Chuiko Institute of Surface Chemistry
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SYNTHESIS AND PROPERTIES OF COMPOSITES BASED ON POLYMERS AND MULTIWALLED CARBON NANOTUBES

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Materials:

Multiwalled carbon nanotubes (MWCNTs) ТУ У 24.1-03291669-009:2009

Polystyrene (pSt) FLUKA

2-Hydroxyethylmethacrylate (HEMA) FLUKA

Synthesis approaches:

-Nanotubes surface modification by adsorption of electrolytes or active compounds;

-Oxidation of the nanotubes boundary layers;

-Chemisorptions of chemically active compounds;

-Synthesis of the polymer filled composites in the magnetostatic field.

Methods:

Scanning electron microscopy (SEM), Transmission electron microscopy (TEM), Infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), Potentiometry, Differential scanning calorimetry (DSC), Thermogravimetric analysis (TGA), Thermomechanic analysis (TMA).

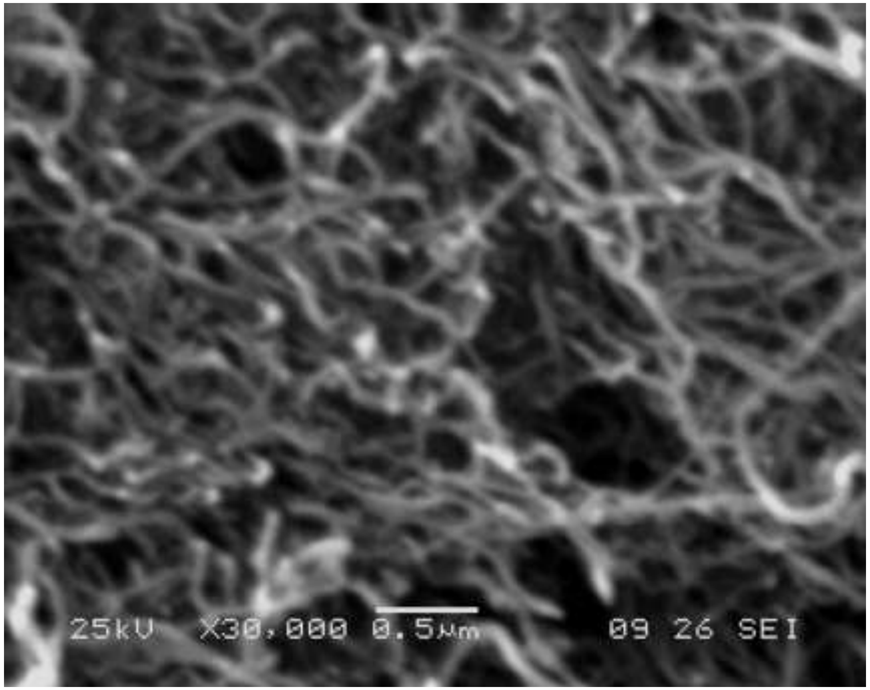
MWCNTs characterization

MWCNTs were synthesized by pyrolysis of propylene on ferric catalyst (CVD) and purified by mixture of HCl and HF in order to remove the residual catalyst and amorphous carbons, followed washing with water until pH is neutral. Purity - 99,8%

Energy Dispersive X-ray analysis)

Elt.	Line	Atomic Wt%	Conc.
C	Ka	92.24	89.00
O	Ka	7.13	9.16
S	Ka	0.07	0.17
Cl	Ka	0.33	0.93
Fe	Ka	**0.04**	**0.49**
Ca, Si	Ka	0.19	0.25
Total		100	100

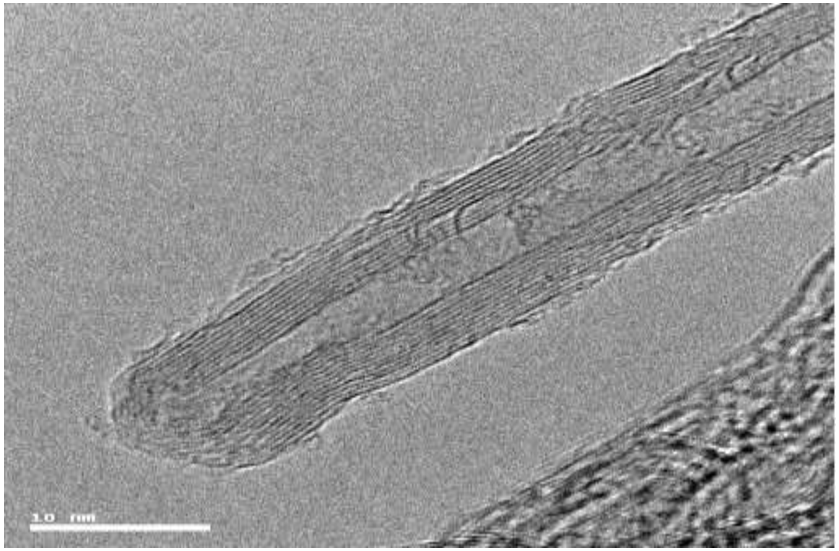
SEM photographs of the pristine MWCNT

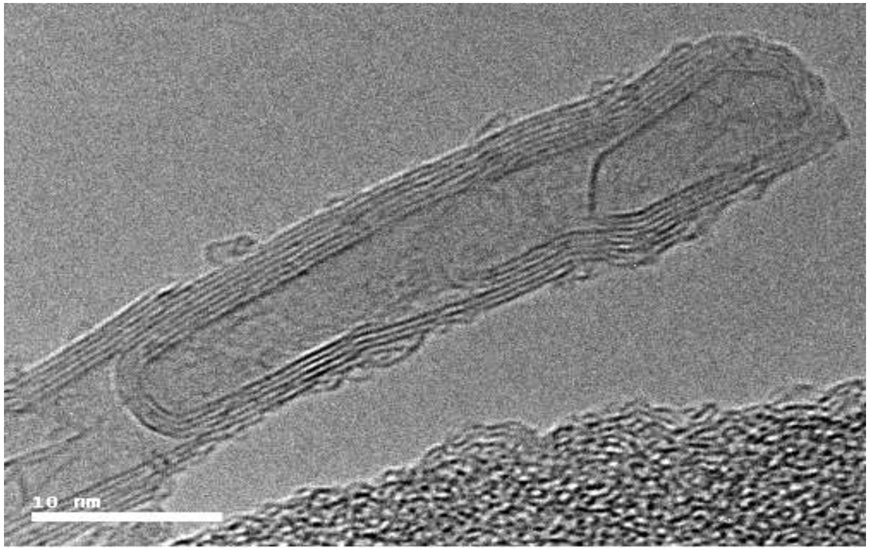


Investigation was particularly supported by FP7 Marie Curie Actions People Project "Hybrid nanocomposites and their applications - Compositum", Grant Agreement Number PIRSES-GA-2008-230790.

TEM photographs of the pristine MWCNT

Length – 100-300 nm, External Diameter -8-10 nm, Internal diameter – 3-5 nm, Number of layers - ~5-10 [*]





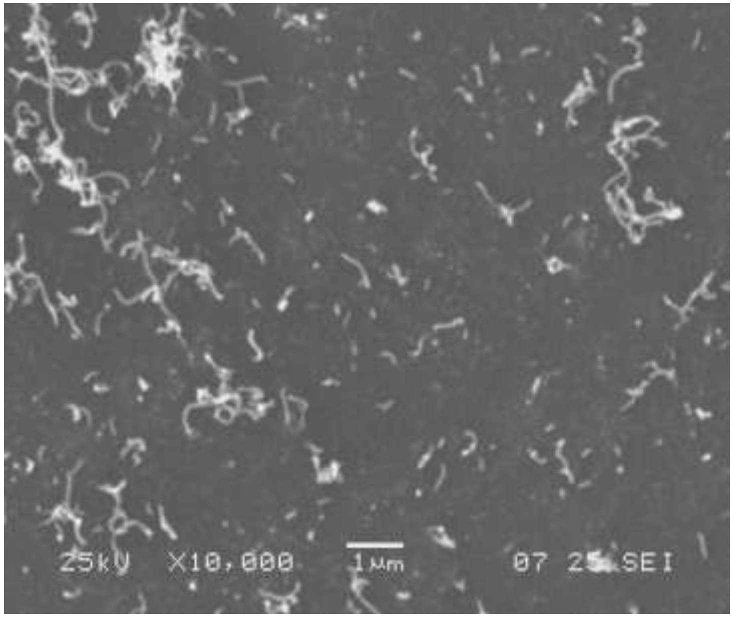
[*Yu.I. Sementsov, A.V. Melezhik, G.P Prikhod'ko et al., Synthesis, structure, physico-chemical properties of nanocarbons materials. In: Physics and Chemistry of Nanomaterials and Supramolecular Structures., A.P. Shak, P.P. Gorbik (eds.), Kyiv, Naukova Dumka, V2 (2007),116.]

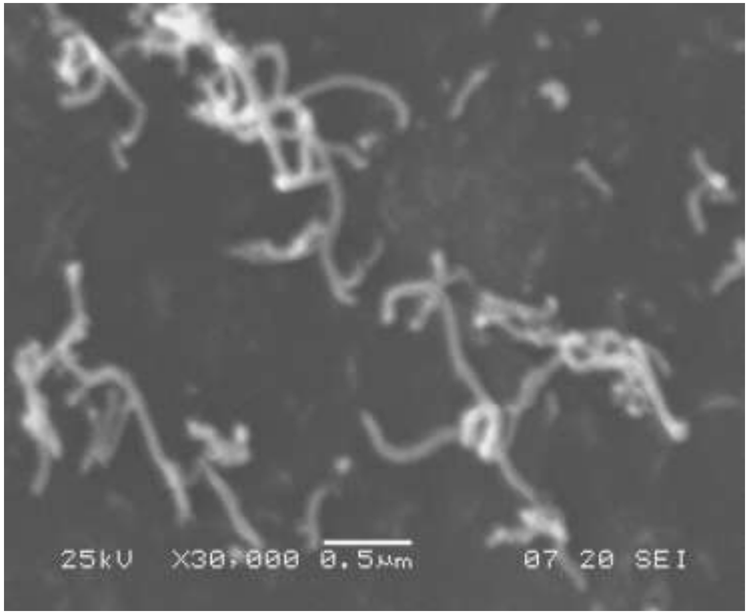
Oxidized MWCNT

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 H2O2 was 30%. The obtained oxidized nanotubes were filtered under vacuum and dried at 150°C

$$2H_2O_2 \rightarrow 2(OH\bullet + OH\bullet) \rightarrow 2H_2O + O_2$$

SEM photographs of the oxidised MWCNT





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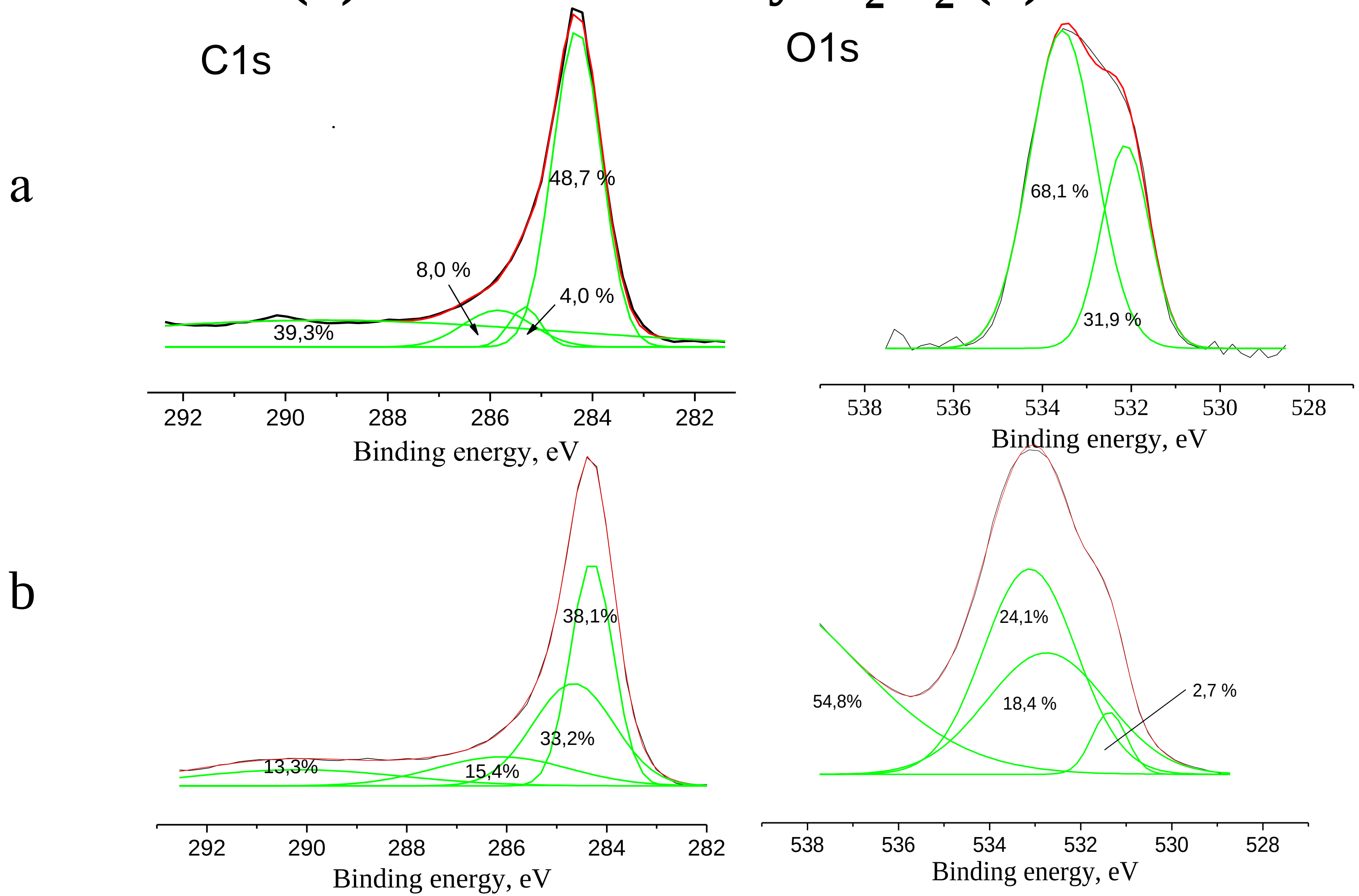
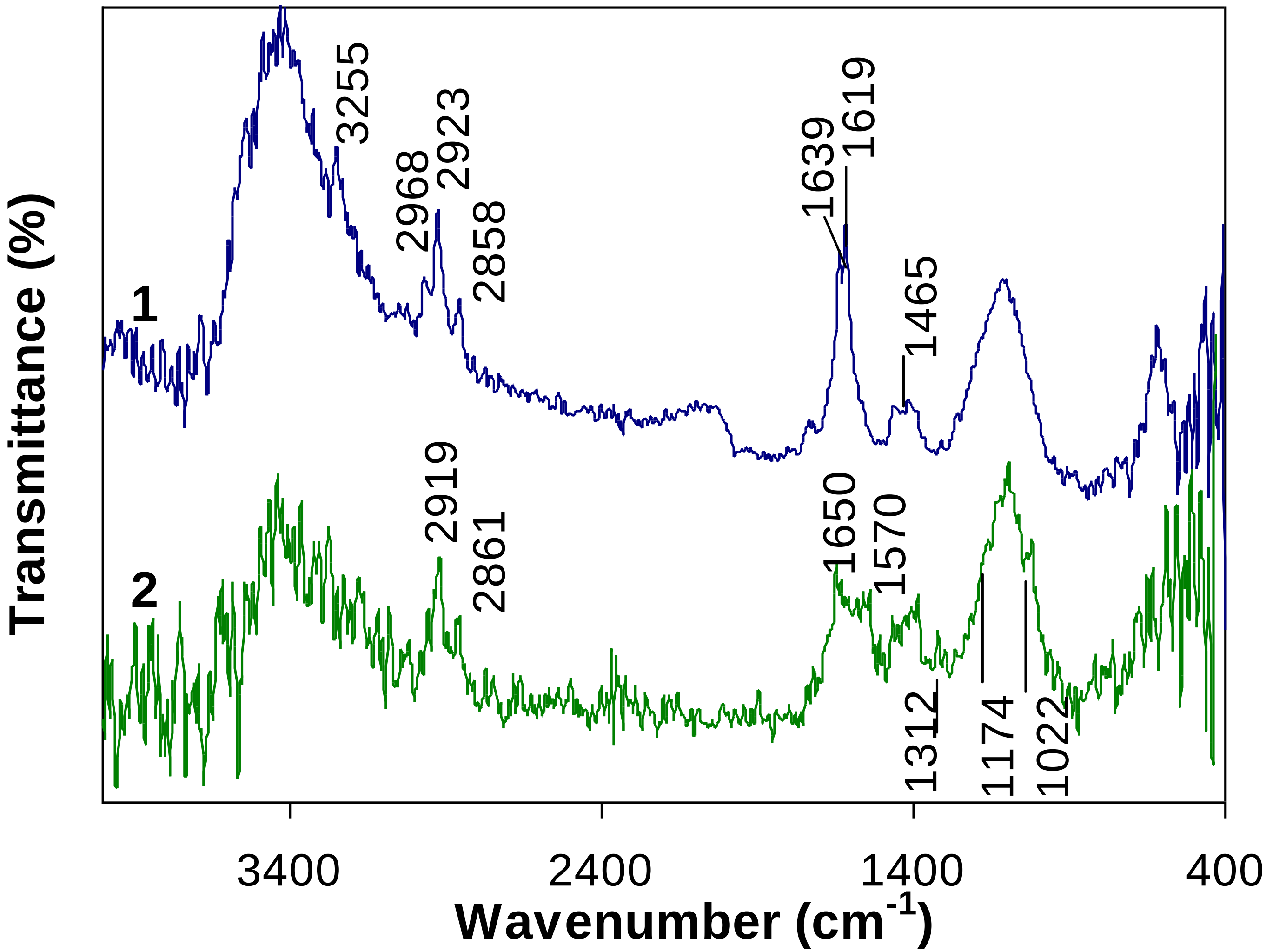
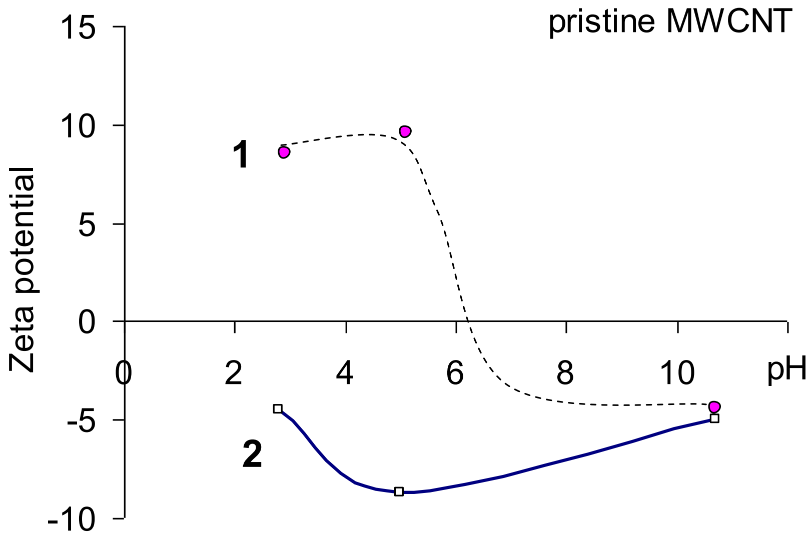
XPS-spectra C1s and O1s MWCNTs: pristine (*a*) and oxidized by H_2O_2 (*b*).

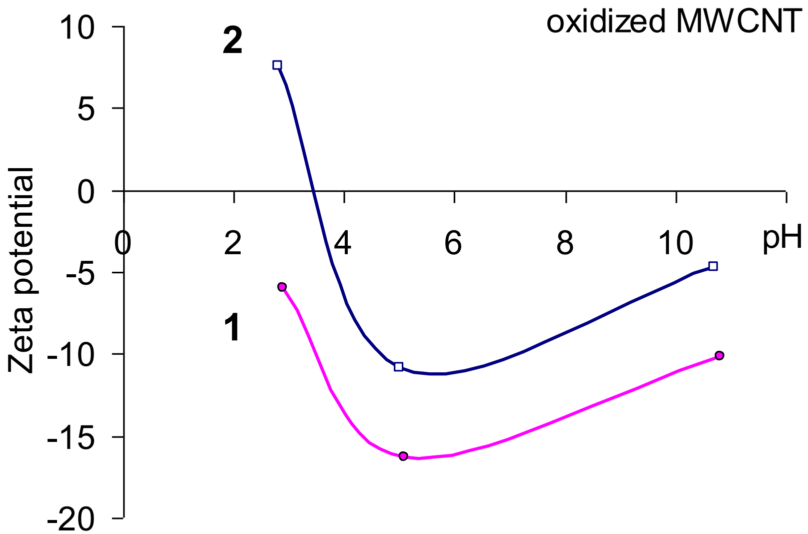


IR-spectrum of the pristine (1) and oxidized MWCNTs (2)

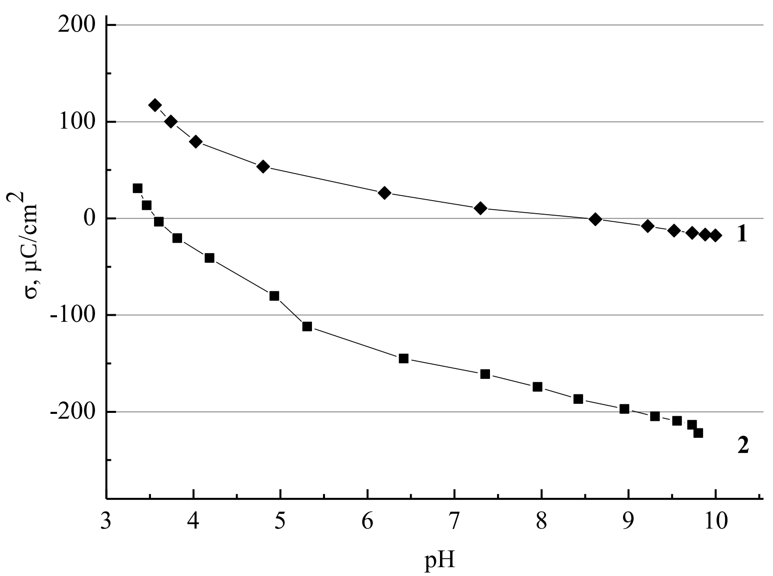


Potentiometric analysis





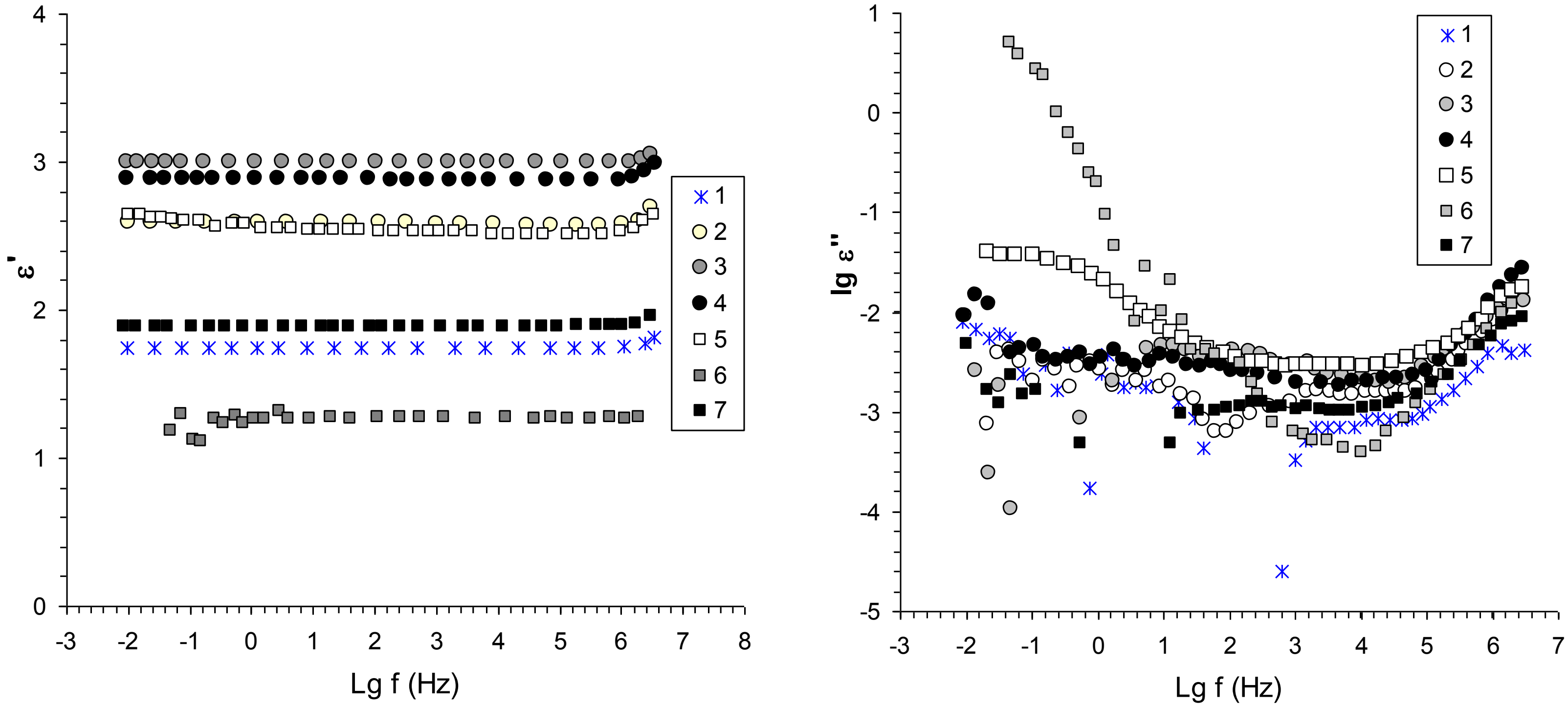
Function of zeta potential from medium pH for pristine or oxidized MWCNTs at concentration of the nanotubes suspension of 0.5 mg/ml in 0.1 (1) or 0.01 mol/l KCl solution (2).



Dependences of surface charge of pristine (1) and oxidized MWCNTs (2) on medium pH

Frequency dependence of real and imaginary parts of the dielectric permittivity for polystyrene (*1*) and polymer filled with pristine (*2-4*) or oxidized MWCNTs (*5-7*); composites were formed without (*2*, *5*) and with magnetic field applying in order to obtain horizontal (*3*, *6*) or vertical (*4*, *7*) orientation of filler nanoparticles.

Filling degree was 0.1 wt%



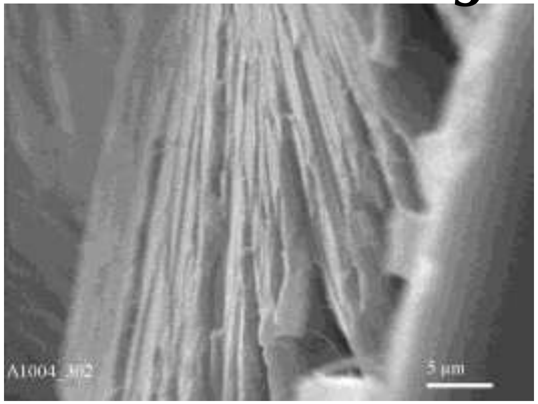
Percolation thresholds and critical exponents for the filled composites (filling degree 0.1-0.8 wt %)

Samples	Percolation threshold wt %	Critical exponent *t*
Polystyrene with pristine MWCNTs	0.05	3.0
Polystyrene with pristine MWCNTs horizontally orientated	**0.16**	**1.75**
Polystyrene with pristine MWCNTs vertically orientated	0.08	3.3
Polystyrene with oxidized MWCNTs	0.18	4.4
Polystyrene with oxidized MWCNTs horizontally orientated	0.19	3.5
Polystyrene with oxidized MWCNTs vertically orientated	0.18	4.6

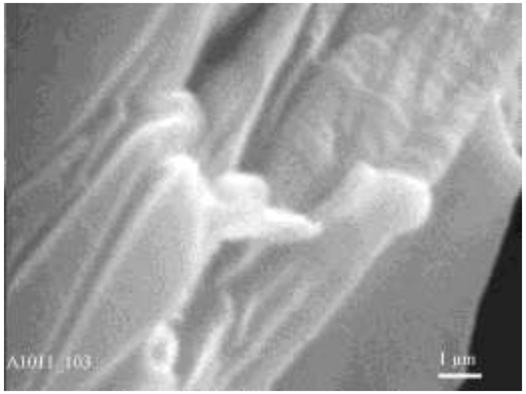
The polystyrene composites filled with MWCNTs

The MWCNTs were treated with hydrochloric acid, ammonium hydroxide, dimethyl-sulfoxide, vinylsilane, or in mixture with the nanosized silica

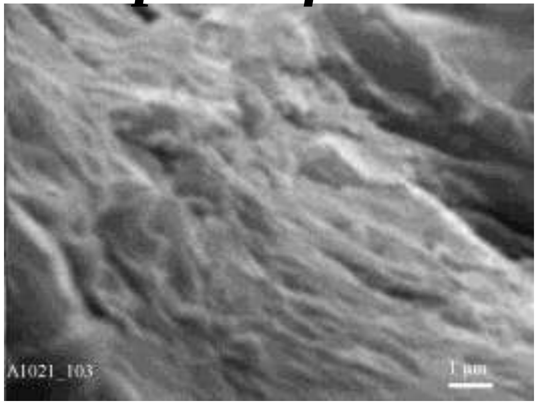
SEM images of the lateral cut of the composite films



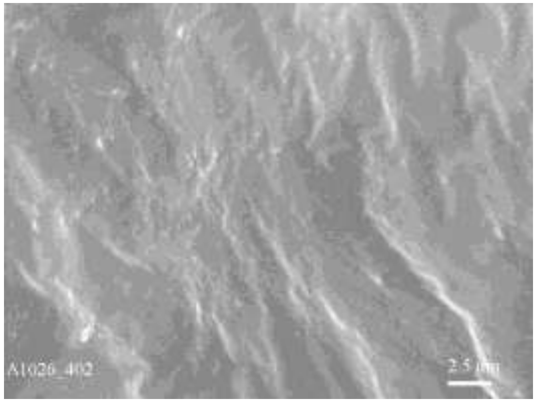
MWCNT + HCl



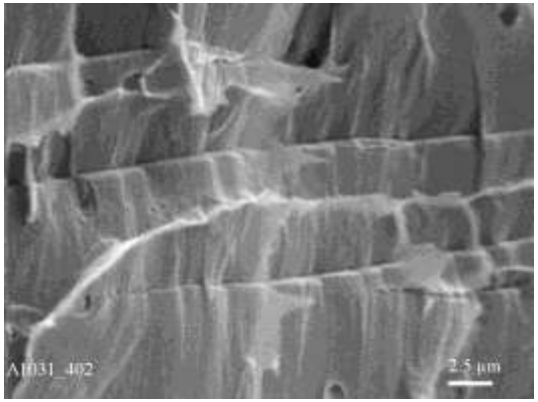
MWCNT + NH_4OH



80% MWCNT + 20%(SiO_2)

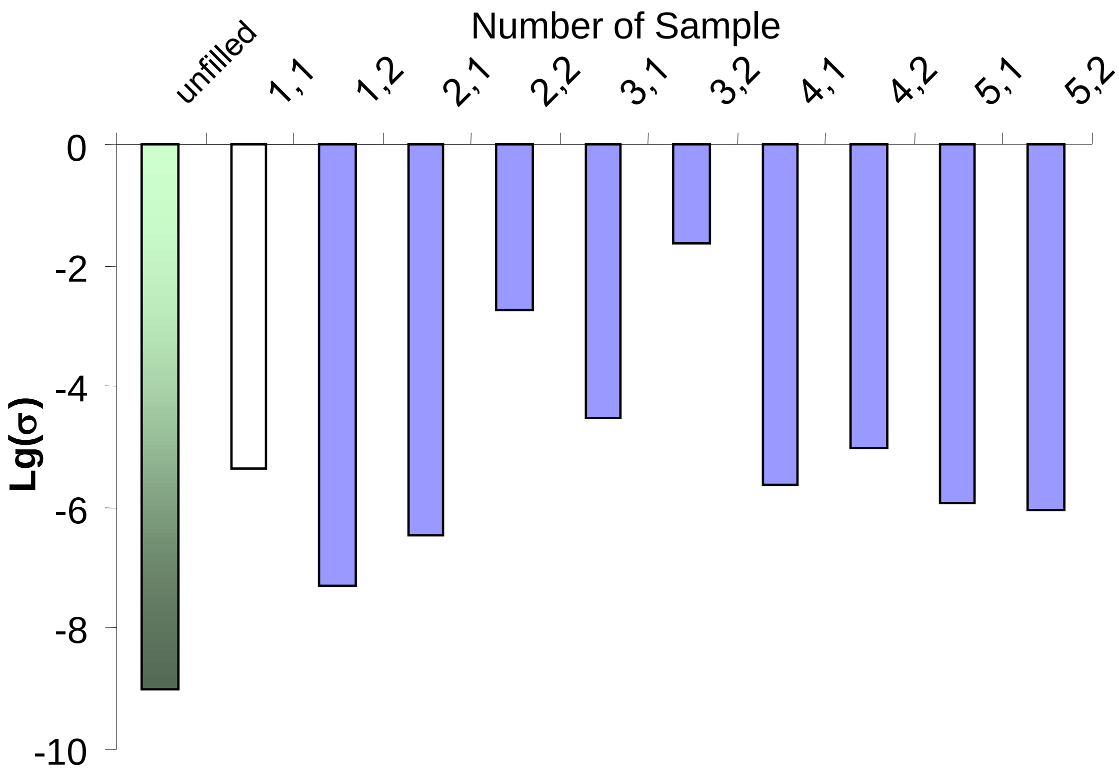


MWCNT + $((CH)_2SO)$



MWCNT + $((C_2H_5O)_3SiCH=CH_2)$

Conductivity measured for the polystyrene composites obtained without and in the magnetostatic field (0.039 T, filling degree – 1 wt%)



Fillers:

1 –pristine MWCNT

2 – MWCNT treated with HCl

3 – MWCNT treated with NH_4OH

4 – Mixture of 80% MWCNT + 20% SiO_2

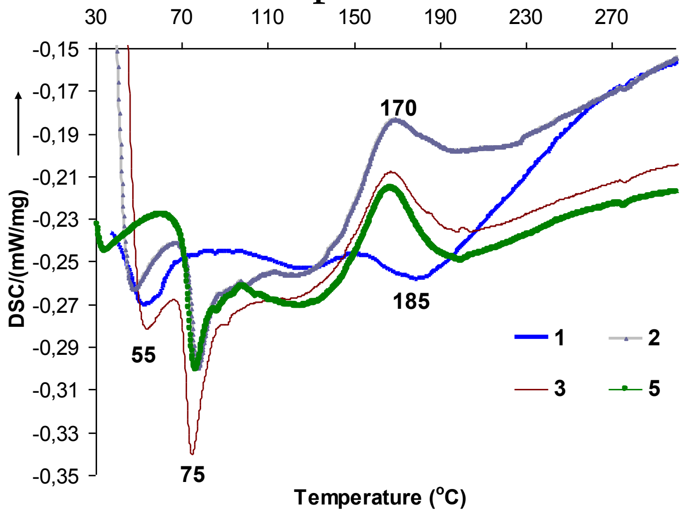
5 – MWCNT treated with $((CH)_2SO)$

Decimal logarithm of conductivity $(Lg(\sigma\times10^{-n})\ (S\cdot cm^{-1}))$

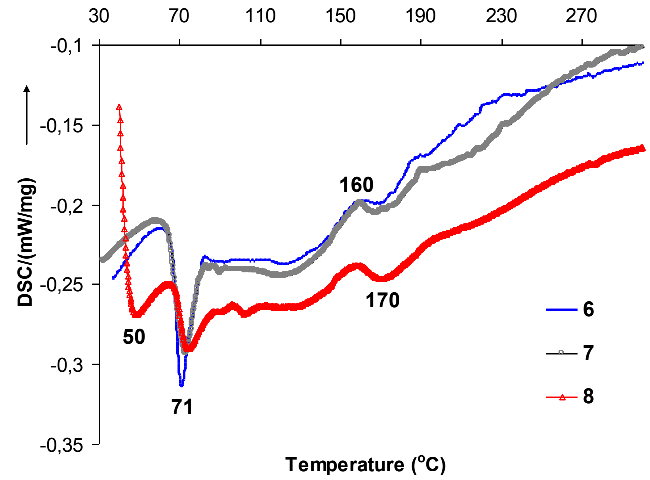
Multiwalled carbon nanotubes /polystyrene composites / Yu.M. Bolbukh, ***G.S. Gunko,*** G.P. Prikhod'ko, V.A. Tertykh // J. Nanostruc. Polym. Nanocomp /-2009.-V. 5.-N1.- P.14-22.

DSC curves for composite films

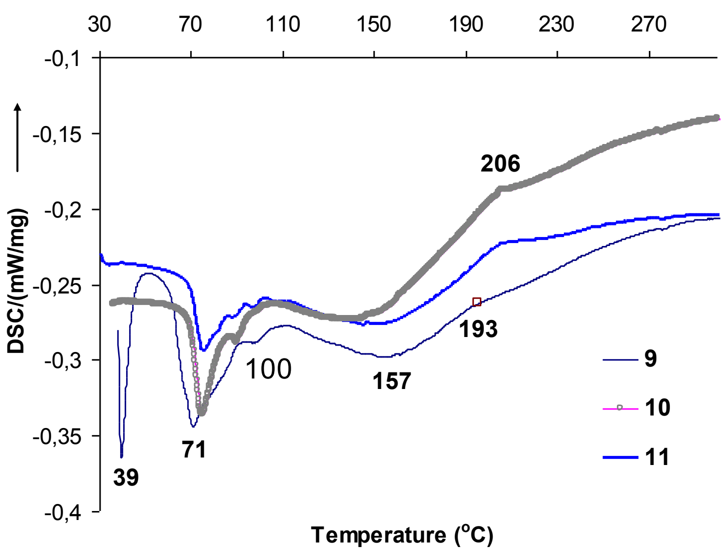
With the pristine MWCNT



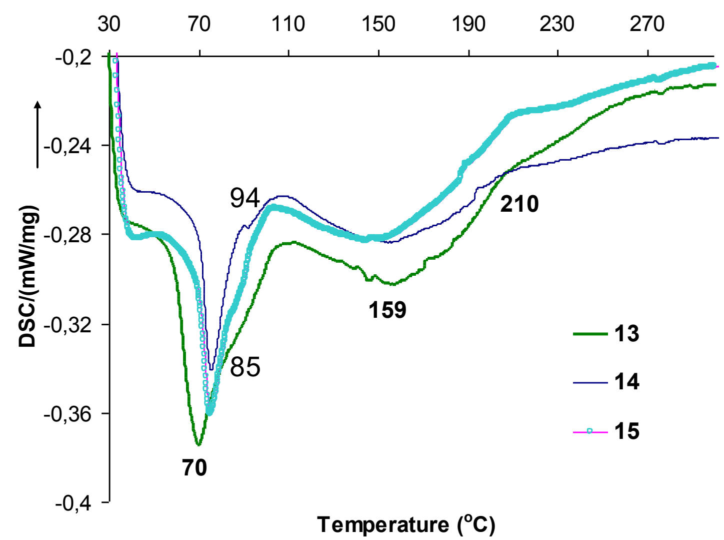
With the oxidized MWCNT



With the pristine MWCNT+HCl

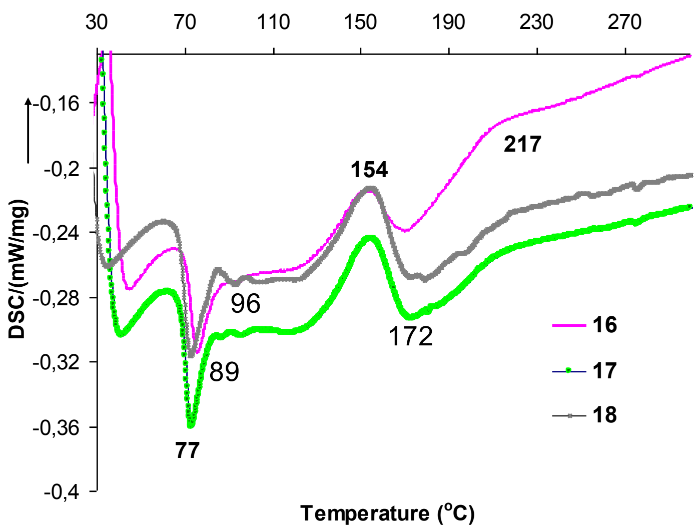


With oxidized MWCNT+HCl

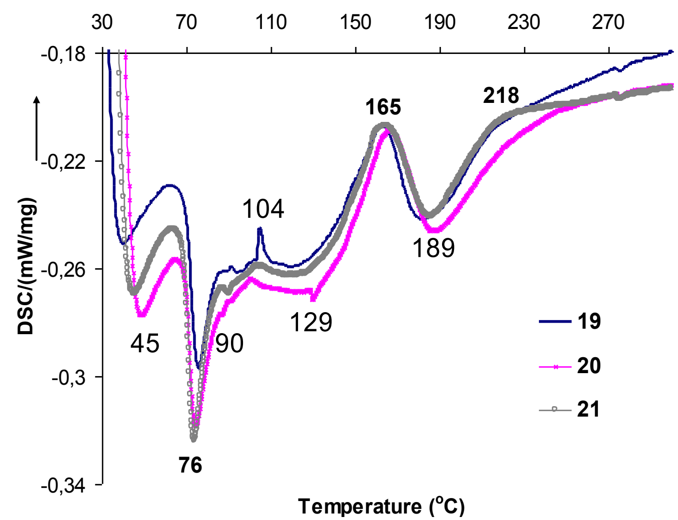


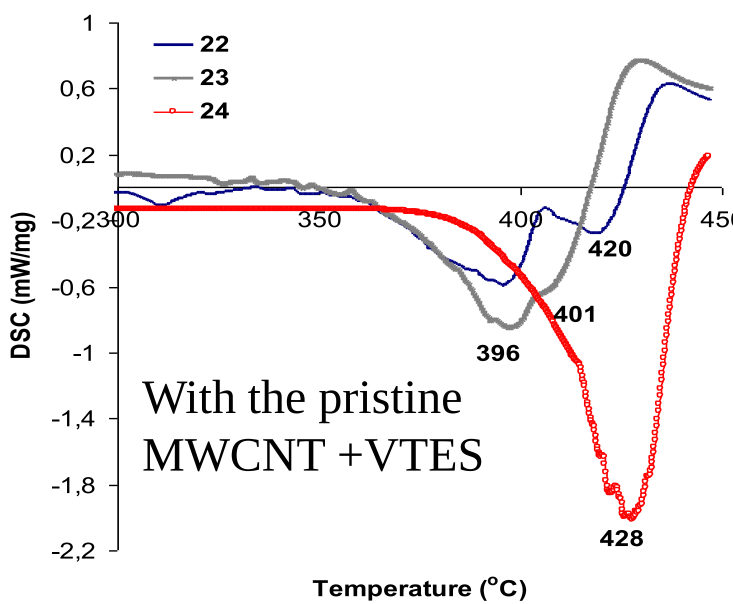
DSC curves for composite films

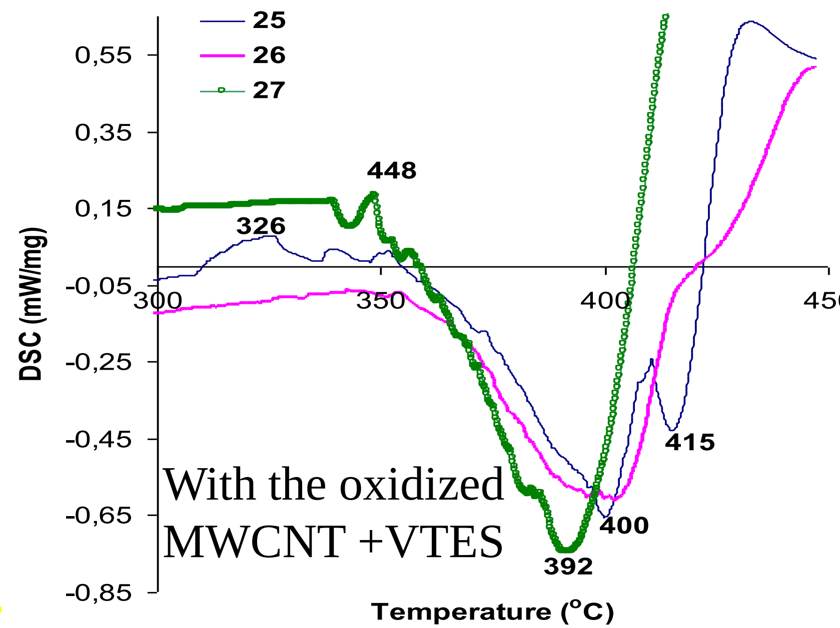
With the pristine MWCNT + NH_4OH



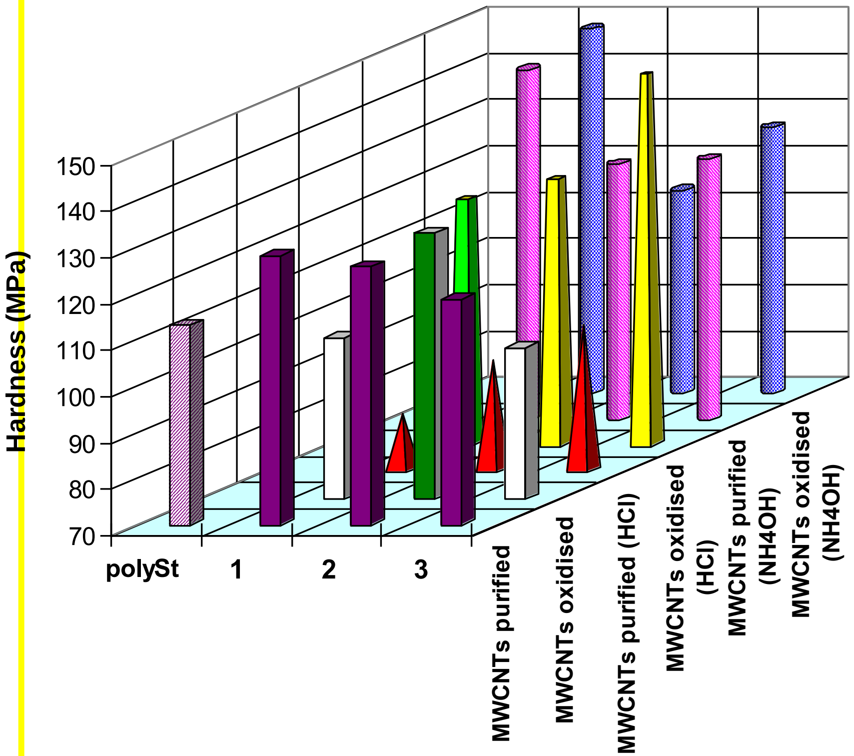
With the oxidized MWCNT NH_4OH

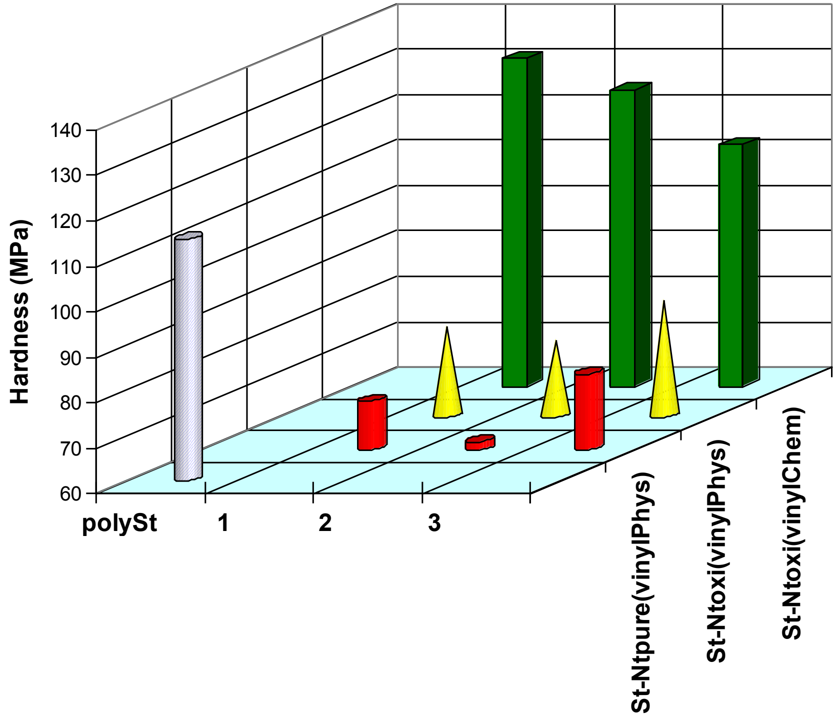




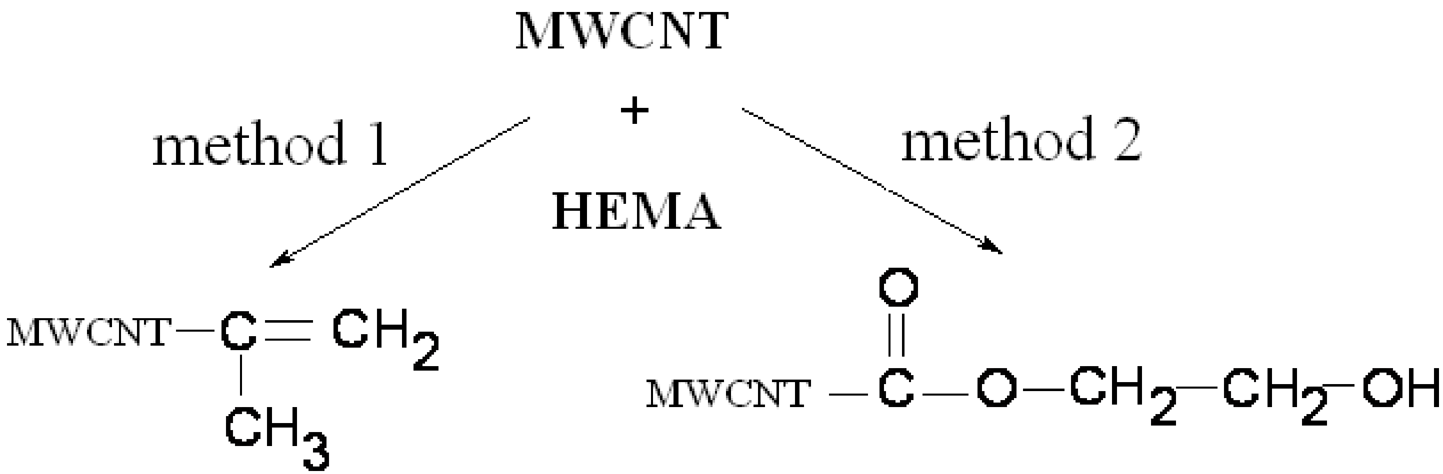


Hardness (MPa) of polystyrene films filled with the pristine and oxidized MWCNT

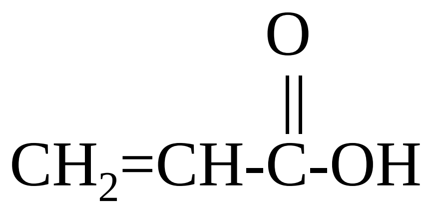




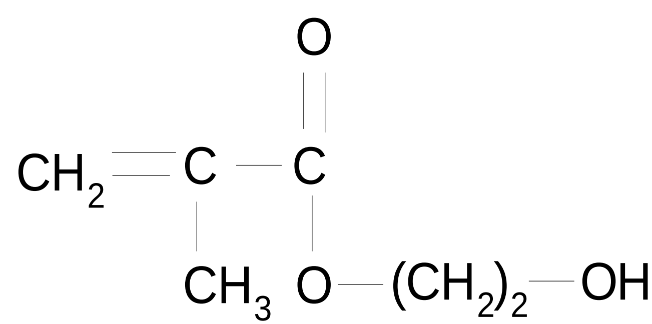
Modification of oxidized nanotubes with acrylates



acrylic acid (AA)



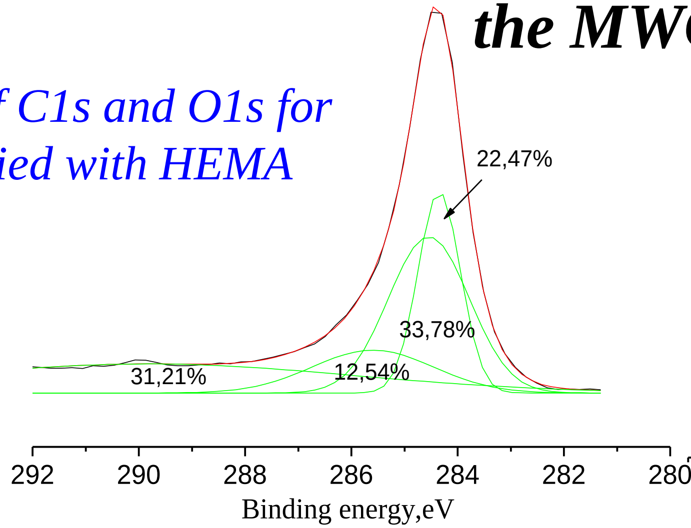
2-hydroxyethylmethacrylate(HEMA)

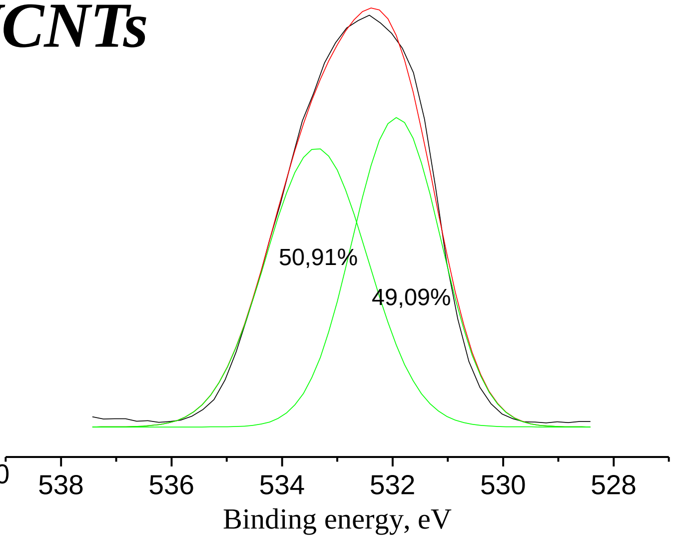


G.S. Gunko, Yu.M. Bolbukh, G.P. Prikhod'ko, V.A. Tertykh, Modification of multiwalled carbon nanotubes with acrylates, *Chemistry, Physics and Technology of Surface*, 2009, Iss. 15, p.343-350.

Method 1 *The attaching via oxygen-containing group of the MWCNTs*

XPS- spectra of C1s and O1s for MWCNT modified with HEMA

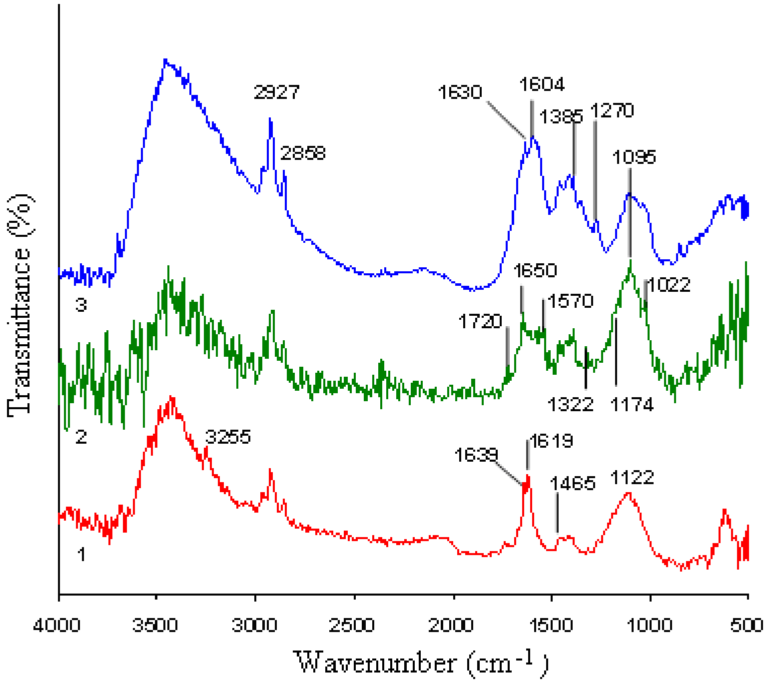




Sample CNT	The relative concentration, %							
	C1s					**O1s**		
	E_b = 284.3 eB C=C	E_b = 285.3 eB C-C	E_b = 286,0-286.5 eB C-OH C-O-C	E_b = 287.3-287.6 eB C=O	E_b = 288.4-288.9 eB -O-C=O	E_b = 531.0-532.1 eB C=O	E_b = 532.8-533.8 eB C-O	E_b = 534.6-535.4 eB $H_2O_{адс.}$
pristine	48.7	3.96	8,04	1	2.7	31.9	68.1	-
oxidized in H_2O_2	38.1	33.3	15.4	~0.3	~0.7	2.7	42.5	54.8
modified HEMA	22.5	33.8	12.5	-	31.2	49.1	50.9	-

Method 1

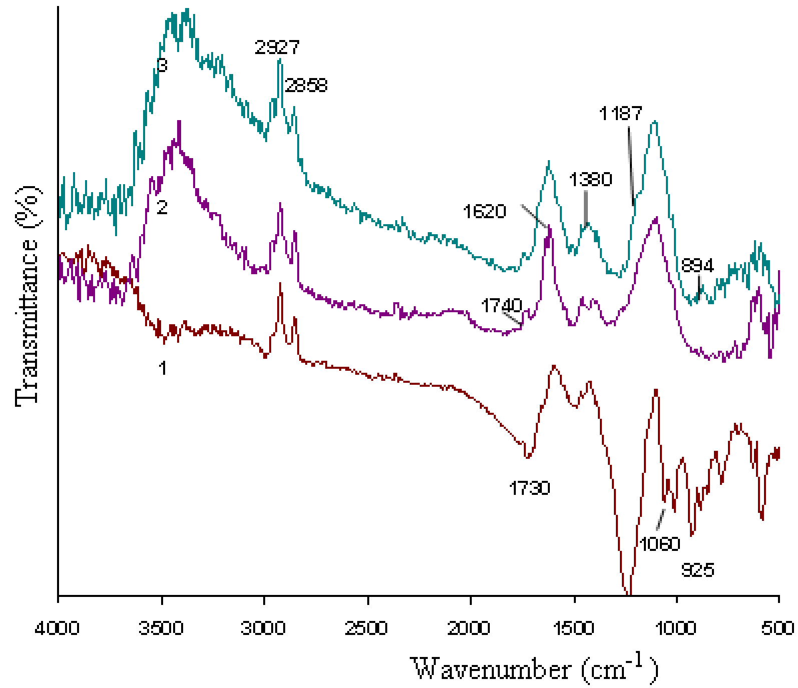
The attaching via oxygen-containing group of monomer



IR spectra of pristine MWCNT (1), oxidized MWCNT (2), and nanotubes modified with HEMA (3)

Method 2

The attaching by methacrylic groups of monomer



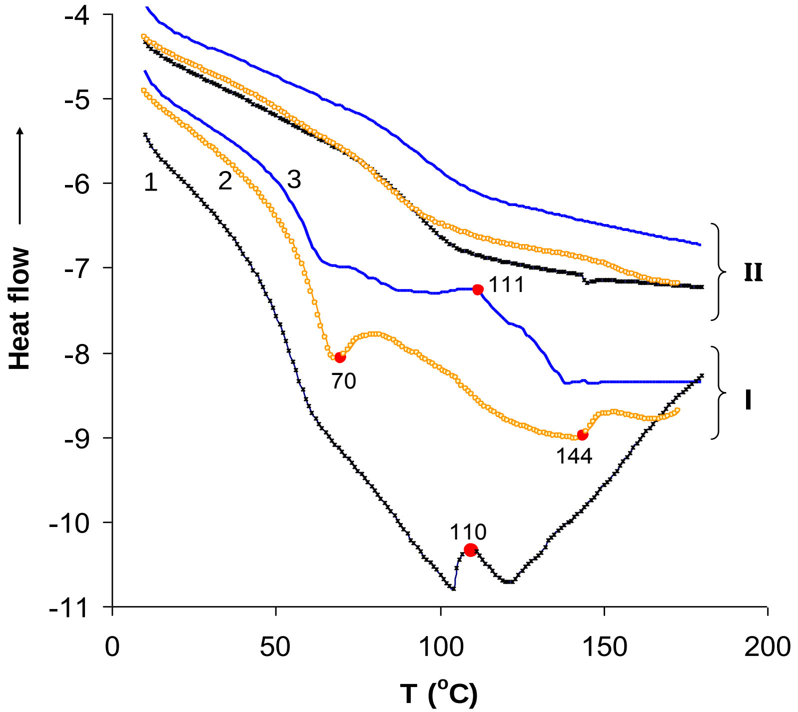
IR spectra of the nanotubes modified with polyHEMA (1), acrylic acid (2) and the AA+HEMA by two step modification approach (3)

Composites based on HEMA filled with MWCNTs

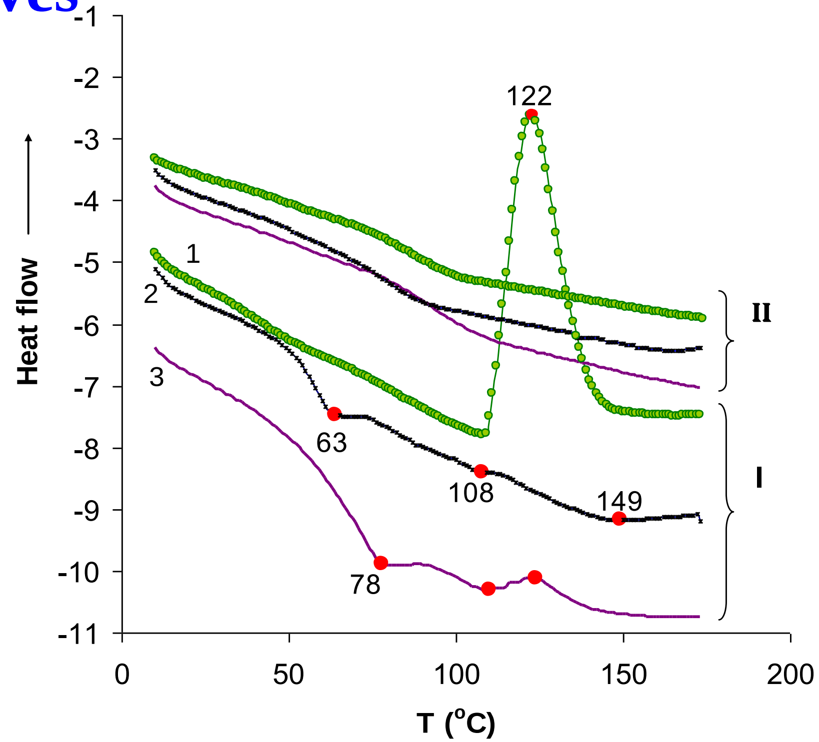
Fillers:

Pristine MWCNTs, oxidized MWCNTs, oxidized MWCNT + HEMA, oxidized MWCNT +CH_2=CH–COOH and oxidized MWCNT +CH_2=CH–COOH +HEMA

DSC curves

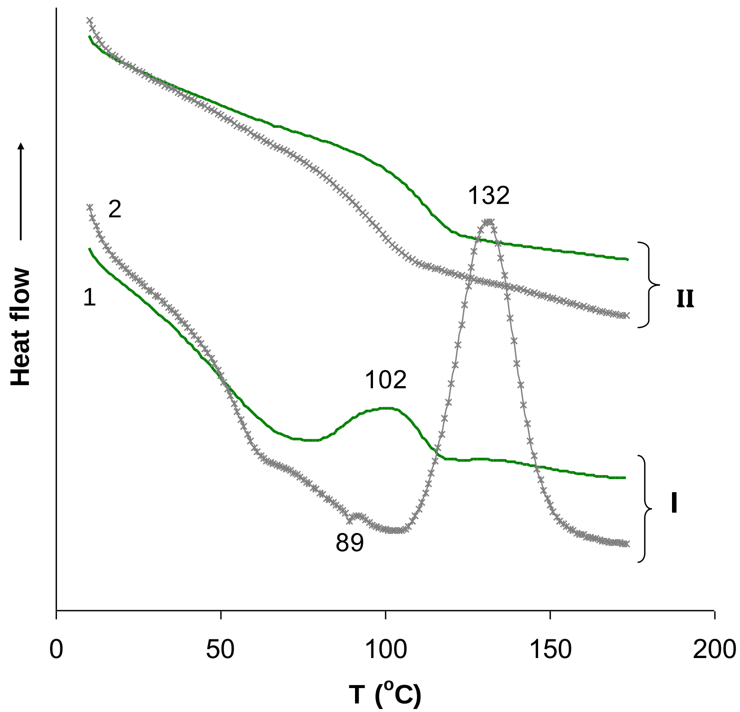


Unfilled polyHEMA (1) and filled with the pristine MWCNTs composites synthesized without (2) and under effect of the magnetic field (3)

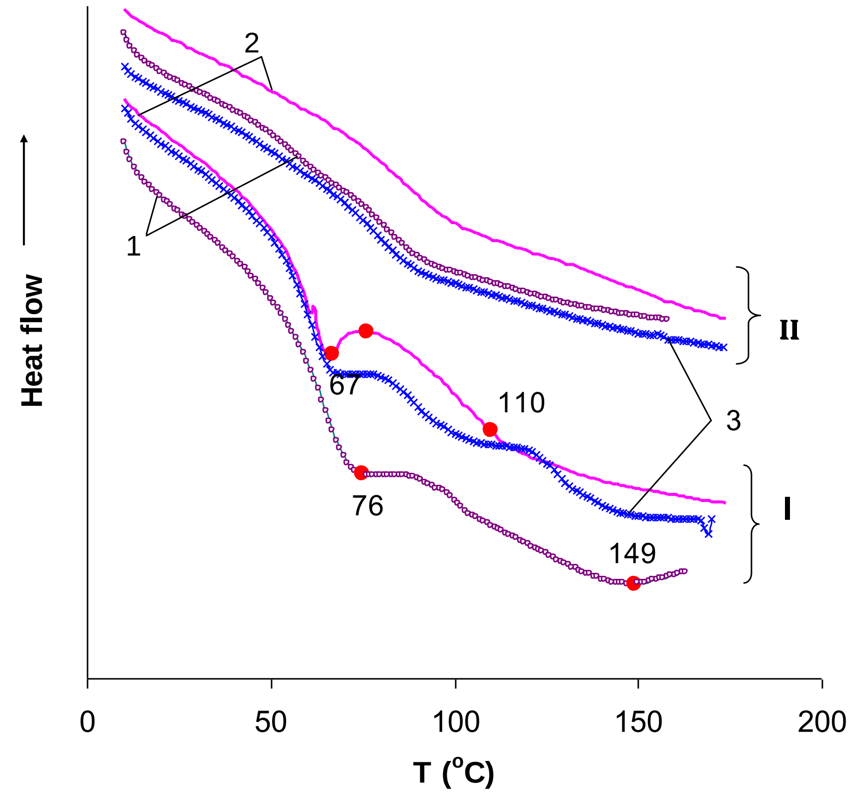


Composite with oxidized MWCNTs synthesized without (1, 2 *) and under effect of the magnetic field (3)

DSC curves



Composites filled with the MWCNT-HEMA synthesized without (1) and under effect of the magnetic field (2)



Composites filled with NT-AA (3) without effect of the magnetic field and filled with NT-AA-HEMA synthesized without (1) and under effect of the magnetic field (2)

21 Kinetic parameters of the thermo-oxidative degradation of composites based on TGA study

Filler/magne-tostatic field	Tm., °C	T*i*/Δm/Ea/n/R^2				Weight loss at 450°C, %
		1	2	3	4	
-	220	280/10/33,83/0,95/0,97	-	**357*/60/181/1,7/0,99**	407/97/-/-/-	99,81
NT pristine	220	264/13/76/1,23/0,98	**330*/59/48/0,7/0,99**	356/82/80/2,8/0,94	377/95/-/-/-	98,57
NT pristine / +	210	270/18/54/0,8/0,99	325/53/28/0,5/0,97	**357*/79/68/1,6/0,97**	367/88/267/8/0,99	97,73
NT oxidized (> initiator)	175	196/6/182/0,2/0,97	254/23/83/0,1/0,98	**300*/61/35/1,2/0,99**	-	98,05
NT oxidized	191	196/3/131/0,1/0,97	280/13/63/0,3/0,99	**357*/72/69/0,5/0,98**	-	98,5
NT oxidized/+	230	-	260/10/77/0,1/0,97	**340*/60/44/0,6/0,99 368*/80/-/-/-**	388/96/187/1,5/0,99	99,32
NT-HEMA	230	-	**243*/21/121/0,4/0,95**	353/85/88/0,8/0,98	419/93/-/-/-	99,3
NT-HEMA/+	210	237/8/87/2/0,96	244-256/13/104/1,5/0,99	**289*/66/180/1,0/0,98**	-	96,6
NT-AA	165	215/7/9/0,3/0,75	225/10/34/1,3/0,89	**300*/63/76/1,2/0,99**	-	98,7
NT-AA-HEMA	165	233/18/49/0,9/0,84	250/28/17/0,3/0,94	**300*/63/41/0,87/0,99**	-	98,4
NT-AA-HEMA/+	220	-	262/10/66/1,3/0,96	**351*/72/58/0,9/0,99**	385/97/-/-/-	99,07

Thermomechanical characteristics of composites based on the polyHEMA

Filler/magnetostatic field	**Tc,°C**	**ε, %**	**$\alpha \times 10^{-4}$, K^{-1}**	**$E_g \times 10^4$, кPa**
-	61	11.3	0,96	473,5
	81	10,1	0,94	526,7
NT pristine	61	**9,1**	1,21	568,9
	80	**4,5**	0,85	**1164,8**
NT pristine / +	61	14,9	0,91	661,0
	76	9,0	0,8	595,83
NT oxidized (> initiator)	57	21,8	0,93	248,5
	67	18,3	0,22	300,7
NT oxidized	50	**5,03**	2,53	860,7
	81	**5,6**	0,66	960,3
NT oxidized/+	59	12,1	0,49	450
	78	11,7	0,55	463
NT-HEMA	85	19,5	0,67	278
	90	16,5	0,91	327
NT-HEMA/+	60	8,2	1,08	634
	76	1,2	0.87	**3650**
NT-AA	52	18,8	1,06	286
	67	20,0	0,16	276
NT-AA-HEMA	65	13,4	1,26	390
	62	39,4	0,46	140
NT-AA-HEMA/+	60	**8,02**	0,14	688
	76	**7,45**	0,85	713

Conclusions

- Oxidation of the nanotubes with hydrogen peroxide leads to formation of a functional layer, consisting mainly of hydroxyl groups.
- Modification of the oxidized multiwalled carbon nanotubes with HEMA and acrylic acid allowed to obtain the layer containing methacrylate (hydrophobic) or hydroxyl (hydrophilic) groups.
- Surface treatment of the MWCNT allows to control properties and structure of the polymer.
- Acrylates (methacrylates) chemisorbed on the nanotubes boundary layers promotes an increase the conversion degree of the monomer HEMA during polymerization
- External magnetostatic field applying allows to obtain oriented polymer matrix through the influence on the filler orientation. The MWCNTs sensitivity is caused by the boundary layer functionality.

Thank you for your attention!