

Polymer Nanocomposite Films with Functionalized MWCNTs

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Abstract: Polymer nanocomposites with carbon nanotubes (CNTs) have become very attractive class of materials for numerous engineering applications since carbon nanotubes exhibit a high aspect ration, unique electrical, mechanical and structural properties. Functionalization of CNTs offer new potentials for other technical challenges of the polymer based nanocomposites associated with their specific interactions.

A biocompatible polymer matrices PMMA and PCL were used to provide good interfacial bonding between carbon nanotubes. MWCNT (d=30-50 nm, purity>95%) were used for preparation of polymer based nanocomposites with 0.2, 0.5 and 1.0 % w/w MWCNT's content. PMMA-based nanocomposites were prepared via the mixing of the MWCNT and polymer in a dichloromethane solution for 24 h, while for the PCL-based nanocomposites as a solvent tetrahydrofuran was used. Functionalization of the CNTs was performed in acid (HNO₃) and alkali (NH₄OH+H₂O₂) medium as well as by additional thermal oxidation at 490°C. Characterization of the nanocomposite films was performed by DSC, TGA, WAX, FTIR and SEM. The obtained results have shown that introducing MWCNT into polymer matrix significantly changes have been found in the properties of the obtained nanocomposites.

Introduction

Polymer nanocomposites based on CNTs and biopolymer matrices are still subject of great research interest, especially with respect to the effects of carbon nanotubes on the thermal and mechanical behavior of the composites. In order to prepare CNT/polymer nanocomposites, several problems had to be overcome. Namely, one is to obtain uniform dispersion of CNTs in a polymer matrix despite the insolubility of CNTs and the inherently poor compatibility between the CNTs and the polymers. In direct blending of CNTs and polymers, the nanotubes tend to aggregate; such nonuniform dispersions in the polymer matrix often results in deteriorious effects. The second main approach is utilization of biodegradable and biocompatible polymeric materials such as Poly Methyl Methacrylate (PMMA), Polylactide (PLA), Poly(ϵ -caprolactone) (PCL) and Poly(3-hydroxybutyrate)(PHB) [1,2,3].

Kang et al. from the University of Cincinnati have worked on polymethylmethacrylate (PMMA) based CNT/PMMA nanocomposites for strain sensors for structural health monitoring [4]. Bio-nanocomposite sensors have been a research topic also at the Florida Advanced Center for Composite Technologies. Here MWCNT/PMMA strain sensors were studied, comparing solution prepared sensors with dry-blended ones. In this paper, a novel carbon nanotube/biocompatible polymer nanocomposite films were study in order to develop a bio-nano gas sensor utilizing the effect of a MWCNTs/polymer nanocomposites chemiresistor for the detection of organic vapors. Multi-walled carbon nanotubes were used because they can be grown longer than single wall carbon nanotubes, they are stiffer and more resistant, and they have larger diameter (~70nm). MWCNTs were also select in order to reduce the cost for real application. They can be integrated into the material (composite) and serve both sensor and structural functions.

Experiment

The PMMA/MWCNT nanocomposite films were prepared by the solution casting method, via ultrasonic mixing of the MWCNT and the polymer matrix in a dichloromethane solution (Figure 1), while for the PCL-based nanocomposites tetrahydrofuran solvent was used. MWCNT ($d=30\text{-}50$ nm, purity $>95\%$), untreated, functionalized and thermally oxidized, have been used for preparation of Poly (Methyl Metacrylate) and Poly (ϵ -caprolactone) based nanocomposites. The main reason why this solution casting method was used is because of the satisfied dispersion (dispersion is consistent and reproducible) obtained due to the low viscosity of the mixture and this method works with small sample sizes. Functionalization of the CNTs was performed in acid (HNO_3) and alkali ($\text{NH}_4\text{OH}+\text{H}_2\text{O}_2$) medium as well as by additional thermal oxidation at 490°C for 40 min.

Characterization of the polymer/MWCNTs nano composite films was performed by differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), Fourier-transform infrared (FTIR) and Raman spectroscopy, X-ray analysis (WAX) and scanning electron microscopy (SEM).

DSC measurements were performed with a DSC (Mettler Star) under N_2 atmosphere in the non-isothermal regime ($V_{\text{heating}}=10$ K/min, $V_{\text{cooling}}=10$ K/min). All specimens were weighted to be in the range of 8-9 mg. TGA was performed in the range of 50 to 800°C with heating rate of 20 K/min (in nitrogen) using a Perkin Elmer Pyris DIAMOND TGA/DTA system. FTIR spectroscopy was used to characterize the structure of the PMMA/ MWCNT and PCL/MWCNT nanocomposites. FTIR spectra were recorded with a Perkin Elmer Paragon 500 analyzer, using 64 scans and a resolution of 2 cm^{-1} . SEM microphotographs were recorded with a FA SEM microscope mode 2000.

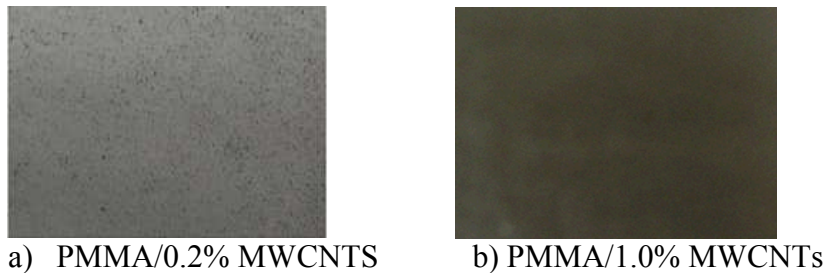


Figure1. Cast films of PMMA/MWCNTs nanocomposites
(a- 0.2% MWCNTs, b-1%MWCNTs)

X-Ray diffraction (WAX) spectra of PMMA and PMMA/MWCNTs nanocomposite films were recorded using a PAN-analytical X'Pert Pro diffractometer using $\text{CuK}\alpha$ radiation between 2 and 40° . Raman spectra were collected using a 785 nm (Titan sapphire laser), Jobin-Yvon HR640 spectrometer fitted with an Andor Technology CCD detector. The changes in the nanocomposite resistance were followed after exposure of PMMA/MWCNTs nanocomposite films to different gases (chloroform, acetone, toluene, hexane) where the pressure of all solvents was controlled at 25°C .

Results

Structural and morphological changes of functionalized MWCNTs were registered by Raman, TGA and SEM analysis. Raman spectra are shown in Fig. 2, while characteristic TGA/DTA thermograms of untreated and thermally oxidized MWCNTs are shown in Fig. 3.

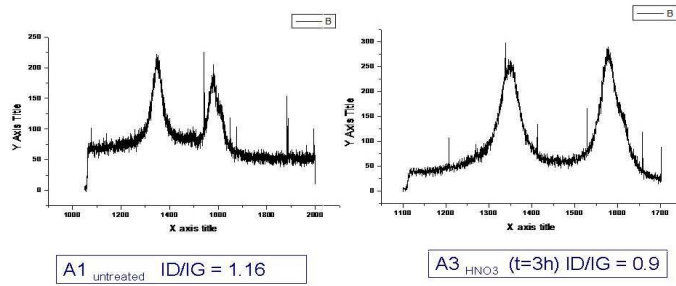


Fig. 2. Raman spectroscopy of MWCNT-untreated and acid functionalized CNTs

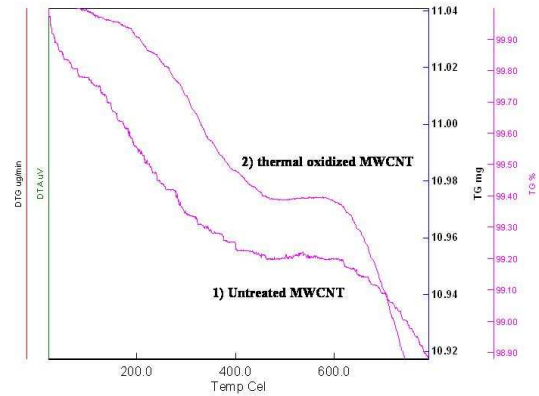


Fig. 3. TGA/DTA thermograms for untreated and thermally oxidized MWCNTs

Characteristic thermal data such as the onset temperature T_o , and the glass transition temperature T_g , were determined from DSC curves and the results are shown in Table 1. It is evident that as the MWCNT content increased, both transition temperatures (T_o and T_g) were shifted to lower temperatures which indicate on changes in the elastic behavior. The PMMA/MWCNT nanocomposites have lower T_g values than the pure PMMA.

Table 1. Characteristic thermal data for PMMA/MWCNT nanocomposites

SAMPLE	T_g [°C]	T_{onset} [°C]	ΔC_P [J/gK]
PMMA	116,8	110,9	0,288
PMMA/0,2% MWCNT	114,8	110,5	0,233
PMMA/0,5% MWCNT	113,9	109,5	0,295
PMMA/1,0% MWCNT	112,6	108,7	0,296

Using the DSC technique, characteristic non-isothermal crystallization data such as T_o -the onset crystallization temperature, T_c -the end temperature of crystallization and T_p - the exothermic peak temperature of the crystallization were determined. The results are shown in Table 2. It is evident that as the cooling rate increased, all the parameters (T_o , T_c and T_p) were shifted to lower temperatures. The lower the cooling rate, the earlier the crystallization starts. It was noted that the PCL/MWCNT nanocomposites have higher T_p values than the pure PCL at all cooling rates (except for PCL/0.5% MWCNT at 40 K/min). This phenomenon could be explained by the heterogeneous nucleation of the MWCNTs suggesting that the melted PCL macromolecule segments can be easily attached to the surface of the rigid nanotubes, which leads to the crystallization of PCL macromolecules at higher temperature. For the PCL/MWCNT nanocomposites obtained, also the linear growth G and the activation energy ΔE_a were determined (Table 3). Generally, for increasing MWCNT contents, the values of both parameters increase. A higher content of MWCNTs means more steric hindrance and a reduction of the transportation ability of the polymer chains (higher ΔE_a).

Thermogravimetric analysis was used to study thermal stability of the MWCNTs and PMWCNTs/Polymer based nanocomposites (Table 4).

Table 2. The nonisothermal parameters for PCL and PCL/MWCNT nanocomposites determined by DSC exotherms

Cooling rate [C/min]	Crystallization parameter [°C]	PCL	PCL/0.25% MWCNT	PCL/0.5% MWCNT	PCL/1.0% MWCNT
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

Table 3. Linear growth rate G and activation energy ΔE_a for PCL and PCL/MWCNT nanocomposites

Parameter	PCL	PCL/0.25% MWCNT	PCL/0.5% MWCNT	PCL/1.0% MWCNT
ΔE_a [kJ/mol]	308.6	250.2	257.9	317.0
G [min^{-1}]	3.60×10^3	1.19×10^3	2.06×10^3	3.01×10^3

Table 4. Degradation temperatures for PMMA/MWCNT nanocomposites

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

It was shown that MWCNTs improved the thermal stability of nanocomposites based on PMMA. T_d was shifted for five degrees. For the MWCNT/PCL system it was found that temperature of thermal decomposition for MWCNT/PCL nanocomposites was slightly shifted to lower temperatures compared to the pure PCL ($T_{d \text{ PCL/1\%MWCNT}} = 393$ °C, $T_{d \text{ PCL}} = 395$ °C) probably due to the lower level of dispersion of the MWCNTs in semicrystalline polymer matrix. Characteristic diffraction curves for PMMA and PMMA/MWCNT are present in Figure 4. The curve for PMMA (series 2) has shown wider diffraction peak in the range of $2\Theta=14^\circ$ which suggest that it is amorphous PMMA.

Decreased intensity of this peak in the WAX-curve of the nanocomposite film (series 1) suggests that it is a compatible nanocomposite system, with compatible mixing of the polymer matrix and MWCNT. Also, some shifting of the diffraction peaks to the lower values have been registered for the nanocomposite films which indicate on changes in the interlayer distance. For the PMMA also, sharp peak is registered at $2\Theta=29^\circ$ which has been shifted to $2\Theta=39^\circ$ in the nanocomposite film. The obtained results are in agreement with the literature data [5].

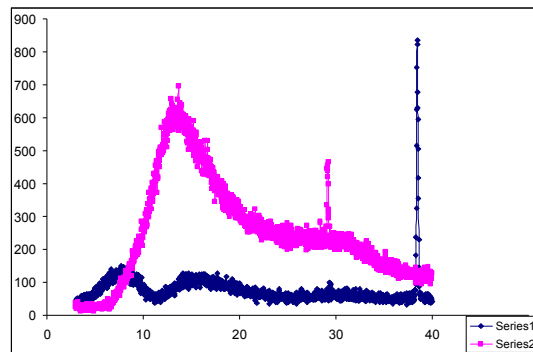


Figure 4. WAX-analysis of PMMA/MWCNT nanocomposite film (series 1- PMMA/MWCNT; series 2 - PMMA)

To evaluate the degree of dispersion of MWCNTs within the polymer matrix, the nanocomposites films have been observed by scanning electron microscopy. The characteristic morphology of the PMMA based nanocomposites was presented in Figure 5 (a: pure PMMA, b: MWCNT, c: PMMA/0,5% MWCNT), while in Figure 6 the obtained morphology of PCL based nanocomposites was shown (a: pure PCL, b: PCL/0.5% CNT, c: PCL/1% CNT). The SEM images clearly show that homogeneous dispersions of MWCNTs (well-dispersed bright dots) throughout the PMMA matrix are achieved at all CNT contents, although at higher MWCNT content of 1% smaller aggregates are also formed.

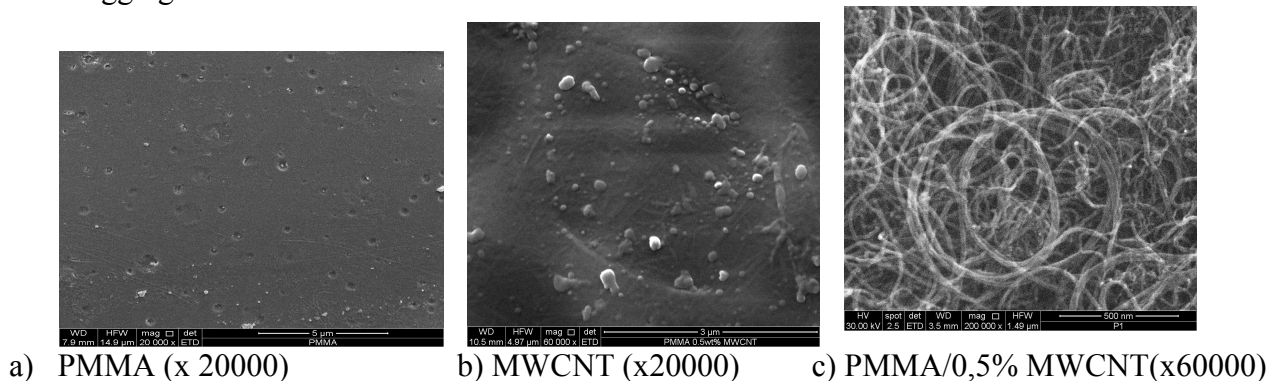


Figure 5. SEM microphotographs of PMMA/MWCNT nanocomposites: a) pure PMMA ($\times 20000$), b) MWCNT ($\times 200000$) c) PMMA/0.5% MWCNT ($\times 60000$)

The FTIR spectra of the pure PMMA matrix and PMMA/MWCNT nanocomposites have shown that besides small peak shifts, there is only one significant change in the compared FTIR peaks of pure PMMA and PMMA/MWCNTs nanocomposites. Namely the C—O stretching bands in pure PMMA matrix at 1583 cm^{-1} and 1611 cm^{-1} remarkably decreased in the PMMA/MWCNTs nanocomposites which indicate the changes induced by the presence of MWCNTs in the polymer structure.

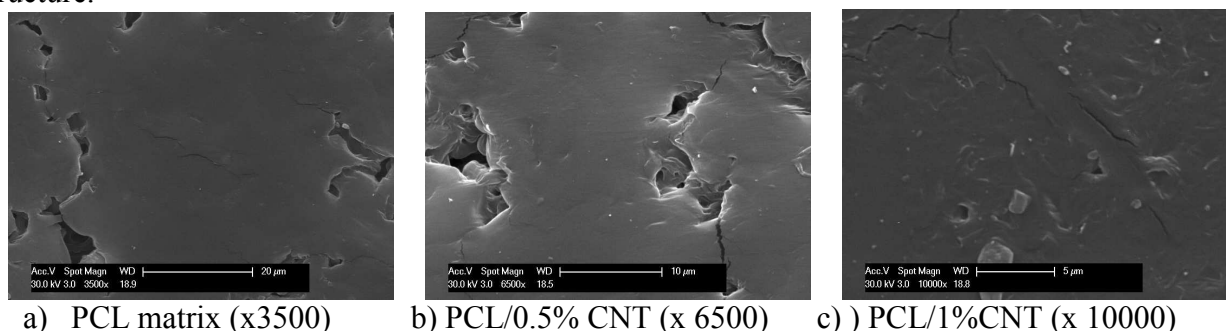


Figure 6. SEM microphotographs of the prepared PCL/CNT nanocomposites; a) pure PCL ($\times 3500$), b) PCL/0.5% CNT ($\times 6500$), c) PCL/1%CNT ($\times 10000$)

Summary

The results presented to the in this paper have shown that due to the functionalization, some changes were registered in the MWCNTs. By introduction of MWCNTs into PMMA and PCL polymers significantly changes of the properties of the obtained nanocomposite films were obtained. Structural changes were shown by X-ray and FTIR spectroscopy. Elastic behaviour was exhibited by DSC data for changes of T_g temperature. TGA/DTA analysis shown improved thermal stability. SEM images shown that a homogeneous dispersion of MWCNT was achieved throughout the PMMA and PCL matrices at all CNT contents.

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