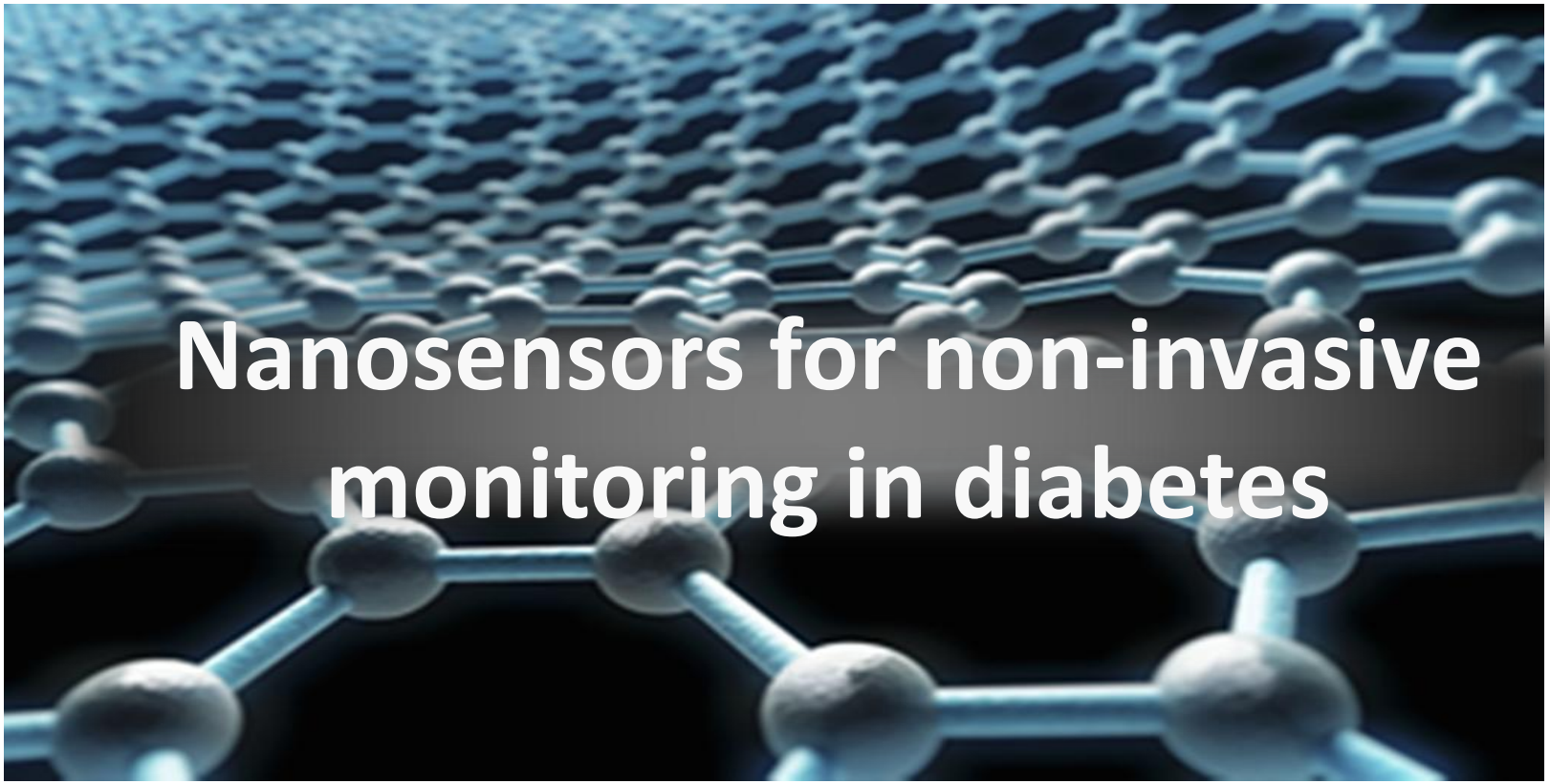

Nanosensors for non-invasive monitoring in diabetes

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Presenting Author

Overview

Up-to-date a research team at the Faculty of Technology and Metallurgy, Ss. Cyril and Methodius University, Skopje, has achieved notable results in the field of polymer-based composites and nanostructures.

One of their recent works was on the design and processing of organic multi nanocomposites for sensors aimed to detect low level of chemical agents (gases) in environmental monitoring.

Since polymer nanocomposite films with functionalized MWCNTs exhibit a large surface-to-volume ratio and unique chemical, optical, and electrical properties; they are a very attractive class of materials for various applications.

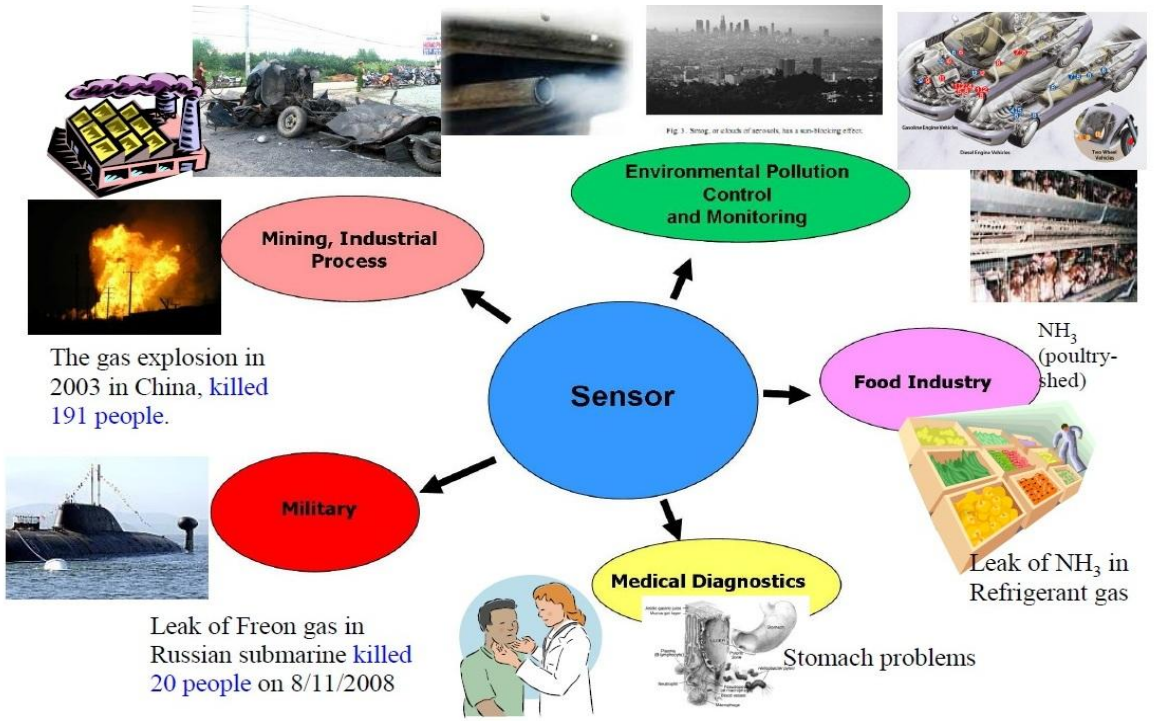
Overview

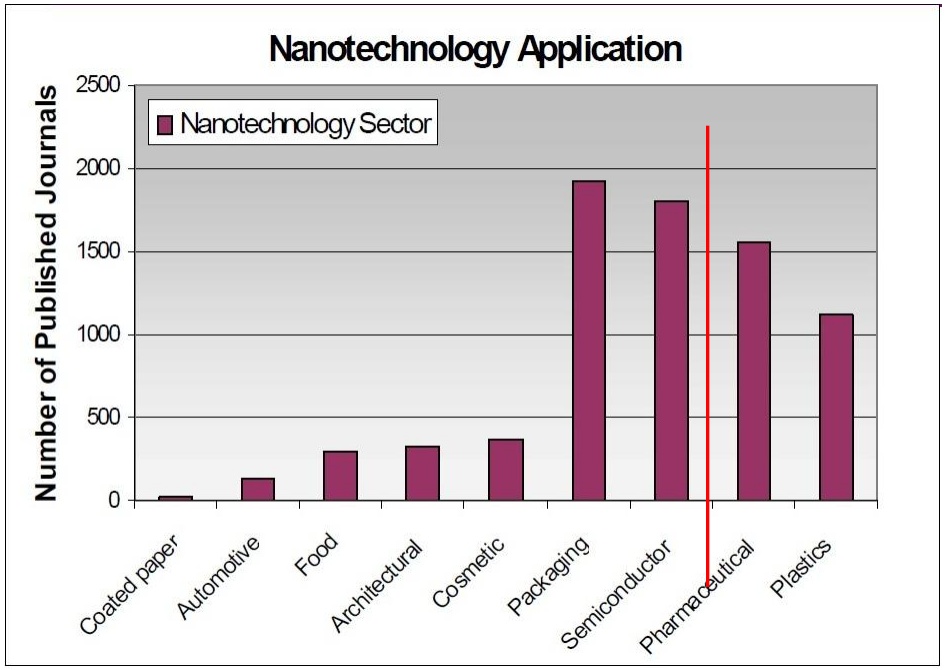
- Furthermore, their functionalization offer new potentials associated with their specific interactions.
- Biocompatible polymer matrices poly (methyl methacrylate) (PMMA) and polycaprolactone (PCL) were used to provide good interfacial bonding between carbon nanotubes.
- In September 2014 the Institute of Public Health of the Republic of Macedonia started a cooperation with the Faculty of Technology and Metallurgy on potential application of these sensors in medical diagnostics and treatment control.
- Therefore, the aim of our future work would be to design, develop and process a nanocomposite (via appropriate modification of CNT and polymer matrix) intended for non-invasive monitoring of diabetes.

Gas sensors are the devices that sense concentration of various gases within an area, usually as a part of a safety system.

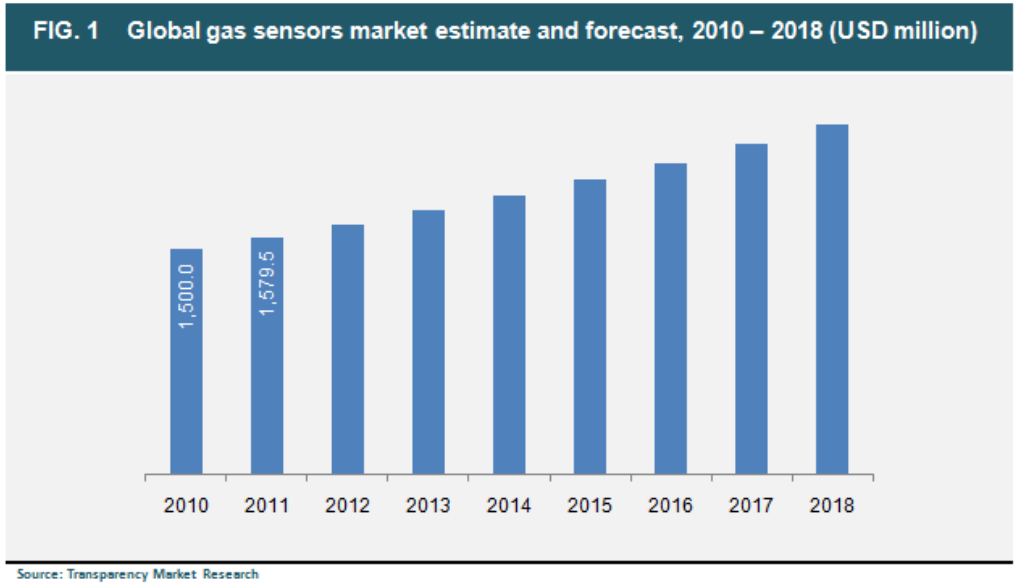
Growing air pollution is the main reason why the gas sensors become more popular in the field of environmental monitoring More than two million people are dying every year from the effects of outdoor air pollution, according to a new study.

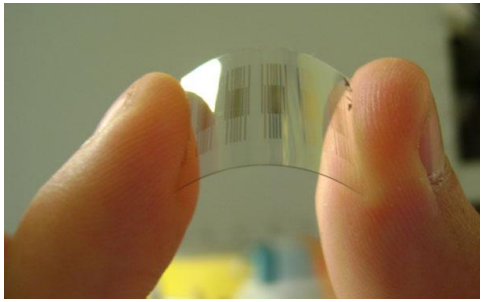
Jason West in Environmental Research Letters said: "Outdoor air pollution is an important problem and among the most important environmental risk factors for health.“





Up to 2009 over £ 1 billion were invested in research and development of gas sensors – acording to the projections the market for gas sensor would reach 2 bilion by 2018.





http://www.transparencymarketresearch.com/gas-sensors-market.html

Sensor	Size	Power	Selectivity	Sensitivity	Stability
Analytical equipment	X	X			
Electrochemical sensors			X		
Catalytic bead sensors		X	X	X	
Metal Oxide Semiconductors		X	X	X	
Conductive polymer sensors			X		X

X = unsatisfactory

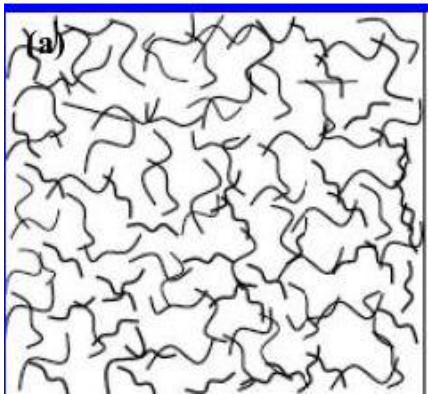
http://www.sensorsmag.com/resources/businessdigest/sbd0704.shtm

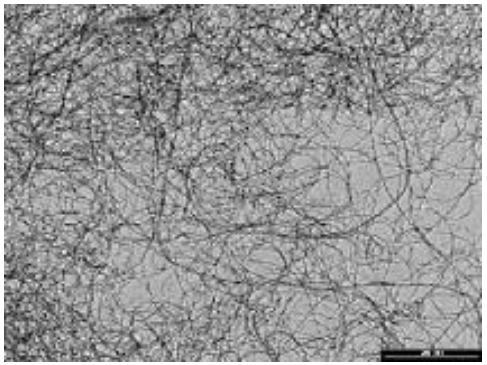
Capone S et. al. Solid State Gas Sensors: State of the Art and Future Activities. Journal of Optoelectrics 2003.

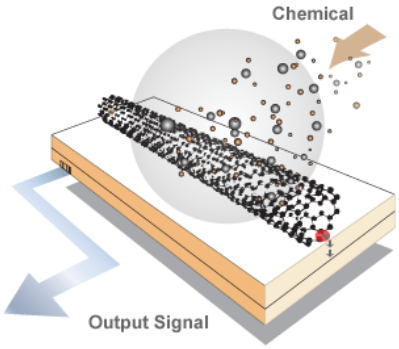
The development of carbon nanotube-(CNTs-)based gas sensors has attracted intensive research interest - because of their potential for selective and rapid detection of various gaseous species and low-power consuming electronics.
The focus was placed by various researchers to improve the sensing performance (sensitivity, selectivity and response time) through the rational functionalization of CNTs with different methods (covalent and non-covalent) and with different materials (polymers and metals).

The aim of the study

- **Therefore, the aim was to develop an efficient gas sensor based on polymer nanocomposites with low cost multiwall carbon nanotubes.**
- **Nanocomposite is composed of biocompatible polymer matrix whose isolationist nature changes after the incorporation of a particular concentration of carbon nanotubes → the electrical, thermal and mechanical properties of polymer nanocomposites are improved.**
- **However, as carbon nanotubes tend to aglomerate in the polymeric matrix – we devote special effort to improve the dispersion of the carbon nanotubes.**
- **The aim was to syntethize polymer nanocomposite – it could be applied as a sensitive part of chemical resistor for detecting of chemical emmision.**





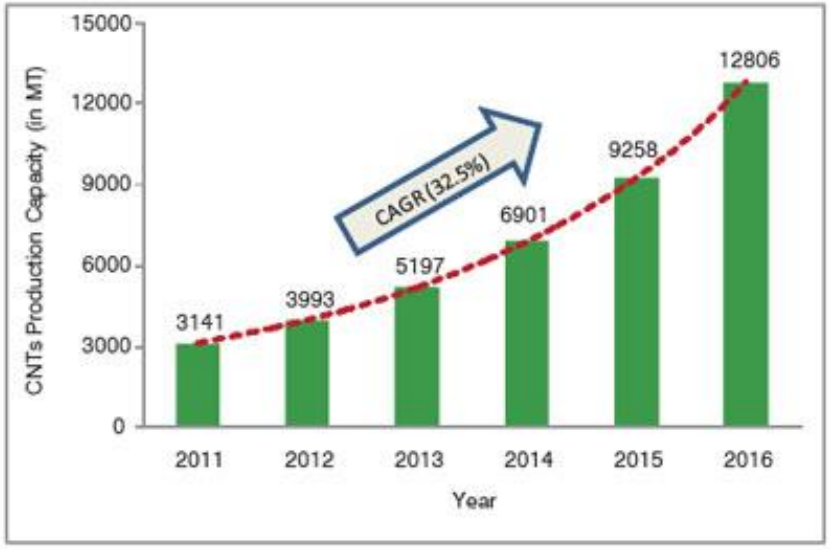


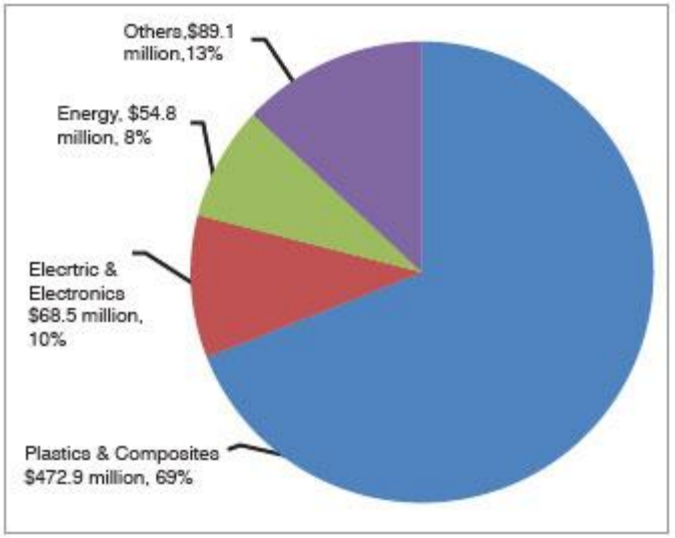
Carbon nanotube-(CNTs-)based gas sensors

—Kong et al. (2001) were among the first to report a type of sensors based on carbon nanotubes .

—Carbon nanotubes are characterized by high specific surface area, hollow-tube structure, nanometer dimensions, excellent electronic semiconductivity and conductivity which favors the adsorption of gas molecules on their atoms arranged entirely on the surface.

—Their application leads to reduction in size and weight of the gas sensors, power consumption and low cost of production.





http://www.nanowerk.com/spotlight/spotid=23118.php

Potential problems

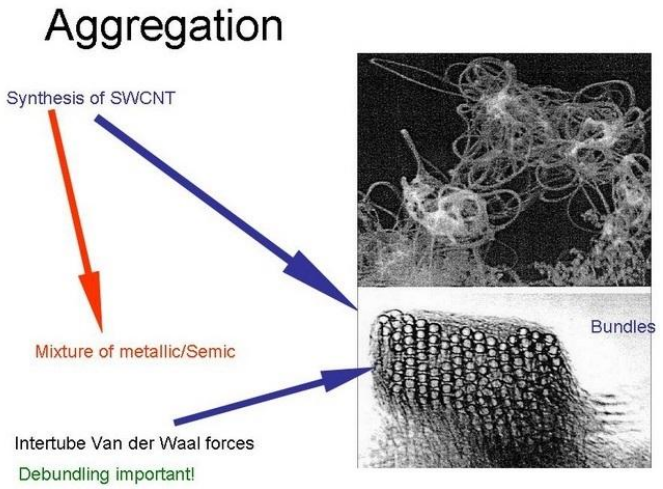
Performance of a polymer / CNTs nanocomposite depend on several factors, among which the most important are:

- **the dispersion of carbon nanotubes in the matrix ,**
- **the interaction between the tubes and the polymer, and**
- **the content of CNTs in nanocomposite.**

Carbon atoms in nanotubes are connected by strong van der Waals forces – they are very stable and inert.

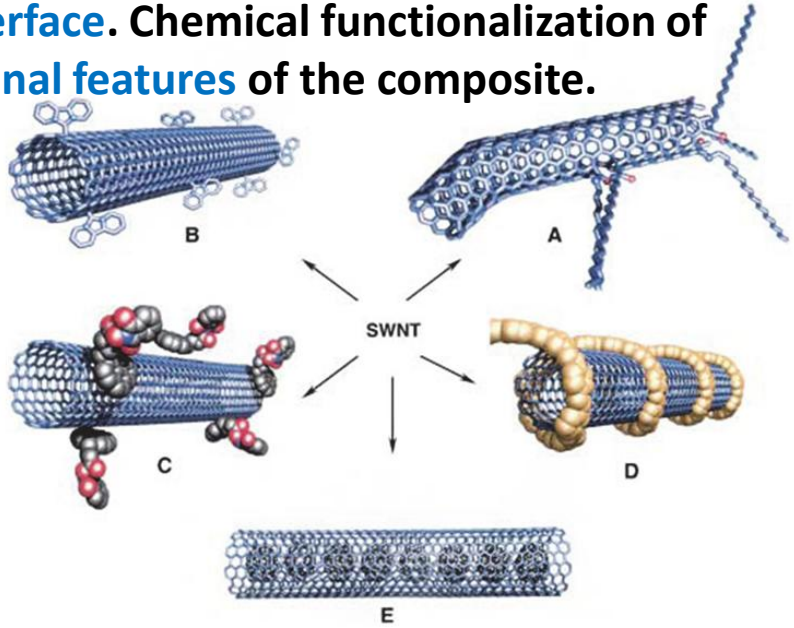
We use funcionalization in order to improve dispersion of CNTs and interaction between the CNTs and the by actually modifying the surface of the tubes.

Electrical properties of composites depend on the content of the CNTs . According to the percolation theory, the application of CNTs reduces the percolation threshold to a much lower volume of filler, than in composites consisted of polymer and activated carbon. The optimal content of carbon nanotubes in a nanocomposite for sensing application is is just after the percolation threshold.



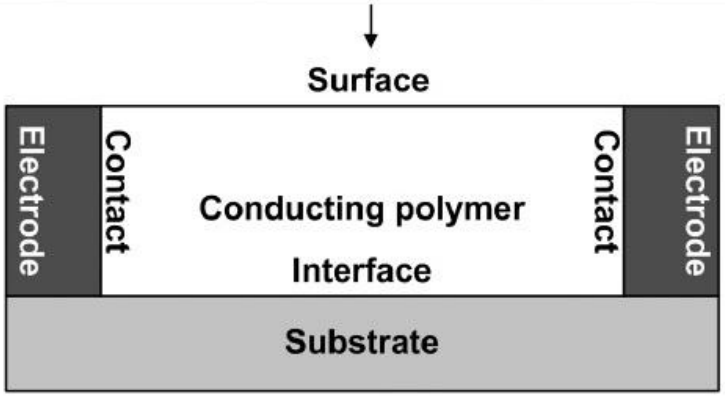
CNTs Functionalization

- To overcome the problem associated with the dispersion of CNTs in polymer nanocomposites we did a functionalization before impregnation in a composite.
- The most common case is a chemical functionalization, which is based on covalent binding of functional groups to the carbon atoms of nanotubes (e.g. carboxyl, carbonyl or hydroxyl groups).
- CNTs functionalized in this way are very soluble in solvents because their hydrophobic nature is changed in hydrophilic as a result of binding of these polar groups.
- These functional groups resulting from the surface modification of the carbon nanotubes can interact with the functional groups in the polymer matrix, which also results in a strong adhesion at the interface. Chemical functionalization of CNT also improved mechanical and functional features of the composite.

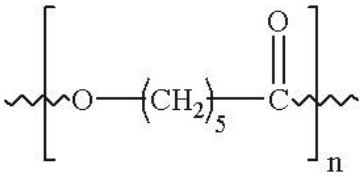


Performance of some of the commonly used gas sensors with polymers and CNTs

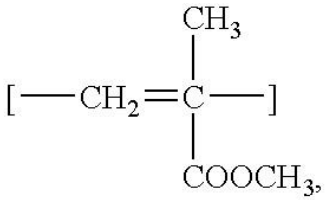
Organic polymer	CNT type	Sensor configuration	Targeted analytes	Detection limit	Response time [s]	Reversibility
PMMA	MWCNT	Chemiresistor	Acetone, Chloroform	N/S	2-5	Reversible
Poly(3methyl thiophene)	MWCNT	Chemiresistor	CH_2Cl_2 $CHCl_3$ CCl_4 CH_4	N/S	60-120	Reversible
Poly (vinyl acetate)	MWCNT	Chemiresistor	Ethanol, Cyclohexane Tetrahydrofuran,	N/S	1200	Reversible
Polyaniline	MWCNT	Chemiresistor	Triethylamine	500 ppb	200-400	Reversible



All these are chemiresistors - the resistance is increased in contact with analytes - with the shortest response time of PMMA composites with CNTs. All these devices are cheap, they have good selectivity , sensitivity, and low power consumption.



ПолиКапролактам



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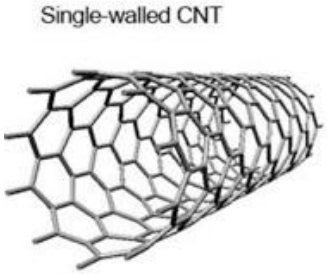
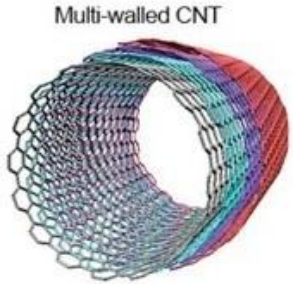




Therefore, the aim was to create a chemical gas sensor which can detect different types of gases.

First, the suitable polymer matrices were chosen (PMMA and PCL) based on previous experiences and literature. These polymers possess many advantages over other polymers, primarily - their high elasticity, increased resistance to moisture, speed of processing, long life, recyclability and biocompatibility.

We used a few types of cheap multiwall carbon nanotubes (for a comparison - single wall carbon nanotubes).

Before deploying the nanotubes in both types of polymer, they were purified and functionalized in different ways for 3 hours, defined as optimal time in previous researches.

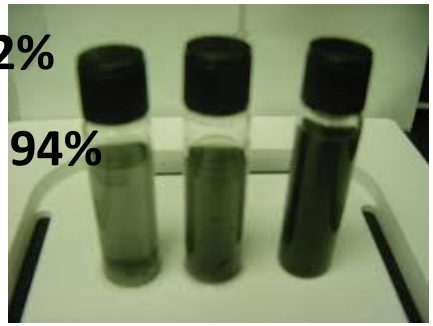
The initial and functionalized tubes were structurally characterized by several techniques and impregnated in the polymer matrix. The synthesized nanocomposite films were structurally characterized , and then exposed to vapors of acetone and chloroform. Sensor activity of nanocomposite films was determined by electrical measurements, and their sensitivity was monitored by the change of their electrical resistance.

Chemicals and Materials

Types of MWCNTs:

A (obtained by pyrolysis) ⇨ d = 50÷100 nm, purity ~ 82%

P (obtained by CVD process) ⇨ d = 10÷40 nm, purity ~ 94%



SWCNTs: d = 1÷2 nm, purity ~ 94%

2 types of polymer:

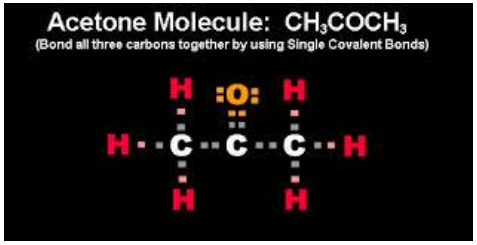
PMMA $(C_5H_8O_2)_n$ ⇨ ρ =1,15÷1,19 g·cm^{-3}; Tt = 130°C; Tg = 100÷105°C

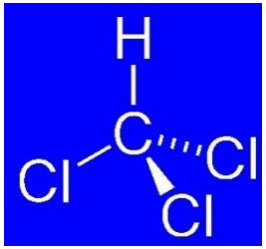
PCL $(C_6H_{10}O_2)_n$ ⇨ ρ=1,145 g·cm^{-3}; Tt = 59÷64°C; Tg = –60°C

Solvents: CCl_4 и CH_2Cl_2 (carbon tetrachloride and dichloromethane)

Funcionalization : HNO_3 и $NH_4OH+H_2O_2$

Agents to vaporize: acetone and chloroform and dimethylformamide.





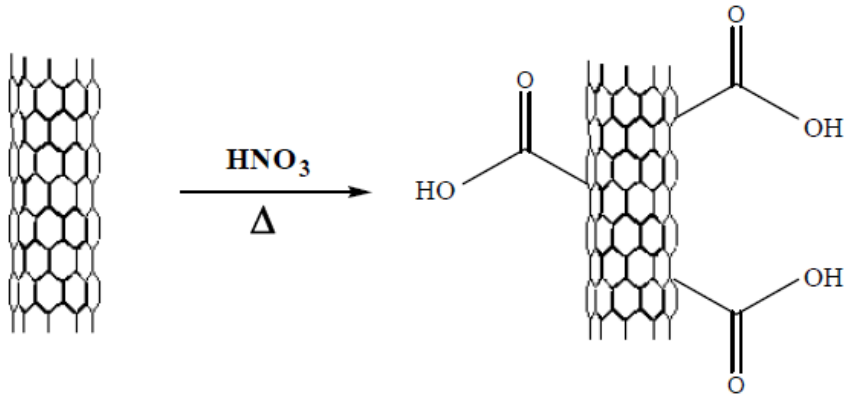
MWCNTs Purification

MWCNTs always contain impurities, such as amorphous carbon, fullerenes, metal particles and other. They adversely affect the thermal stability of the nanotubes, contributing to accelerated oxidation - combustion of carbon in the tubes.

Therefore, to purify these undesirable impurities and enhance their thermal stability, they were subjected to further purification treatment .

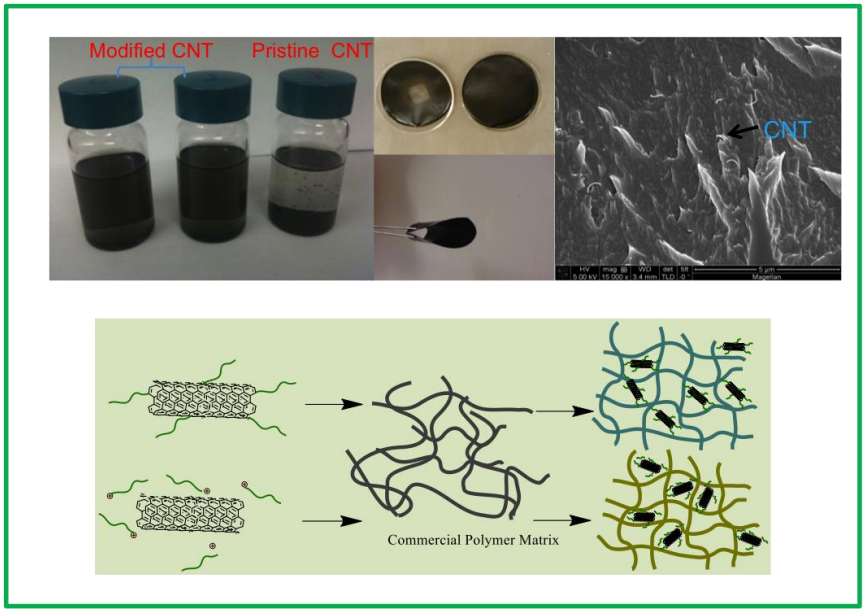
MWCNTs were purified and activated by two alternate methods: with acid and with base.

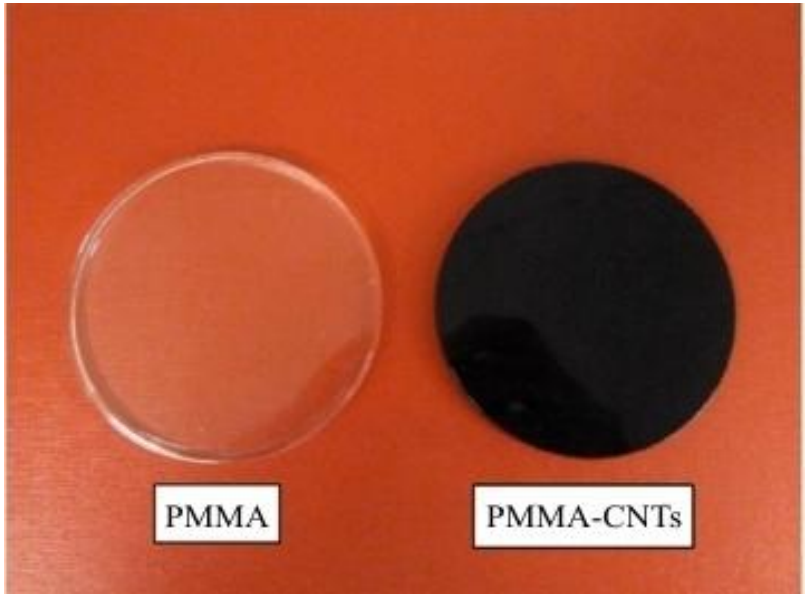
During purification process opening of MWCNTs ocurred - thus generating larger active surface area. The different types of MWCNTs that were used, were activated in 28 % nitric acid and ammonium hydroxide with hydrogen peroxide (1:50).



Method of preparation

—Nanocomposites were prepared by the method of solvent evaporation.
—Firstly, MWCNTs were immersed in the solvent carbon tetrachloride.
—Then we prepared a solution of the polymer matrix (poly (methyl methacrylate) - PMMA in the same solvent (20%). After dissolving the polymer we mixed the polymer matrix solution with the nanotubes in the solvent, and then the resulting solution was mixed further for 30 minutes in an ultrasonic bath at room temperature.
— Then , the solution was poured into a Petri dish and th esolvent was allowed to evaporate at room temperature After three days of drying at ambient conditions, the resulting film was dried in a vacuum dryer at a temperature of 50 °C

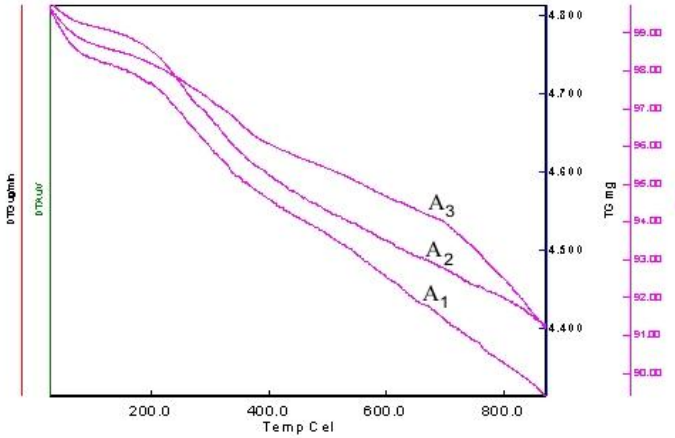


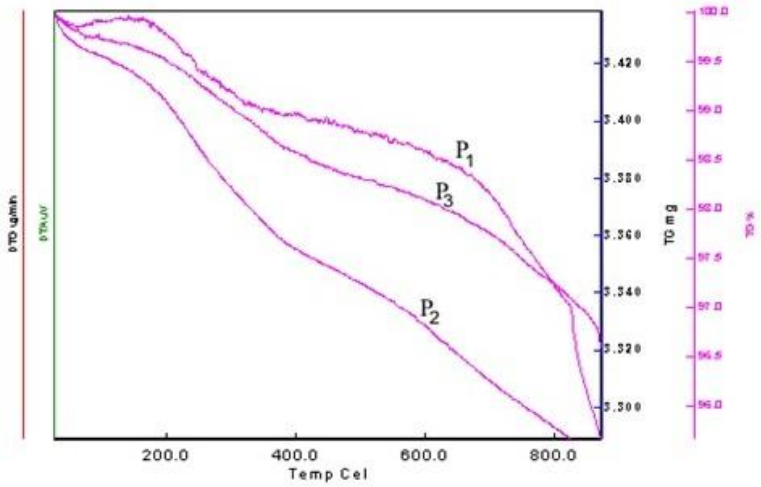


Thermal gravimetric analysis (TGA) of modified MWCNTs

1. TGA/DTA

Примерок	T_{d1} [°C]	T_{d2} [°C]	T_{d3} [°C]	T_{d4} [°C]	T_{d5} [°C]
A1 MWCNTs	48,7	212,3	532	669	761
A2 MWCNTs	52,2	174,6	310	/	799,3
A3 MWCNTs	49,6	202,2	334	539	704
P1 MWCNTs	/	146,8	/	657,6	825
P2 MWCNTs	/	177,1	/	555	812
P3 MWCNTs	/	189,6	/	673,2	870



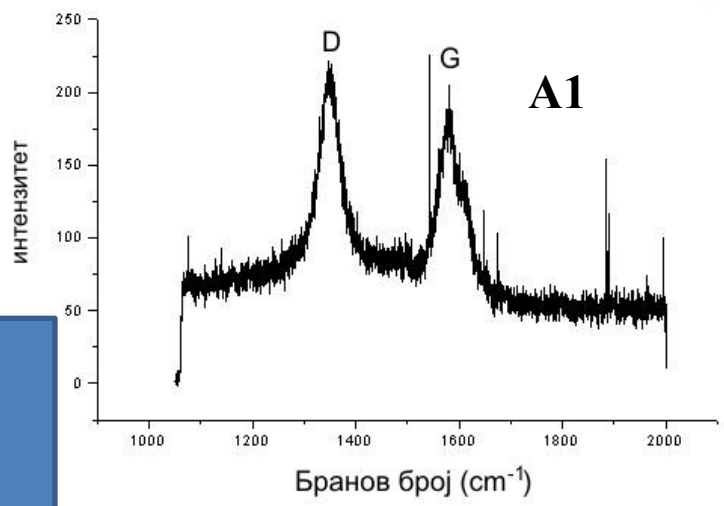


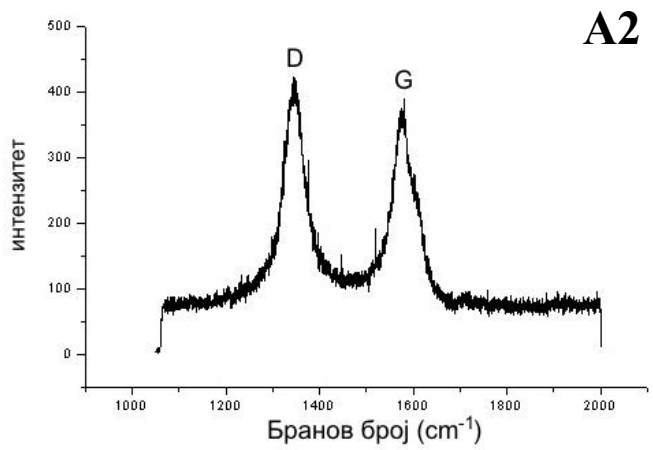
Samples A2 and P3 showed the highest thermal stability whose complete combustion temperatures are higher than in the initial sample → funcionalization affects and improves the thermal stability of the two series of tubes

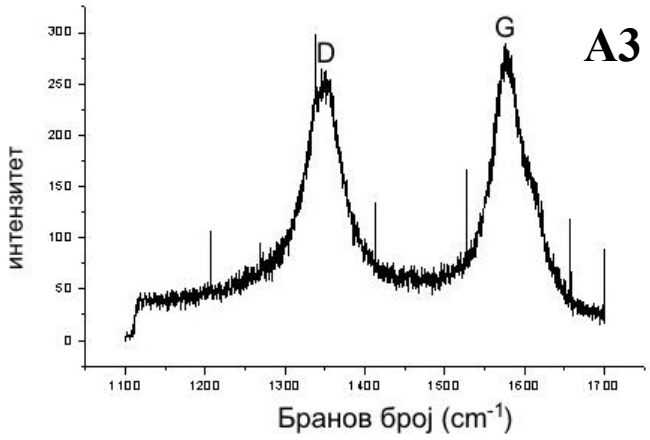
Raman spectroscopy of modified MWCNTs

Примерок	I_D/I_G
A1	1,2
A2	1,1
A3	0,9

—The values of the ID / IG ratio is greater in CNTs before than after treatment with the smallest value for the sample A3.
—A2 - a relatively large amount of amorphous carbon remains unchanged.
—A3 - the modifition was more effective in CNTs modified with base

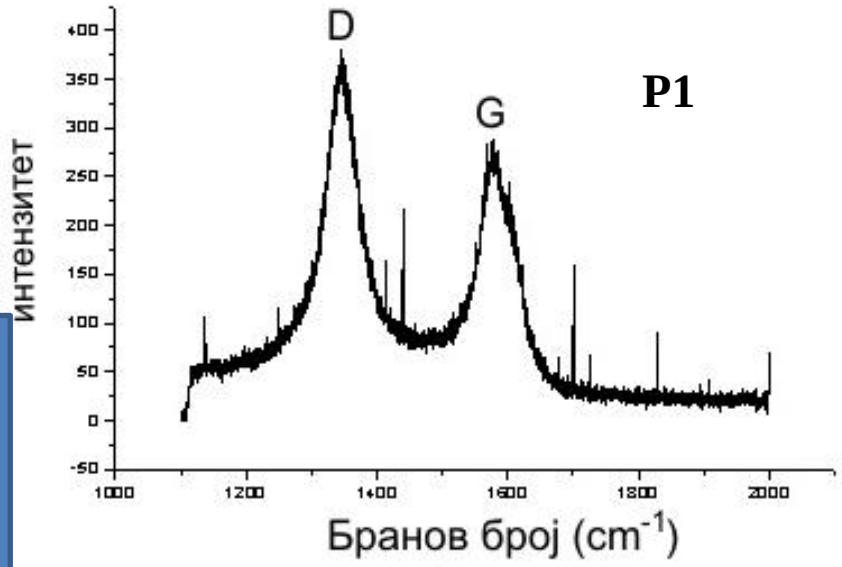


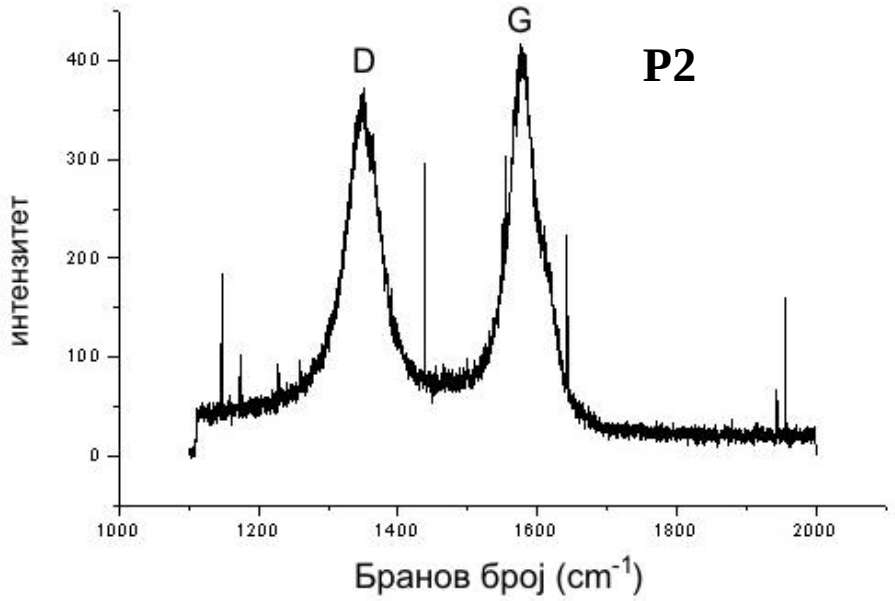


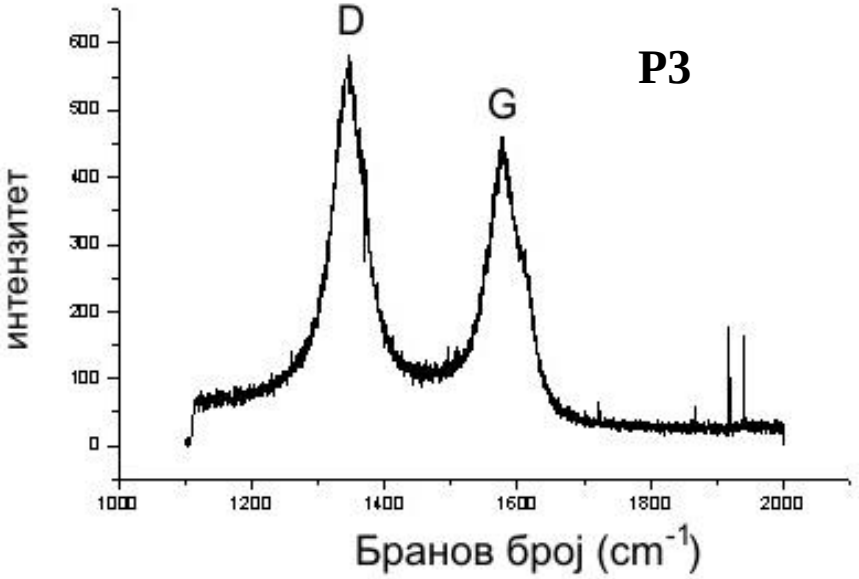


Примерок	I_D/I_G
P1	1,3
P2	0,89
P3	1,25

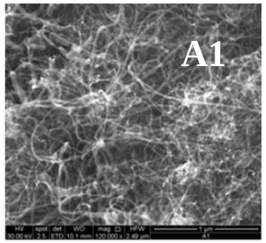
Funcionalization affected ID / IG ratio reducing its value after treatment with acid and base, with acid treatment showing more intensive reduction.
G – peak indicates more efefective purification and better structure arrangement in sample P2.

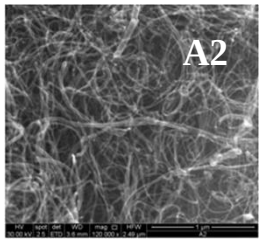


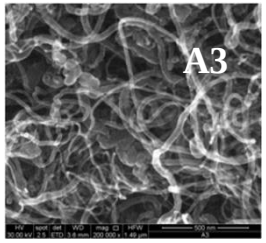




Energy Dispersive X-Ray Analysis (EDAX)

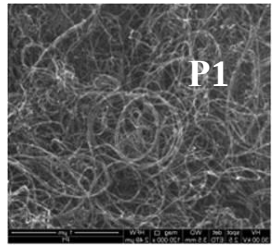


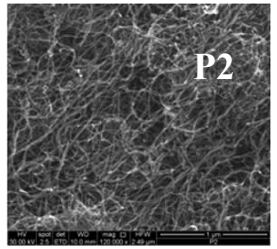


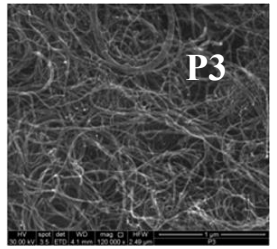


Sample	C	O	Al	Si	Ca	Fe	Co	Cu	Σ
A1	85.12	9.08	4.31	0.12	0.05	0.76	0.47	0.09	100
A2	85.10	8.16	5.33	0.04	0.00	0.79	0.52	0.06	100
A3	85.25	7.92	5.16	0.07	0.09	0.90	0.56	0.07	100

EDAX- to identify elemental composition before and after funcionalization with acid and base treatment → weak purification and generation of COOH groups (weak funcionalization).



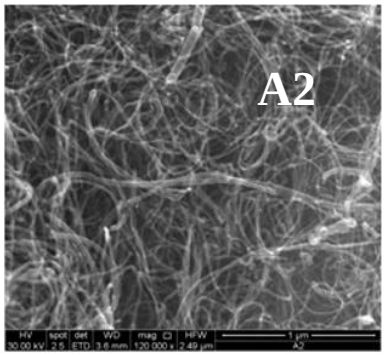


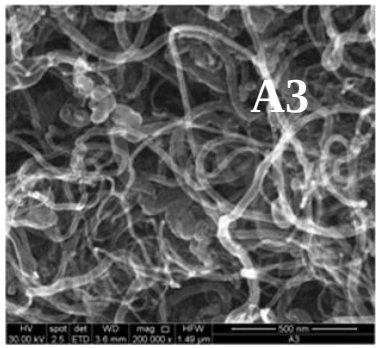


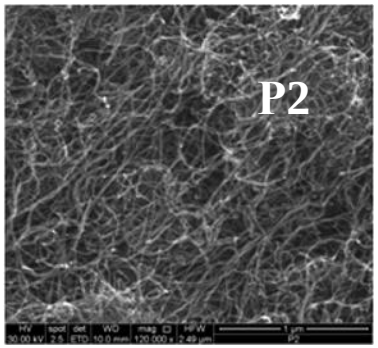
Sample	C	O	Al	Si	S	Fe	Ni	Cu	Σ
P1	94.72	2.89	1.63	0.02	0.03	0.54	0.09	0.08	100
P2	92.49	4.79	2.10	0.02	0.04	0.40	0.06	0.10	100
P3	92.43	4.07	2.45	0.13	0.03	0.72	0.08	0.10	100

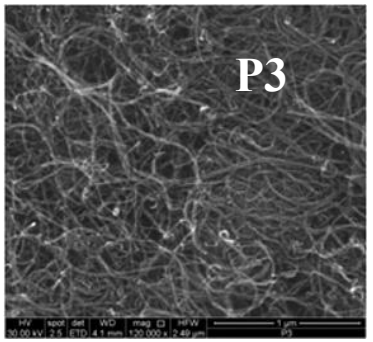
The higher oxygen content after modification →succesful funcionalization and creation of new COOH groups (especialy in sample purified with acid).

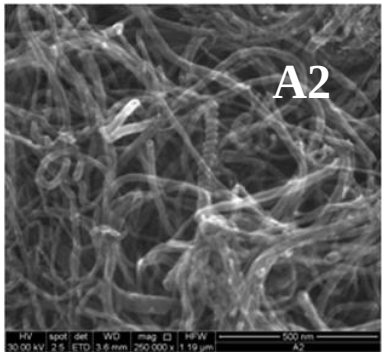
Scanning electron microscopy (SEM) of modified MWCNTs

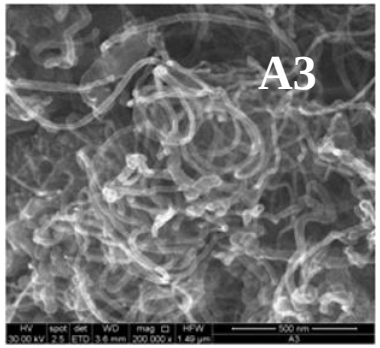


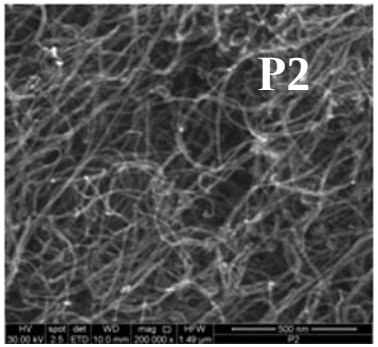


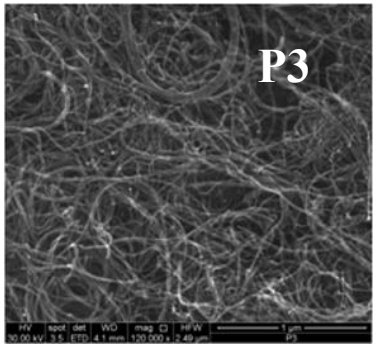


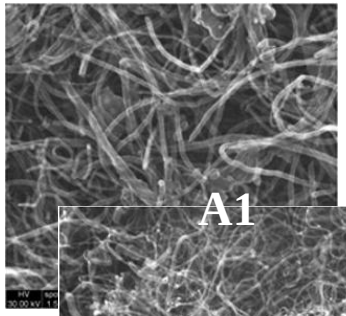


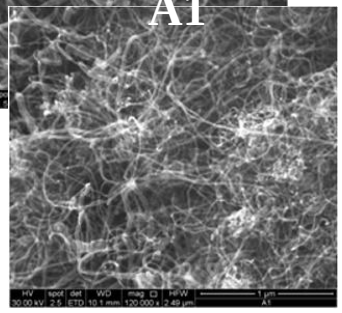










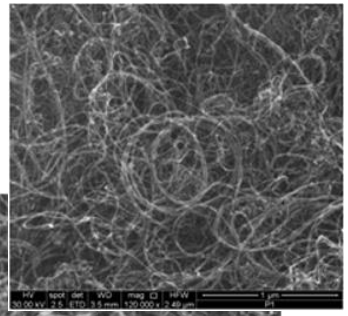


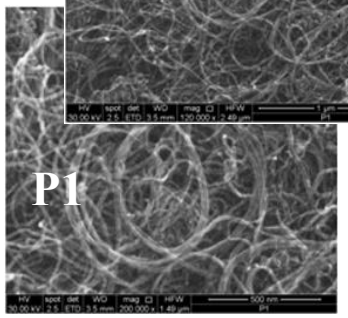
—SEM to access changes in morfology after chemical treatment.

—The clusters are detected in all samples.

—The samples have an uneven surfaces and curved ends, with slight shortening of their lenght.

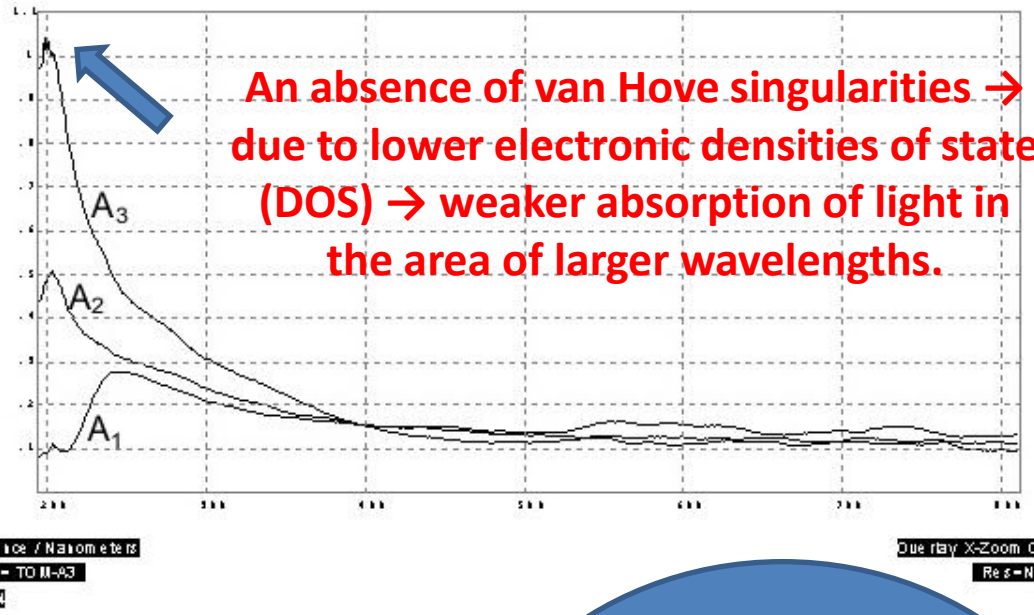
—In general, MWCNTs retained the same morfology and formation after the modification.





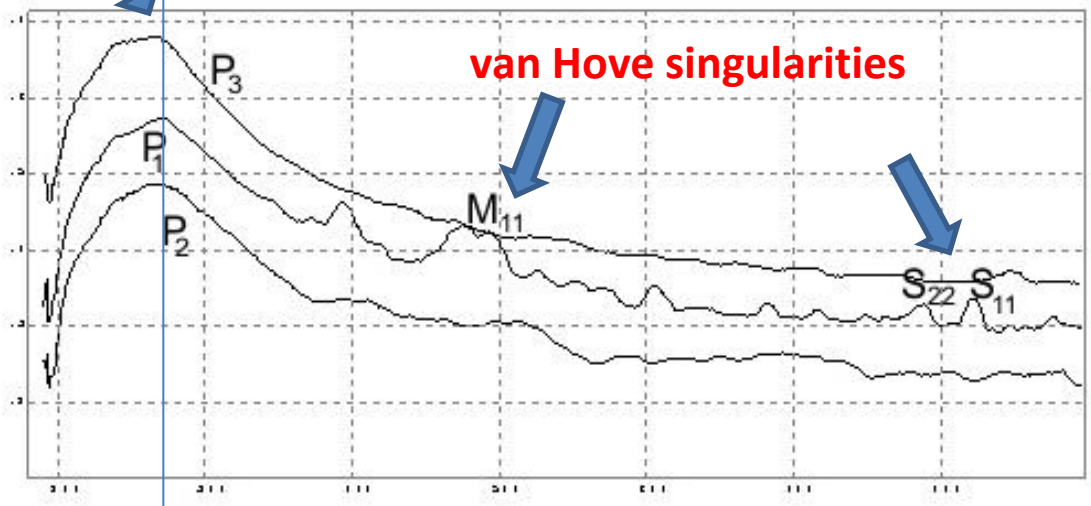
UV spectroscopy of modified MWCNTs

An intense absorption peak at 200-230 nm (the result of the excitation of π electrons



An absence of van Hove singularities → due to lower electronic densities of state (DOS) → weaker absorption of light in the area of larger wavelengths.

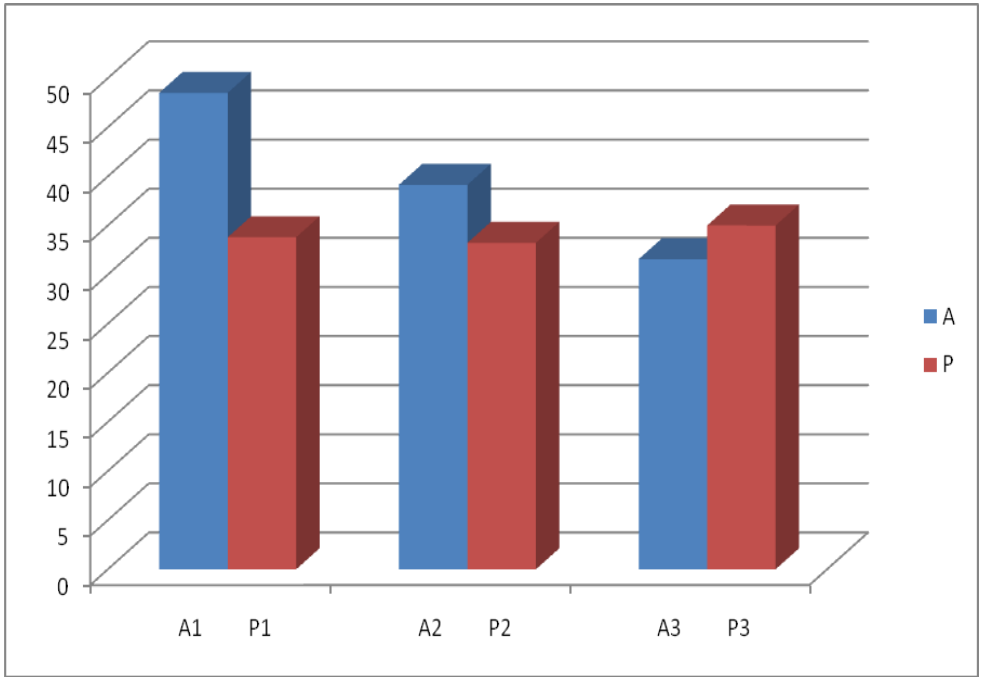
Broad intense peak at about 250 nm.



After funcionalization (P2 and P3), peak that marks the highest energy transition S22 disappears - the treatment changes the electronic structure of the CNTs - their conductivity.

Zeta potential of modified MWCNTS

Sample	T (^{0}C)	Напон(V)	ZP(mV)
SW2	15	100	43.20
MW3	15	100	34.60
A1	15	100	48.50
A2	15	100	39.14
A3	15	100	31.57
P1	15	100	33.80
P2	15	100	33.23
P3	15	100	35.00



—The stability of dispersions was followed by the analysis of zeta potential.
—All CNTs have a positive surface charge ranging from 31 to 48.5 MW.
—It is known that nanoparticles with zeta potential (negative or positive) higher than 25 mV have a high degree of stability → that the modified MWCNTs are stable nanostructures with less tendency to agglomerate.

Structural characterization of nanocomposites (TGA)

Sample	$T_{d10\%}$ [°C]	T_{dmax} [°C]
PCL	395	420
PCL/0.25% MWCNTs	393	☑ 426
PCL/0.5% MWCNTs	401	☑ 437
PCL/1.0% MWCNTs	413	☑ 492

Sample	T_d [°C]
PMMA	334,2
PMMA/0,2% MWCNTs	☑ 338,2
PMMA/0,5% MWCNTs	☑ 338,8
PMMA/1,0% MWCNTs	☑ 339,0

☑ Higher termal stability

—Thus, CNTs were impregnated in the polymer matrix and nanocomposites analyzed for structural characterization. TGA analysis examined the thermal stability of composites through their characteristic degradation temperatures.

—The Table - values of temperatures at which 10 % of weight loss occurs (Td 10 %) and a max degradation temperature of PCL and PMMA composites with different content of CNTs.

—Impregnation of MWCNTs in PCL matrix shifts both temperatures to higher areas.

—The composite with 1% CNTs has the highest value for both the Td 10% and Tdmax.

—The increasing concentration of CNTs is a factor that affects the thermal stability - higher thermal stability results from higher concentrations of CNTs in the polymer matrix.

—Similarly, dispersion of the CNTs in PMMA matrix shifts both temperatures to higher temperature areas.

—Again, the biggest increase in Td is observed in the nanocomposite film with 1 % MWCNTs.

Differential scanning calorimetry of nanocomposites

v на ладење [Kmin^{-1}]	Кристал. [^{o}C]	PCL	PCL/0.25% MWCNTs	PCL/0.5% MWCNTs	PCL/1.0% MWCNTs
5	T_o	34.2	39.7	40.0	44.6
	T_c	26.1	32.1	29.5	34.9
	T_p	30.3	36.7	36.0	39.9
10	T_o	31.2	37.2	37.7	42.3
	T_c	20.8	26.7	23.9	29.6
	T_p	27.4	33.3	31.7	36.9
20	T_o	28.8	34.1	35.1	39.7
	T_c	15.4	19.2	16.3	21.9
	T_p	24.9	28.9	27.2	33.3
40	T_o	26.8	30.5	31.8	37.1
	T_c	8.0	7.7	5.4	9.3
	T_p	22.7	28.9	21.6	28.3

⬅The bigest change

—We use differential scanning calorimetry to study the thermal transitions of a polymer - to monitor changes in nanocomposite sand to detect the shifts of melting, crystallization, degradation etc.

—We study PCL alone and PCL + various % of CNTs in nanocomposite.

—Temperature of cristalization shift toward higher areas with increasing the % of CNTs.

Differential scanning calorimetry of nanocomposites

Примерок	T_g[^{O}C]	T_o[^{O}C]	ΔC_P [Jg^{-1}K^{-1}]
PMMA	116,8	110,9	0,288
PMMA/0,2% MWCNTS	114,8	110,5	0,233
PMMA/0,5% MWCNTS	113,9	109,5	0,295
PMMA/1,0% MWCNTS	112,6	108,7	0,296

Примерок	T_g [^{O}C]
PMMA	116,8
PMMA/M1 MWCNTS	114,8
PMMA/ A1 MWCNTS	116,1
PMMA/ A2 MWCNTS	115,7
PMMA/ A3 MWCNTS	116,0
PMMA/ P1 MWCNTS	113,7
PMMA/ P2 MWCNTS	114,5
PMMA/ P3 MWCNTS	119,7

Differential scanning calorimetry of PMMA and PMMA + MWCNTs showed a change in the transition temperature - an important parameter for amorphous polymers is a major indicator of their stability.

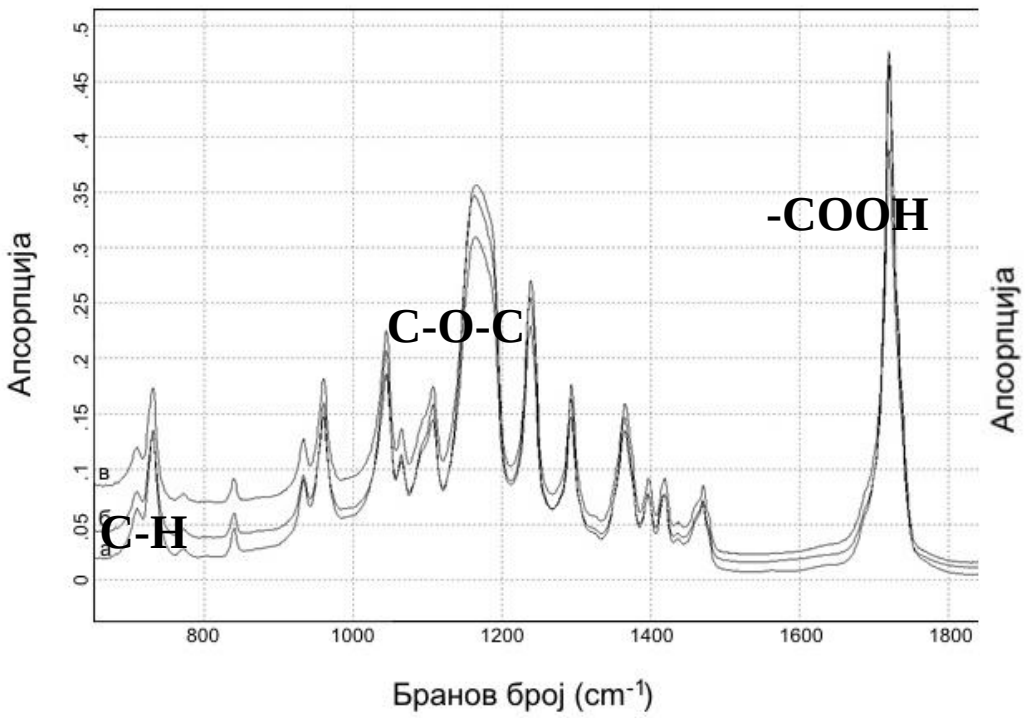
By increasing the concentration of CNTs, TG showed a declining trend, indicating a change in the elastic behavior - improve the elasticity of the nanocomposite films.

In all samples, except in P3, a lowering of TG - improvement in elasticity.

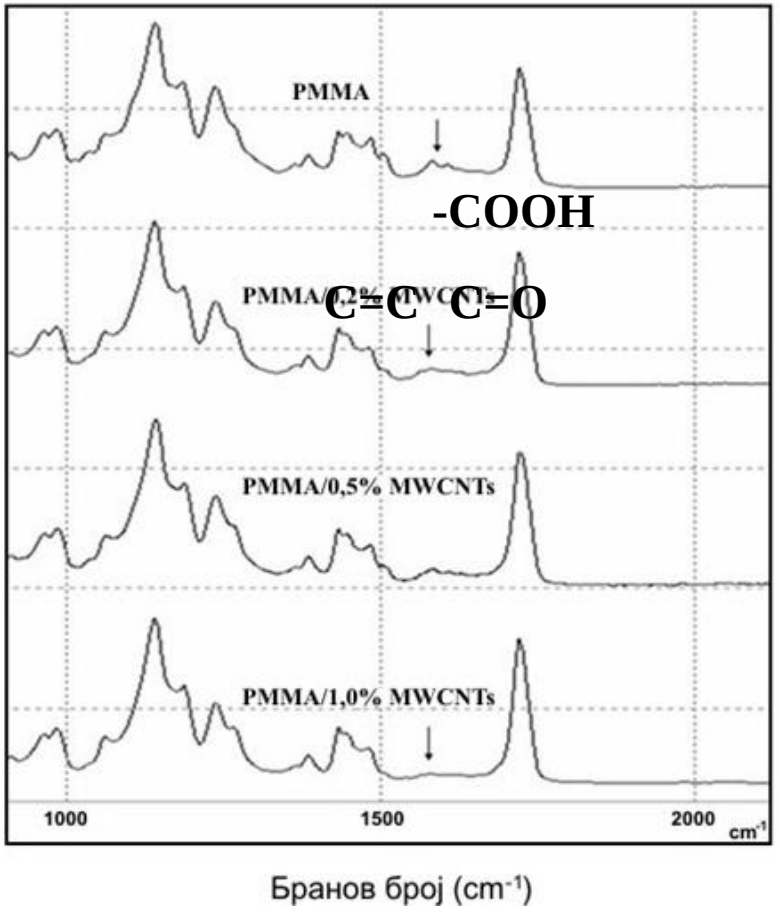
In P3 sample we registered an increase of Tg - an increased rigidity of the film.

glass

FTIR of nanocomposites



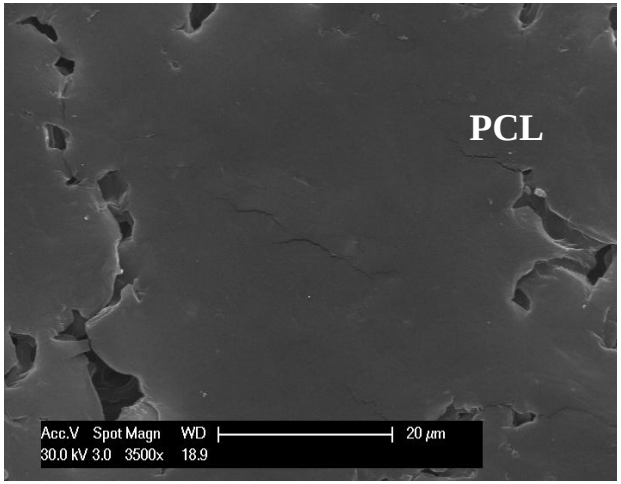
а) PCL matrix only; б) PCL/0,5%MWCNTs;
в) PCL/1%MWCNTs

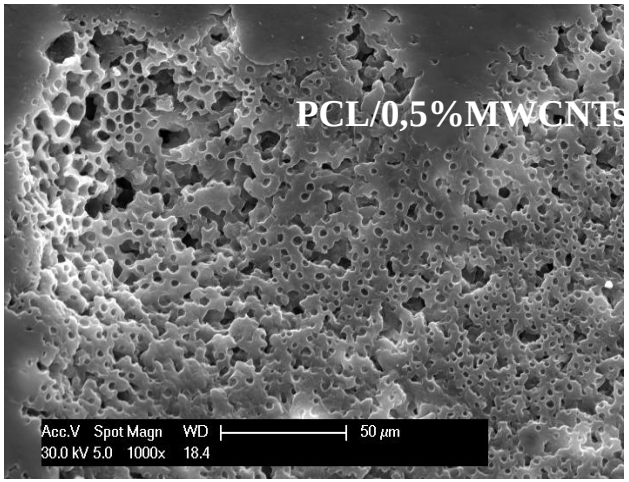


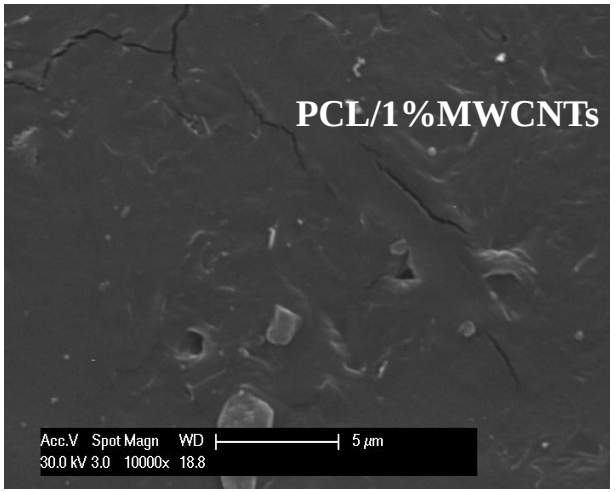
All three curves have identical appearance
No interaction between PCL matrix and CNTs.
Increase in % of CNTs in nanocomposites does not affect the intensity of peaks originating from the carboxyl groups.

C-C and C=O peaks – more intensive in pure PMMA – decrease with increasing % of CNTs (oxidation of carbon). Peak due to COOH becomes sharper with increase of % of CNTs – strong interaction between PMMA and CNTs.

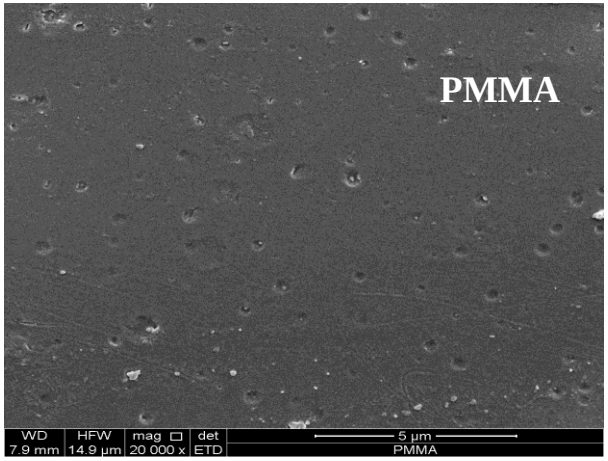
Scanning electron microscopy (SEM) of nanocomposites

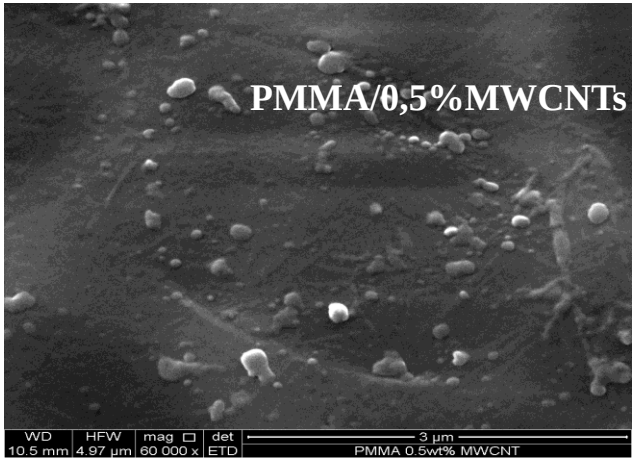


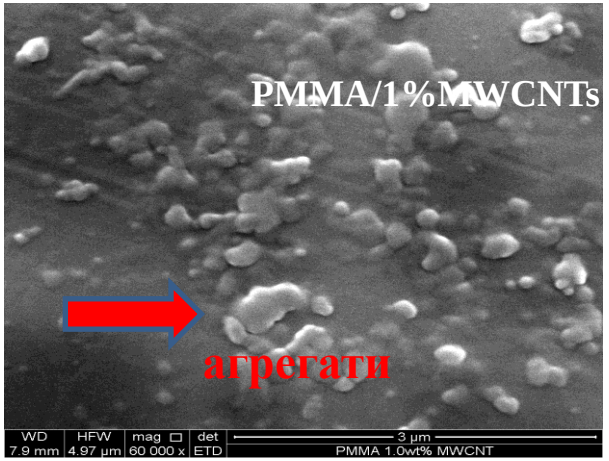




Bright lines and points are CNTs - uniform dispersion of PCL in polymer matrix

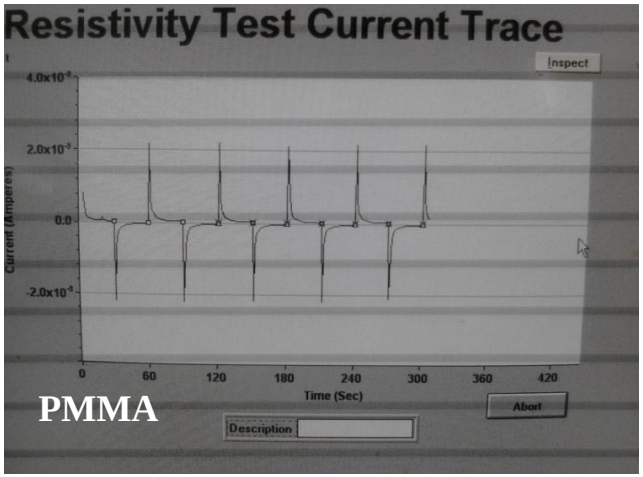


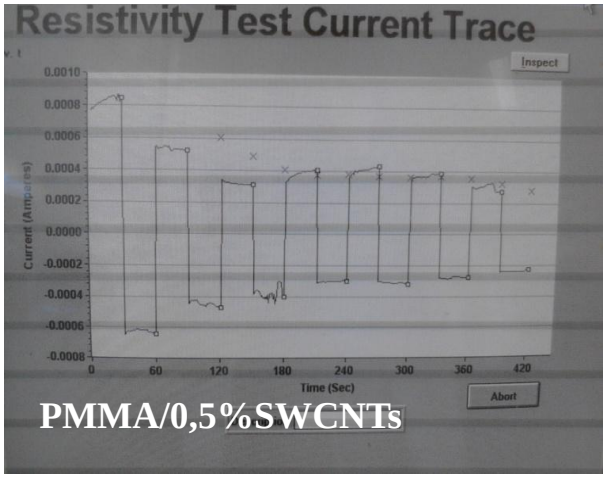




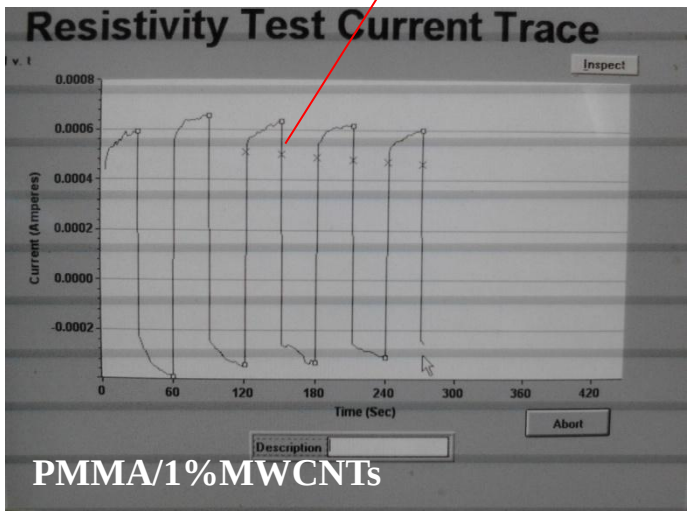
Only higher content of 0,1% MWCNTs lead to the formation of smaller aggregates.

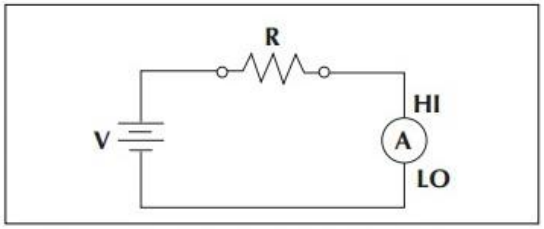
Sensor activity of nanocomposites





Mean values for the current





The sensor activity of nanocomposites was determined by monitoring electrical resistance. Measurements are done with method of constant voltage. Amperometer measures the current passing through the nanocomposite at a constant voltage of 200 volts and calculate the value for 8 cycles. Resistance is calculated by the formula:

R = U/I

Sensor activity of PMMA/CNTs nanocomposites

Sample	R [Ω·cm] Initial	R[Ω·cm] 30 min with acetone	R[Ω·cm] 30 min with chloroform
PMMA	1.37×10^{16}	6.89×10^{14}	9.46×10^{14}
PMMA/1% SWCNTs	1.38×10^{9}	5.09×10^{9}	2.12×10^{9}
PMMA/0.5% SWCNTs	7.03×10^{8}	2.87×10^{9}	1.62×10^{9}
PMMA/1% MWCNTs	2.81×10^{8}	1.14×10^{10}	3.91×10^{9}
PMMA/0.5% MWCNTs	4.37×10^{8}	2.43×10^{10}	4.96×10^{9}
PMMA/0.25% MWCNTs	3.32×10^{8}	5.23×10^{8}	1.15×10^{9}

PMMA / MWCNTs nanocomposites were subjected to vapors (acetone and chloroform) 30 min and then sensitivity was determined again - change of resistance before and after 30 min with organic vapors at various % of CNTs nanocomposite are shown.

—PMMA matrix has the highest electrical resistance.

—For all nanocomposites the increased electrical resistance is measured as compared to initial (10 to 100 times for acetone) – they are good sensors for -CO groups .

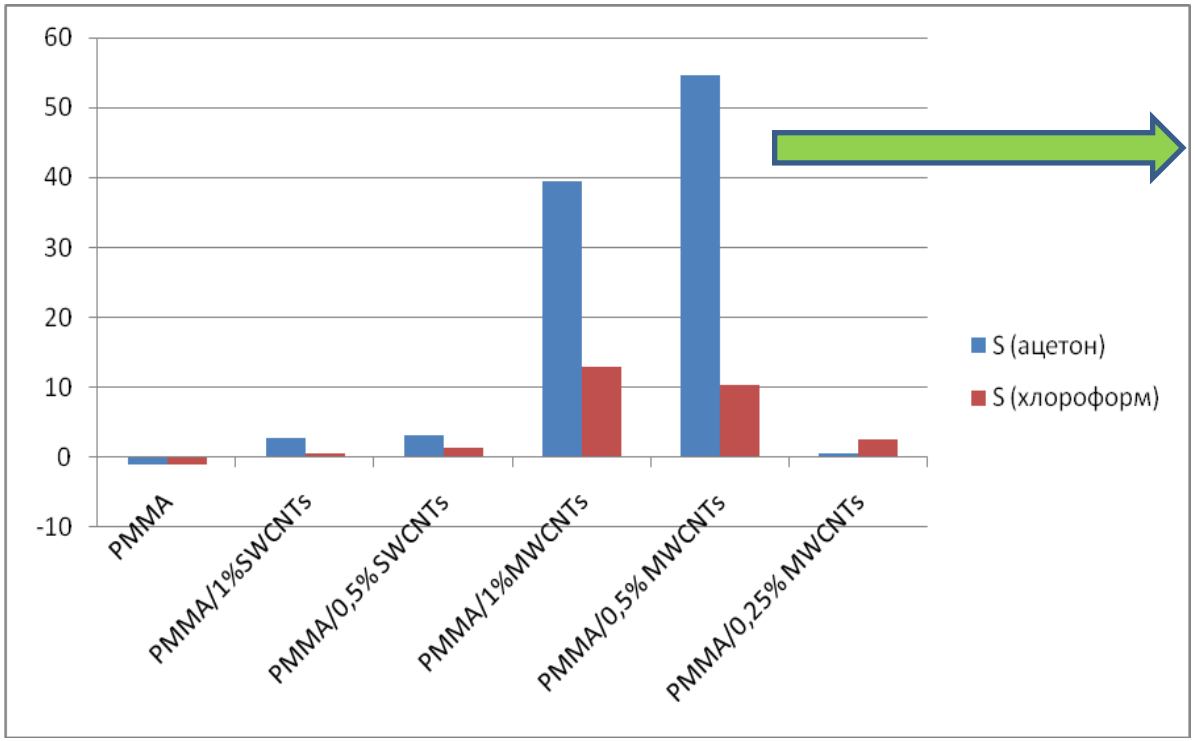
—After chloroform vapors, the resistance of nanocomposites increases by 10 times.

—The nanocomposites show higher sensitivity to acetone than to chloroform. In addition, the biggest change in resistance after chloroform was observed in PMMA with 1 % MWCNTs, while for acetone, the greatest resistance has sample with 0.5 % MWCNTs.

SAMPLE	S (30 min acetone)	S (30 chloroform)
PMMA	1	1
PMMA/1%SWCNTs	2,7	0,54
PMMA/0,5%SWCNTs	3,1	1,3
PMMA/1%MWCNTs	39,5	13
PMMA/0,5%MWCNTs	54,6	10,35
PMMA/0,25%MWCNTs	0,58	2,5

$$S = \left| \frac{R-Ro}{Ro} \right|$$

Sensitivity of PMMA/CNTs with various % of CNTs



Sensitivity S is a ratio of the difference of resistance after and before subjecting to vapors and the initial resistance.

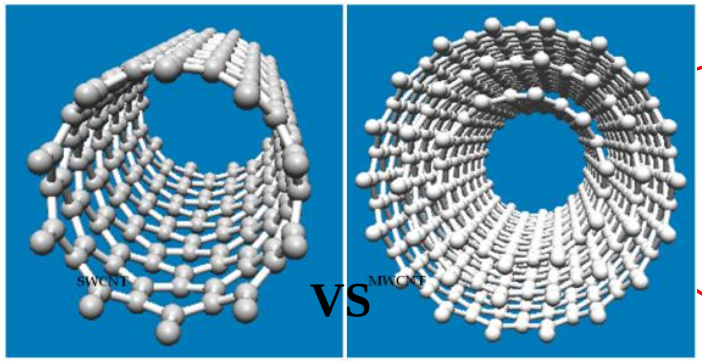
—MWCNTs show higher to acetone and chloroform than SWCNTs.

—The highest sensitivity to acetone - PMMA/0,5% MWCNTS.

Примерок	R_0 [Ω·cm] без напарување	R [Ω·cm]30 min напар. со ацетон
PMMA	1.37×10^{16}	6.89×10^{14}
PMMA 1% SWCNT	1.38×10^{9}	5.09×10^{9}
PMMA 1% MWCNT	2.81×10^{8}	1.14×10^{10}
PMMA 1% P1 MWCNT	5.83×10^{12}	5.88×10^{12}
PMMA 1% P2 MWCNT	5.32×10^{8}	3.83×10^{12}
PMMA 1% P3 MWCNT	3.14×10^{12}	1.01×10^{9}
PMMA 1% A1 MWCNT	1.74×10^{8}	4.83×10^{12}
PMMA 1% A2 MWCNT	6.00×10^{12}	1.41×10^{9}

2. Sensitivity of PMMA/CNTs with different types /treatment of CNTs

the biggest change in electrical resistance has the PMMA / MWCNTs (functionalized with acid obtained by CVD) sample P2)



Weak purification

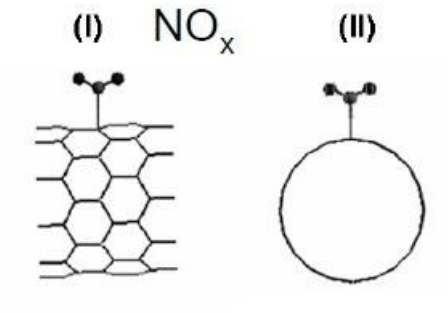
Примерок	S (со ацетон)
PMMA	1
PMMA 1% SWCNTs	2,7
PMMA 1% MWCNTs	39,5
PMMA 1% P1 MWCNTs	0,009
PMMA 1% P2 MWCNTs	7198
PMMA 1% P3 MWCNTs	1
PMMA 1% A1 MWCNTs	27757,6
PMMA 1% A2 MWCNTs	1

Electro resistance of PCL/CNTs and PMMA/CNTs

Матрица/%MWCNTs	R_0 (без напарување)	R (5 min напар. со диметилформамид)
PCL/1% MWCNTs	100 MΩ	145 MΩ
PMMA/1% MWCNTs	186 MΩ	130 Ω
PMMA/0.25% MWCNTs	61 KΩ	20 KΩ

PCL and PMMA with different % of CNTs were examined when subjected to the vapors of dimethylformamide. DMF in its structure contains nitroso group. These groups have electron acceptor nature- in contact with the surface of the CTs they accept negative charge and increase the number of gaps - This results in a decreasing of the electroresistance.

Thus, in the case of PMMA a drastic reduction of resistance occurs (10^6). This indicates that this type of nanocomposites are good sensor for NO groups.



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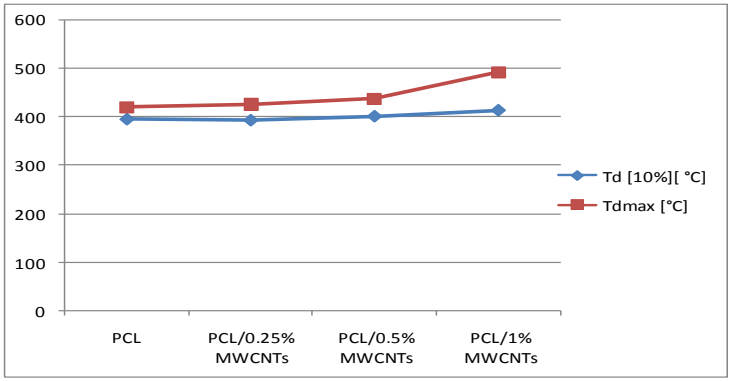
Conclusions

1. The modified CNTs showed the changes in their structure as a result of the chemical treatment and funcionalization.

2. PCL/MWCNTs: The composite have improved thermal stability; MWCNTs are uniformly dispersed through the matrices.

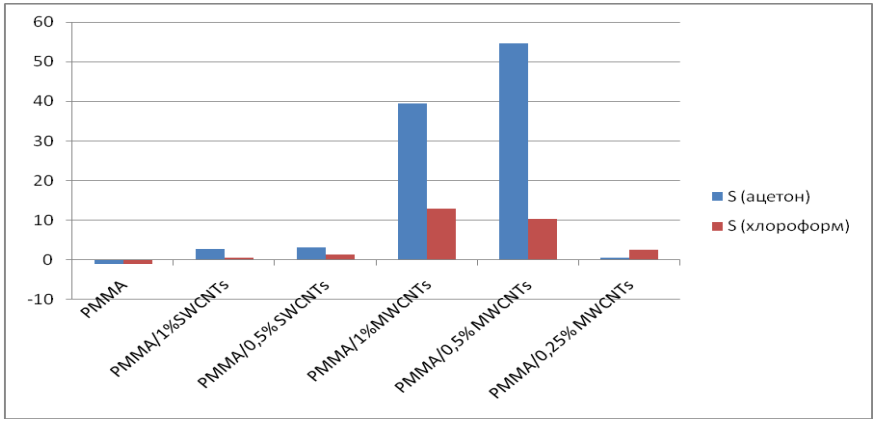


3. PMMA/MWCNTs: The composite have improved thermal stability; their stability increases with increasing of the content of the carbon tubes, however – the possibility of agglomeration at the higher percentages should be considered; the improved elastic behavior in most cases

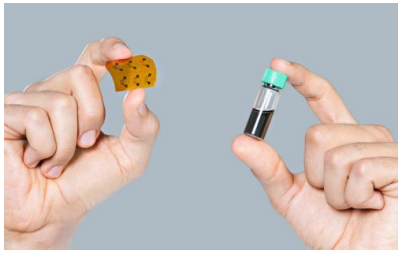
4. **The increasing of the electrical resistance after subjecting to the organic vapors (acetone and chloroform) with better sensitivity to acetone, so - the highest sensitivity to acetone was shown in PMMA with 0.5 % CNTs and the highest sensitivity to chloroform was shown in PMMA/1%MWCNTs.**

5. **The nanocomposites with CNTs that have been functionalized show better sensitivity.**

6. **PMMA/1%MWCNTs nanocomposites showed a drastical decreasing of the electro resistance – they are good sensors for –NO groups.**



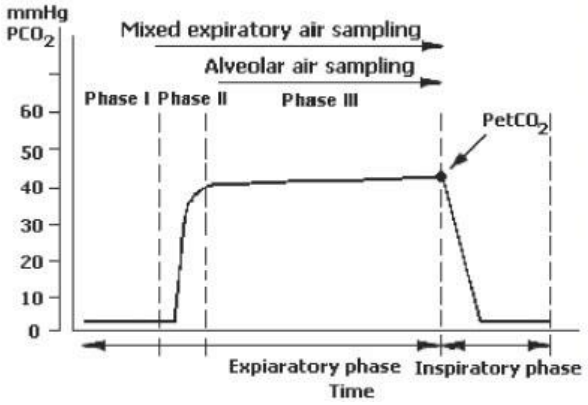
Future plans



- **The aim of our future work would to evaluate the applicability of the sensors to detect acetone in a human breath as a biomarker of diabetes.**
- **According the World Health Organization (WHO), 347 million people worldwide suffer from diabetes, with type 2 diabetes accounting for approximately 90% of all cases.**
- **Furthermore, there are 183 million people worldwide that are currently undiagnosed and able to benefit from affordable and convenient early detection technology.**
- **Breath tests are gaining popularity as non-invasive testing alternatives for numerous traditional disease diagnoses, due to their quick results and ease of use.**
- **Exhaled breath consists of many different molecular species, and their composition gives valuable information about biochemical processes in the body.**

Future plans

- **Acetone (2-propanone) is the major ketone in exhaled human breath. It is believed that the fruity odor in the breath increases significantly during periods of glucose deficiency and has long been known as a useful biomarker of type I diabetes.**
- **This acetone is absorbed into the blood stream and excreted in the breath along with the normal constituents of human exhaled breath. Acetone concentrations in the plasma of diabetic patients were shown to be elevated by at least two orders of magnitude. The acetone in expired air from lungs follows the diffusion law and is approximately 1/330 of the acetone in plasma.**



Future plans

- **SnO2 thin film sensor arrays were employed by Wang *et al*. to monitor acetone exhaled from the nose of 32 volunteers (18 idiopathic diabetics and 14 non-diabetics), before a meal and at intervals up to 2 h after the meal.**
- **They were able to achieve 100% discrimination between diabetic and non-diabetic patients 1 h after the meal, but at much lower discrimination percentages during other sampling times.**
- **Metal oxide sensors require very high operating temperatures and voltages, thereby affecting the sensitivity of the device.**
- **The obvious advantage of breath analysis of acetone is that it is non-invasive and painless technique, that provides quick results and it is easy to use.**

Wang, L.; Yun, X.; Stanacevic, M.; Gouma, P.; Pardo, M.; Sberveglieri, G. An Acetone Nanosensor For Non-invasive Diabetes Detection. *AIP Conf. Proc.* ***2009, 1137, 206–208.***

Future plans

Hence, in order evaluate the applicability of the sensors to detect acetone in a human breath as a biomarker of diabetes the following characteristics of the sensors should be established:

- **Accuracy:** This defines how correctly the sensor output represents the true value. In order to assess the accuracy of a sensor, either the measurement should be benchmarked against a standard measurand or the output should be compared with a measurement system with a known accuracy.
- **Error:** It is the difference between the true value of the quantity being measured and the actual value obtained from the sensor.
- **Precision:** Precision is the estimate which signifies the number of decimal places to which a measurand can be reliably measured. It relates to how carefully the final measurement can be read, not how accurate the measurement is.

Future plans

- **Resolution:** Resolution signifies the smallest incremental change in the measurand that will result in a detectable increment in the output signal. Resolution is strongly limited by any noise in the signal.
- **Sensitivity:** Sensitivity is the ratio of incremental change in the output of the sensor to its incremental change of the measurand in input.
  - For example, if we have a gas sensor whose output voltage increases by 1 V when the oxygen concentration increases by 1000 ppm, then the sensitivity would be 1/1000 V/ppm, or more simply 1 mV/ppm.
- **Selectivity:** A sensor's ability to measure a single component in the presence of others is known as its selectivity.
- For example, an oxygen sensor that does not show a response to other gases such as CO, CO2 and NO2, may be considered as selective.

Future plans

- **Minimum Detectable Signal (MDS):** This is the minimum detectable signal that can be extracted in a sensing system, when noise is taken into account.
- **Detection Limit:** It is the smallest magnitude of the measurand that can be measured by a sensor.
- **Repeatability:** Repeatability is the sensor's ability to produce the same response for successive measurements of the same input, when all operating and environmental conditions remain constant.
- **Reproducibility:** The sensor's ability to reproduce responses after some measurement condition has been changed.
- For example, after shutting down a sensing system and subsequently restarting it, a reproducible sensor will show the same response to the same measurand concentration as it did prior to being shut down.