWCNTs covered by CTAB display a ζ-potential of 61.5 mV) [33]. However, for MWCNTs-HEMA the low potential values (15 to -20 mV) were detected in all range of pH that is insufficient for suspension stability (stability from electrostatic considerations is achieved for zeta potential values beyond the -15 to 15 mV range). Positive surface charge of MWCNTs-HEMA indicates a low ionization of the modifying layer in the wide pH range of 3–9, consequently, the oxygen-containing groups, capable to dissociation, are replaced (or screened) by the modifier molecules. Grafted HEMA, likely copolymer Disperbyk-2150, behaves as a cationic surfactant and shields the nanotubes surface with lyophobic methacrylate groups.

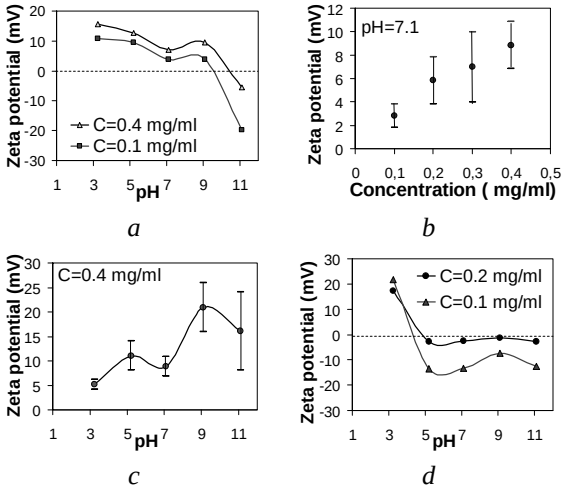


Fig. 9. Dependences of zeta potentials of MWCNTs-HEMA (*a*), MWCNTs-HEMA-HEMA (*b, c*) and MWCNTs-CTS (*d*) on medium pH (*a, c, d*) and on suspension concentration (*b*)

According to the results obtained, the zeta-potential is diminished with the suspension concentration decrease, and the dispersion stability is reduced at pH below 10 (Fig. 9*a*). For MWCNTs-HEMA this dependence is linear and insignificant. However, with the modifier molecules elongation (MWCNTs-HEMA-HEMA sample) decrease in the zeta potential value was more substantial (Fig. 9*b*). It is significant that at the lowest suspension concentration the zeta potential values were close to zero and with less dispersion. DEL becomes more stable with the suspension concentration decrease.

For the MWCNTs-HEMA-HEMA sample zeta potential is positive throughout the pH range studied (Fig. 9*c*). Similar results were reported in [33] where the zeta-potential distribution for carbon nanotubes wrapped by cationic surfactant CTAB was presented. Zeta potential

values of MWCNTs-HEMA-HEMA in the pH range of 5–9 were significantly higher in comparison with the MWCNTs-HEMA sample. MWCNTs-HEMA-HEMA forms fairly stable dispersion in water (Fig. 9*a*, *c*). The least suspension stability was observed at pH=3 and pH=11.

For the MWCNTs-HEMA-HEMA sample the highest value of zeta potential was detected at pH 9 (Fig. 9*c*). With the following pH increase the potential tends to zero and the IEP for this sample was found above pH=11. Perhaps, at this pH the polymer chains became more linear that results in the DEL compaction.

With pH increase the solubility of chitosan is decreased and it could reduce the suspension stability. However the MWCNTs-CTS suspension was shown to be stable throughout the pH range studied. The IEP was in the pH range of 4–5 depending on the suspension concentration (Fig. 9*d*). In spite of small values of the zeta potential in the pH range of 7–11 at C=0.2 mg/ml, nanotubes sedimentation was not observed. The suspension was the least stable at pH=5.2 that was close to IEP. Chemical and conformational changes of CTS, while changing pH, may be responsible for such dispersion behaviour. Usually chitosan is precipitated at pH above 6.5. Some properties of the chitosan-MWCNTs system have been studied in [34]. In the acidic solutions adsorbed onto MWCNTs surface chitosan acts as a polymeric cationic surfactant and stabilizes the nanotubes suspension. The polymeric chains of CTS repulse one another in the acidic solution owing to $–NH_2$ groups protonation. Groups $–NH_3^+$ are gradually deprotonated with pH increasing, and then MWCNTs-CTS precipitate because of intramolecular hydrogen bonding. In the basic solution, both $–NH_3^+$ and –COOH groups of chitosan are deprotonated forming $–NH_2$ and $–COO^–$ groups. The negatively charged $–COO^–$ groups could also promote to formation of the homogeneous dispersion of carbon nanotubes. When the medium pH was close to the isoelectric point, the $–NH_2$ and –COOH groups form intramolecular and intermolecular complexes, and nanotubes sedimentation takes place [35].

Cross-linking of adsorbed chitosan with glutaraldehyde results in lowering of amino groups content. Properties of the obtained sample are comparable with the characteristics of the nanotubes modified with cellulose [36]. With decrease in concentration of MWCNTs-CTS suspension the value of the zeta potential (as an absolute value) is increased. This indicates an interaction between aggregates in the suspension. Comparison of the results obtained for the modified nanotubes allows one to conclude that modification with chitosan provides the most stable aqueous suspensions of carbon nanotubes.

CONCLUSION

Modification of oxidized MWCNTs with HEMA and chitosan could be used to change surface charge, to disperse nanotubes homogeneously in suspension and to impart them biocompatibility. The data presented testify that during oxidation with hydrogen peroxide the tangles of nanotubes are crushed, ports are opened while the modification with polymers resulted in formation of agglomerates. For all the samples, a decrease of the suspension concentration leads to shift of the zeta potential value into the negative range. The interaction between particles (aggregates) into suspension has a significant effect on the DEL structure. For each sample there is the concentration when the dispersion is the most stable. After the oxidized MWCNTs modification with HEMA the isoelectric point is shifted to pH=10. Elongation the modifier chains attached to nanotubes (MWCNTs-HEMA-HEMA), along with change of the terminal groups nature, provides the positive and stable surface charge increase in nanotubes concentration at pH range of 3–9. For nanotubes modified with polymer the zeta potential depends on the conformation of the grafted molecules, since at the different pH the polymer chains can be expanded or collapsed. Increase of the zeta potential value provides enhancement of the dispertion stability. An exception to the general dependences found for the zeta potential values was detected for the chitosan-modified nanotubes. The isoelectric point of the MWCNTs modified with chitosan was close to pH=4.5. At relatively small zeta-potential values, which became more negative with decrease in nanotubes concentration, such suspensions were the most stable due to features of the modifier morphology and the nature of terminal groups.

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Багатошарові вуглецеві нанотрубки, модифіковані біосумісними речовинами

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Досліджено фізико-хімічні властивості, морфологію та характер поверхні вихідних і модифікованих 2-гідроксіетилметакрилатом (НЕМА) і хітозаном багатошарових вуглецевих нанотрубок (БШВНТ). Вимірювання дзета-потенціалу БШВНТ проводили при різних pH розчину електроліту і концентраціях суспензії. Показано, що при окисненні БШВНТ відбувається їхнє дроблення з утворенням портів, що обрамлені переважно гідроксильними групами. Кисеньвмісні групи визначають негативний дзета-потенціал окиснених нанотрубок в досліджуваному діапазоні pH (3-11), але залежність дзета-потенціалу від концентрації дисперсії у кислому і основному середовищах обернена. Після модифікування БШВНТ НЕМА ізоелектрична точка зміщується з pH=2 до pH=10. Подовження ланцюжка прикріпленого до нанотрубок модифікатора (БШВНТ-НЕМА-НЕМА) разом із зміною кінцевих функціональних груп забезпечує позитивний і стабільний заряд поверхні, що збільшується симбатно концентрації нанотрубок в діапазоні pH 3-9. Ізоелектрична точка БШВНТ-хітозан близька до pH=4,5. За відносно невеликих значень дзета-потенціалу, який стає більш негативним зі зменшенням концентрації нанотрубок, такі суспензії є найбільш стійкими.

Многослойные углеродные нанотрубки, модифицированные биосовместимыми веществами

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Исследованы физико-химические свойства, морфология и характер поверхности исходных и модифицированных 2-гидроксиэтилметакрилатом (НЕМА) и хитозаном многослойных углеродных нанотрубок (МУНТ). Измерение дзета-потенциала МУНТ проводили при разных pH раствора электролита и концентрациях суспензии. Показано, что при окислении МУНТ происходит их дробление, а образующиеся порты обрамлены преимущественно гидроксильными группами. Кислородсодержащие группы определяют отрицательный дзета-потенциал окисленных нанотрубок в исследуемом диапазоне pH (3-11), но зависимость дзета-потенциала от концентрации дисперсии в кислой и основной средах обратная. После модифицирования МУНТ НЕМА изоэлектрическая точка смещается от pH=2 к pH=10. Удлинение цепочки прикрепленного к нанотрубкам модификатора (МУНТ-НЕМА-НЕМА) вместе с изменением концевых функциональных групп обеспечивает положительный и стабильный заряд поверхности, который увеличивается симбатно концентрации нанотрубок в диапазоне pH 3-9. Изоэлектрическая точка МУНТ-хитозан близка к pH=4,5. При относительно небольшом значении дзета-потенциала, который становится более отрицательным с уменьшением концентрации нанотрубок, такие суспензии являются наиболее устойчивыми.