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## Characterization of thermoelectric and thermogravimetric properties of conductive PEDOT:PSS films blended with SWCNTs and PVA

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# Characterization of thermoelectric and thermogravimetric properties of conductive PEDOT:PSS films blended with SWCNTs and PVA

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**Abstract.** Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) was blended with polyvinyl alcohol (PVA) and single-walled carbon nanotube (SWCNT) filler to form composites with thermoelectric properties. Studied samples were obtained by drop coating and solution casting methods. Thermoelectric measurements of PEDOT:PSS demonstrated that the addition of 5 wt. % SWCNTs increased the Seebeck coefficient value from 8.0  $\mu\text{V/K}$  to 23.6  $\mu\text{V/K}$ , while in the case of PEDOT:PSS/PVA blended with 5 wt. % SWCNT Seebeck coefficient value of 20.3  $\mu\text{V/K}$  was achieved. Thermogravimetric analysis showed slight SWCNT effect on thermal stability of the investigated systems.

## 1. Introduction

In recent years poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) has reached attention as a perspective material for applications in electronics and energetics due to decent thermoelectric properties [1]. Water-soluble PEDOT:PSS is also non-toxic and it is easy to use to obtain uniform conductive films and coatings by means of drop coating and film casting methods that can be applied in laboratory environment [2]. PEDOT:PSS organic nature and thin film properties in future could be applied for commercial manufacturing of small-scale thermoelectric devices for waste energy transformation into electrical power [3].

Addition of conductive nanofillers could be beneficial to further improve PEDOT:PSS thermoelectrical properties. For this purpose single-walled carbon nanotubes (SWCNTs) can be a good candidate due to their wide usage for electrical conductivity enhancement in polymer composites and fact that they can be directly dispersed in PEDOT:PSS without additional surfactants [4]. A good SWCNT dispersion can improve electrical junctions between PEDOT:PSS particles giving contribution to electrical conductivity and thus the thermopower improvement at the same time keeping the increase in thermal conductivity relatively low.

However from PEDOT:PSS composite with carbon nanotubes it is difficult to form freestanding films leaving great negative effect on its flexibility, that may reduce its applicability. Therefore additionally blending of PEDOT:PSS with other polymers offers means to combine the useful and desired properties exhibited by the individual polymer components. In the current case polyvinyl alcohol (PVA) was chosen to modify PEDOT:PSS as it is environmentally friendly, flexible and also water-



soluble that can facilitate mixing of these two polymers. Previous studies show that PEDOT:PSS/PVA blends can form free-standing films and reduce the drawbacks of brittleness [5-6] however sacrificing a part of thermoelectric properties due to PVA insulating nature.

## 2. Experimental

### 2.1. Materials

PEDOT:PSS aqueous dispersion (Clevios PH 1000) with solids content of 1.3 wt. % was purchased from Heraeus, Germany. SWCNTs with outer diameter 1 – 2 nm, length 5 – 30  $\mu\text{m}$  and purity > 90 % were provided from Timesnano, Chengdu Organic Chemicals Co. Ltd., Chinese Academy of Sciences. PVA (Celvol E 04/88S), 88 % hydrolyzed, was obtained from Celanese, USA.

### 2.2. Preparation of PEDOT:PSS/PVA/SWCNT films

To prepare PEDOT:PSS/SWCNT composites, SWCNTs were dispersed in PEDOT:PSS solution by ultrasonic probe UIS250V (Hielscher Ultrasonics GmbH). To induce an efficient SWCNT dispersion, sonication time was approximately 20 min. For PEDOT:PSS/PVA/SWCNT sample preparation, first PVA was added to PEDOT:PSS solution at the same concentration (1.3 wt. %) and stirred at 80 °C until the PVA was fully dissolved. Then SWCNTs were added in the same manner as previous. Obtained dispersions were cooled down to room temperature and applied by drop coating method on clean glass substrates for thermoelectric properties characterization. Free standing films were obtained by solution casting on flat polypropylene surface.

### 2.3. Characterization

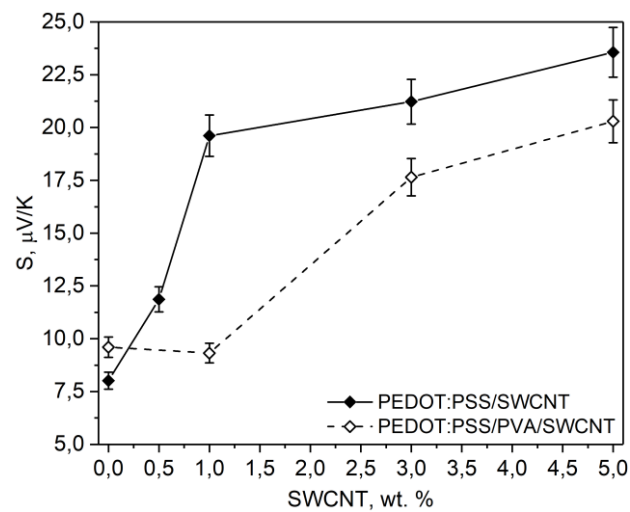
The Seebeck coefficient was measured by a custom made device based on the Peltier effect. It consists of two separate Peltier plates which temperature can be adjusted from –20 to +80 °C. Three samples of each PEDOT:PSS nanocomposite system were used. The sample was put into the gap between the Peltier plates to generate temperature gradient. The temperature difference  $\Delta T$  across the sample was registered with a thermocouple, and the thermovoltage  $\Delta V$  generated was measured with an HP34401A multimeter. The Seebeck coefficient was determined from the slope of  $\Delta V$ – $\Delta T$  curves. Thermal gravimetric analysis (TGA) according to EN ISO 11358 was carried out using TGA1/SF device (Mettler Toledo Inc.). The change in sample weight was determined at temperature range of 25 – 800 °C at a heating rate of 10 °C/min. Each sample mass was ~ 10 mg and the measurements were performed in nitrogen atmosphere.

## 3. Results and discussion

### 3.1. Thermoelectric performance

Measurements of thermopower properties (Figure 1) show that addition of SWCNT filler to PEDOT:PSS up to 1 wt. % results in steep increase in Seebeck coefficient by doubling its value from 8.0  $\mu\text{V/K}$  to 19.6  $\mu\text{V/K}$ . This indicate that dispersed SWCNT filler improves Seebeck coefficient which is governed by formation of electrical percolation network in PEDOT:PSS matrix volume where distance between individual SWCNTs decreases to form electrical contacts between SWCNTs thus improving electrical conductivity of PEDOT:PSS. By further increasing SWCNT concentration up to 5 wt. % the improvement of Seebeck coefficient does not show noteworthy changes. The main reason for such an effect could be that at 1 wt. % SWCNT concentration the composite has reached percolation threshold where additional increase in filler concentration gives no considerable effect.

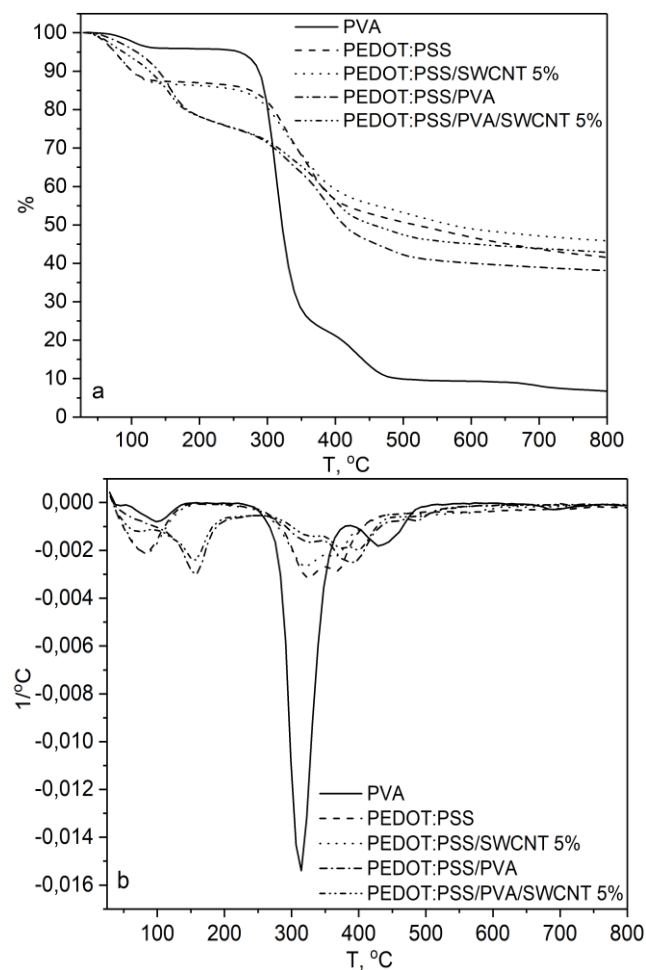
As expected, addition of PVA, as a typical dielectric polymer, to PEDOT:PSS/SWCNT, reduces the measured thermopower value. However, at higher SWCNT concentrations (> 3 wt. %) it is still possible to achieve some increase in Seebeck effect. The less pronounced enhancement in Seebeck coefficient arises from lower electrical conductivity of the polymer blend matrix due to the fact that PVA hydroxyl groups form hydrogen bonds with PSS sulfonate groups, reducing the negative charge in the PSS [7].



**Figure 1.** Seebeck coefficient of PEDOT:PSS/SWCNT and PEDOT:PSS/PVA/SWCNT composites.

### 3.2. Thermal gravimetric analysis

Thermal gravimetric behaviour of the investigated materials is depicted in Figure 2a-b.



**Figure 2.** TGA (a) and DTG (b) curves of PEDOT:PSS/PVA/SWCNT composites.

The first weight loss region of PEDOT:PSS sample from 20 to 120 °C is related to release of absorbed water [8], which makes up approximately 12 wt. %. Later, the second weight loss stage, with two overlapping first derivative curve (DTG) peaks, describes decomposition of PSS at 320 °C by rupturing of the sulfonate groups from styrene and PEDOT thiophene chain decomposition at 365 °C [9]. Whereas the first PVA weight loss step with loss of 4 wt. % of absorbed water is located in the temperature range from 50 to 125 °C. Next step is decomposition of hydroxyl groups with peak at 307 °C, followed by smaller weight loss stage at 430 °C (scission of C-C bonds in PVA backbone) [10]. In PVA and PEDOT:PSS blend and its nanocomposite with SWCNT this weight loss step is shifted towards the direction of higher temperatures, most probably due to release of the bound water as a result of hydrogen bonding between PVA hydroxyl groups and PSS sulfonate groups.

In the presence of SWCNT filler residual weight of PEDOT:PSS and PEDOT:PSS/PVA based composite samples is correspondingly increased as well as weight losses of the composites, especially PEDOT:PSS/PVA, up to ca 300°C are promoted. According to thermogravimetric relationships of the investigated composites, it could be estimated that PEDOT:PSS and PEDOT:PSS/PVA based composites could be used for room temperature thermoelectric applications.

#### 4. Conclusions

Thermopower measurement results indicated SWCNT contribution to Seebeck coefficient improvement due to the increase of PEDOT:PSS electrical conductivity which resulted in sharp increase in Seebeck coefficient at 1 wt. % of SWCNT concentration because of formation of electrical percolation network. Blending of PEDOT:PSS with PVA revealed that at SWCNT concentration higher than 3 wt. % it is possible to keep an increase in Seebeck coefficient, even in the presence of insulating polymer matrix however at 14 – 17 % smaller values. TGA measurements of PEDOT:PSS/PVA blends demonstrated that in the presence of SWCNT filler weight losses of the composites, especially PEDOT:PSS/PVA, up to ca 300°C are promoted.

#### Acknowledgement

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