Stretchable and flexible thermoelectric polymer composites

P. Slobodian¹, P. Riha², J. Matyas¹, R. Olejnik¹

¹Centre of Polymer Systems, University Institute, Tomas Bata University, Trida T. Bati 5678, 76001 Zlin, Czech Republic
²The Czech Academy of Sciences, Institute of Hydrodynamics, Pod Patankou 5, 16612 Prague 6, Czech Republic

Corresponding author’s e-mail: P. Slobodian (slobodian@cps.utb.cz)

Abstract. Polymer composites were manufactured from pristine and oxidized multi-walled carbon nanotubes and ethylene-octene copolymer. The composites had thermoelectric properties and exhibit thermoelectric effect, that is, the conversion of temperature differences into electricity. Fourier transform infrared spectroscopy and X-ray photoelectron spectroscopy of the multi-walled carbon nanotubes in ethylene-octene copolymer matrix showed that the oxidation with HNO₃ or KMnO₄ enhanced its p-type electrical conductivity and that the thermoelectric power increase was proportional to the formation of new oxygen-containing functional groups on the surface of carbon nanotubes.

1. Introduction
Thermoelectric polymer composites as principal parts of thermoelectric devices are capable to convert thermal energy into electricity when there is a different temperature between the hot and cold junctions of two dissimilar conductive composites. In spite of their lower thermoelectric efficiency in terms of the figure of merit, the properties as elasticity, shape formation, light weight, low thermal conductivity, easy processing and low manufacturing cost are advantages in many technological and ecological applications.

The aim of this study is to specify the effect of pristine and oxidized multi-walled carbon nanotubes (MWCNTs) in ethylene-octene copolymer matrix on their thermoelectric power. The thermoelectric efficiency of the composites was calculated on basis of the measured electrical and thermal conductivities and the induced electric voltage.

2. Experimental
The purified multi-walled carbon nanotubes produced by acetylene chemical vapor deposition method were purchased from Sun Nanotech Co. Ltd., China with purity >90% and electrical resistivity 0.12 Ωcm. The ethylene-octene copolymer (EOC) with 45 wt% of octene content (ENGAGE 8842) was purchased from Dow Chemicals. The density of EOC was 0.8595 gcm⁻³.
KMnO$_4$ oxidation: Oxidized MWCNTs were prepared in a glass reactor with a reflux condenser filled with 250 ml of 0.5 M H$_2$SO$_4$, into which 5 g of potassium permanganate (KMnO$_4$) as oxidizing agent and 2 g of MWCNTs were added. The dispersion was sonicated at 85 °C for 15 h using thermostatic ultrasonic bath (Bandelin Electronic DT 103H).

HNO$_3$ oxidation: 2 g of MWCNTs was added to 250 ml of HNO$_3$ (concentrated) and heated at 140 °C for 2 h. After that the dispersion was cooled and filtered. The sediment was washed by deionized water and dried at 40 °C for 24 h.

The X-ray photoelectron spectroscopy (XPS) signals were measured to get information on functional groups attached onto the nanotube surface. The XPS signals from MWCNT, MWCNT(KMnO$_4$) and MWCNT(HNO$_3$) network surfaces were recorded using a Thermo Scientific K-Alpha XPS system (Thermo Fisher Scientific, UK) equipped with a micro-focused, monochromatic Al Kα X-ray source (1486.6 eV). An X-ray beam of 400 mm size was used at 6 mA x 12 kV [1]. The spectra were acquired in the constant analyzer energy mode with pass energy of 200 eV for the survey. Narrow regions were collected using the snapshot acquisition mode (150 eV pass energy) enabling rapid collection of data (5 s per region). The narrow region data was post-processed using Jansson’s algorithm to remove the analyzer point spread function what resulted in improved resolution of the spectra for peak deconvolution [2].

The thermoelectric power of a material is a measure of the magnitude of an induced voltage in response to a temperature difference across that material, as induced by the thermoelectric effect. The thermoelectric power measurement was carried out for all the samples using a set-up illustrated in Fig. 1a. A circular composite sample (diameter 20 mm, thickness 2 mm) was placed between two copper electrodes. The ends of each Cu electrode were immersed in a thermostatic silicone oil bath set to different temperature. The temperature at the copper/composite interfaces was measured by a digital thermometer. The arising thermoelectric current was measured with a Multiplex datalogger 34980A.

![Fig. 1 a) Schematic diagram of the set up for the measurement of voltage induced in the composite in response to a temperature difference. B) Energy harvesting button assembled from MWCNT(pristine)/EOC and MWCNT(KMnO4)/EOC thermoelements.](image)

To demonstrate a possible use of conductive MWCNT/EOC composites as thermoelectrical material, the energy harvesting from temperature gradient was examined. The arrangement of the thermoelectric generator as so called energy harvesting button, which was fabricated from three conductive thermoelements, namely, one MWCNT pristine/EOC and two MWCNT(KMnO4)/EOC composites, is shown in Fig. 1b. The composite stripes were stuck on PET foil while the composite overlaps holder together by proper stickiness of composites. The composite generated electricity was monitored by means of the Multiplex datalogger 34980A while a temperature gradient was induced by a finger touching.
3. Results
The x-ray photoelectron spectroscopy was performed on the MWCNT specimens to get information on the functional groups attached onto the nanotube surface. The surface composition (in atomic %) were determined by considering the integrated peak areas of C1 and the respective sensitivity factors. The fractional concentration of a particular element A was computed using,

$$\% A = \left(\frac{I_A}{s_A}\right) \times \frac{I}{s_n} \times 100\%,$$

where $I_A$ denotes the signal intensity of element A, $I_n$ integrated peak areas, $s_A$ and $s_n$ the Scofield sensitivity factors corrected for the analyser transmission.

The main binding energy peak (284.5 eV) in XPS spectra of MWCNTs was assigned to the C1s-sp2, while the other ones were assigned to C-O (286.2 eV), C=O (287.1 eV), O-C=O (288.6-289 eV) and C1s-π-π* (291.1-291.5 eV). XPS data in Fig. 2a show that all MWCNTs have C-OH, C=O and O-C=O groups on their surface and that MWCNT(KMnO₄) and MWCNT(HNO₃) and MWCNTs have maximum percentage of O-C=O, C-O and C=O, respectively. The XPS analysis was also a useful and simple method for evaluating the content variation of amorphous carbon in MWCNT samples by analyzing the sp³/sp² carbon ratio. According to our XPS results the carbon ratios are 2.50, 3.50 and 1.69 for MWCNTs, MWCNT(HNO₃) and MWCNT(KMnO₄), respectively. The reason why the total oxygen amount for MWCNT(KMnO₄) is less than in case of HNO₃ oxidant could be due to removing away more amount of the oxygen species originated from amorphous carbon structures during the acidified KMnO₄ oxidation process. The decreased number of total groups involving oxygen increased the contact resistance in MWCNT junctions of the network nanotube structure, Fig. 2b.

![Fig. 2](image-url)

**Fig. 2** a) Oxygen content (at %) on pristine and oxidized MWCNTs by different reagents. b) Generated voltage vs. temperature difference for all investigated composites (filler concentration 30 wt.%) together with the indicated thermoelectric power $S = V_{TEV} / \Delta T$ in µV/K at 22 °C.

The values of induced voltage in response to a temperature difference across the measured sample of investigated thermoelectric composites are shown in Fig. 2b. The slope of the linear temperature-difference $\Delta T$ dependence on resulting voltage $V_{TEV}$ defines the thermoelectric power $S = V_{TEV} / \Delta T$, an essential measure evaluating the potential thermoelectric performance. The corresponding values are 13.2, 18.7 and 24.4 µV/K for MWCNTs, MWCNT(KMnO₄) and MWCNT(HNO₃) composites, respectively. However, the enhancement of thermoelectric power by oxidation is accompanied by suppression of the electrical conductivity. Hence, the use of MWCNT(HNO₃)/EOC composite with a high thermoelectric power is only one important factor for the efficient performance of a
thermoelectric generator. No less important step is careful design to enhance also the electrical conductivity $\sigma$ of the composite by adjustment of the nanotube concentration which increases the thermoelectric power factor $S^2 \sigma$. The power factor is an important value since it is directly related to the usable power attainable from the thermoelectric material.

The arrangement of the thermocouple for energy harvesting fabricated from two conductive thermoelements (MWCNT/pristine/EOC and MWCNT(KMnO$_4$)/EOC composites) operates even in a small temperature gradient induced by a touch of finger (Fig. 1b). The system takes in heat from the finger and outputs electricity. Time dependence of generated voltage is shown in Fig. 3a. In practice, the energy harvesting button may use programmable thermal energy source to control electronic devices which need a small amount of electrical energy in a large time scale. The advantage of the composite energy harvesting button is its flexibility and a high level of possible integration which may be useful to remove heat in a network of electronic devices.

Thermoelectric device (thermopile) built up of two conductive thermoelements and the schematic diagram showing the material junctions in series alternating hot/cold temperatures with each junction is shown in Fig. 3b.

![Fig. 3](image)

**Fig. 3** a) Time-dependent generation of voltage after finger touching at A or B ends of the energy harvesting button assembled from MWCNT(pristine)/EOC and MWCNT(KMnO$_4$)/EOC composites (see Fig. 1b). b) Thermoelectric device (thermopile) built up of MWCNT/EOC flexible thermoelements and the schematic diagram showing the material junctions in series alternating hot/cold temperatures with each junction.

4. Conclusions
The thermoelectric power, which specifies the voltage produced per degree temperature difference, increased of 42% for KMnO$_4$ oxidized and 85% for HNO$_3$ oxidize MWCNTs with respect to the thermoelectric power of the composite with pristine nanotubes [9]. The thermoelectric power increase is proportional to formation of the new oxygen-containing functional groups on the surface of carbon nanotubes.

References
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