

# Melt-mixed thermoplastic polymer/carbon nanotube composites for thermoelectric applications

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## ABSTRACT

In our study, polymer composites with an industrially widely used polymer, namely polypropylene (PP) as the matrix, were prepared by small-scale melt processing. Singlewalled carbon nanotubes (SWCNTs) were applied to construct an electrical conducting network in this insulating thermoplastic matrix. In addition, high Seebeck coefficient (S) copper oxide (CuO) microparticles were incorporated into these composites to build up a mixed filler system. The effect of SWCNT content on electrical conductivity ( $\sigma$ ), S, and power factor (PF) was studied. It was shown that the charge carriers injected by SWCNT addition are detrimental to the Seebeck coefficient, leading to an optimised PF at 4 wt% SWCNTs. The addition of copper oxide micro-particles can enhance the thermoelectric (TE) properties. In addition, the use of an ionic liquid during melt mixing leads to higher TE values, whereas the variation of melt-mixing processing conditions did not show much effect. By using special processing additives during the melt mixing, like polyethylene glycol (PEG), doping of the nanotubes can be achieved, resulting in negative Seebeck coefficients.

To construct demonstrators, two composites were selected: p-type PP/ 2 wt% SWCNT composite with 5 wt% CuO (with S up to 45  $\mu\text{V/K}$ ), and n-type composite (with S up to -56  $\mu\text{V/K}$ ) using the same composition and 10 wt% PEG. The two prototypes with 4 and 49 thermocouples of these p- and n-type composites delivered output voltages of 21 mV and 110 mV, respectively, at a temperature gradient of 70 K.

**Keywords:** polypropylene, carbon nanotubes, melt mixing, thermoelectric properties, Seebeck coefficient

## 1 INTRODUCTION

Thermoelectric generators (TEG), which can convert waste heat directly into electricity, are one type of promising energy harvesting devices. The thermoelectric (TE) effect (also called Seebeck effect) describes an electrical potential (voltage  $\Delta U$ ) induced by a temperature difference ( $\Delta T$ ) between the two sides of a material. High Seebeck coefficient (S), high electrical conductivity ( $\sigma$ ) and

low thermal conductivity (k) are favourable for high TE efficiency with high power factor ( $\text{PF} = \sigma \cdot S^2$ ).

An efficient TEG requires high performance p-type (positive S) and n-type (negative S) TE materials. To avoid problems due to different thermal expansion coefficients or corrosion effects of two different materials, it is desired to combine similar p- and n-type materials for device fabrication. An ideal scenario is to apply the same base material, which can be doped both into p-type and n-type.

Compared to traditional TE materials, polymers are flexible and contain abundant atoms (mostly C, H, O). Polymers are widely available, can be easily processed into different shapes and have much lower cost and density. In addition, pure polymers in general have intrinsic low thermal conductivity ranging from 0.1 to 0.6 W/m·K [1], which is desired for high TE parameters.

There are two general possibilities when using polymers for TE applications (compare to Figure 1): (a) use of intrinsically conductive polymers (ICP) and (b) use of polymer composites consisting of insulating/conducting polymer matrix and conductive and/or semiconductor fillers. Insulating thermosetting or thermoplastic polymers can be transformed into conductive ones by adding a certain amount of conductive fillers above the electrical filler percolation. In both cases semiconductor based TE materials can be added to enhance the thermopower. ICPs can be also additionally filled with conductive fillers, like carbon nanotubes, graphite nanostructures etc.

Polymers can be processed either in the solution or melt state, both of which could be scaled up for mass fabrication to reduce the cost. In comparison, melt processing is more environmental friendly as it prevents the use of solvents and enables the production of larger material amount.

In recent years, there has been intensive research on polymer based TE materials with focus on the p-type materials. PEDOT is a very promising solution processable p-type TE material of which a high power factor up to 324  $\mu\text{W/m}\cdot\text{K}^2$  was recorded for PEDOT-Tos, where Tos represents the counterion tosylate [2]. A multilayer thin film of solution processed polyaniline, graphene and doublewalled carbon nanotubes, as a p-type material, exhibited a high power factor of up to 1825  $\mu\text{W/m}\cdot\text{K}^2$  [3] which is comparable to that of semiconductors.

In contrast, n-type polymer based materials are rarely studied, mostly due to their low air stability and poor TE

properties. Also n-type polymer based TE materials can be categorized into two groups: intrinsically conductive n-type polymers and composites. Composites are fabricated either based on (a) p-type conductive polymers with n-type fillers; (b) n-type conductive polymers with p-type fillers or (c) based on insulating polymers (e.g. PVDF) with n-type semiconductors or n-type CNTs.

Powder pressed n-type electrical conductive polymers, poly(Kx(Ni-1,1,2,2-ethenetetrathiolate)s) (poly(Ni-ett)s), were reported with a stable high power factor of  $66 \mu\text{W}/\text{m}\cdot\text{K}^2$  at room temperature [4]. However, they are neither soluble nor processable in the melt state. Solution processed n-type poly(Ni-ett)s were thereby designed but much lower power factors of  $\sim 0.02$  and  $4.7 \times 10^{-4} \mu\text{W}/\text{m}\cdot\text{K}^2$  were found [5,6]. The highest power factor at room temperature for solution processed n-type electrical conductive polymers was reported for self dopable perylene diimides (PDI), of which the power factor reached a value of  $1.4 \mu\text{W}/\text{m}\cdot\text{K}^2$  [7]. N-type polymers, such as polyethyleneimine (PEI) and a conjugated polyelectrolyte (such as poly(fluorene-altbenzothiadiazole)), were applied to produce n-type composites with common p-type CNTs and displayed power factors of  $\sim 10 \mu\text{W}/\text{m}\cdot\text{K}^2$  [8-11] and  $\sim 18 \mu\text{W}/\text{m}\cdot\text{K}^2$  [12], respectively. In fact, most of as produced CNTs are p-type conductors due to the synthesis related oxygen impurities [13]. These p-type CNTs could be treated with nitrogen or salt/crown ether to produce n-type CNTs and used afterwards to fabricate n-type composites [13,14]. However, to retain the n-type behaviour, this polymer has to be stored inside a protected atmosphere. Solution processed n-type polymers are still under development aiming for higher power factor, higher air stability and the prospect for large scale fabrication.

Despite of the advantage of melt-mixing versus solution mixing, there are only few papers focusing on melt mixed composites. This is mainly due to the much lower values of electrical conductivity achievable for polymer/CNT or graphite nanoplate (GNP) based composites. Due to polymer wrapping around CNTs, relatively high contact resistance occurs, requiring electron tunneling/hopping to achieve electrical conductivity. Antar et al. developed melt mixed p-type composites with poly(lactic acid) (PLA), CNTs and expanded graphite (eGR), of which the maximum Seebeck coefficient is  $\sim 18 \mu\text{V}/\text{K}$  for PLA filled with eGR [15]. In this study, high filling levels of up to 30 wt% fillers resulted in electrical conductivities of about 40 S/cm [15]. A strongly increased thermal conductivity to 5.5 W/m·K was also reported. Mixed filler systems of CNT and eGR resulted in synergistic effects in conductivity but not in the Seebeck coefficient [15]. Melt mixed p-type composites based on polycarbonate (PC) and CNTs were presented by Liebscher et al., of which the Seebeck coefficient is lower than  $14 \mu\text{V}/\text{K}$  and the electrical conductivity is less than 0.01 S/cm [16,17]. Melt mixed PVDF composites filled with CNTs also showed low Seebeck coefficient around  $10 \mu\text{V}/\text{K}$  and electrical conductivity lower than  $10^{-4}$  S/cm [18]. Melt mixed PVDF

composites with GNPs displayed a Seebeck coefficient of  $\sim 28 \mu\text{V}/\text{K}$  and the corresponding composites designed with foam structure demonstrated a high Seebeck coefficient up to  $58 \mu\text{V}/\text{K}$  [18]. Nevertheless, the electrical conductivity of this foam structure is extremely low, ca  $10^{-8}$  S/cm.

Another interesting approach is presented in [19] where CNT/ $\text{Bi}_2\text{Te}_3$  hybrid fillers decorated UHMWPE granules were pressed together, leading to a segregated network structure. The segregated composite containing 2.6 vol% MWCNTs and 5.1 vol%  $\text{Bi}_2\text{Te}_3$  exhibited a Seebeck coefficient of  $29 \mu\text{V}/\text{K}$  and thermoelectric figure of merit ZT of  $3 \times 10^{-5}$  at RT. However, this material can not be melt processed anymore into other shapes.

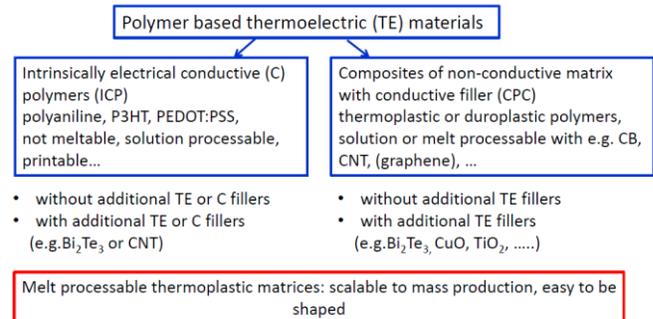


Fig. 1: Classification of polymer based thermoelectric materials

## 2 EXPERIMENTAL

PP Moplen HP400R (LyondellBasell Industries) was selected together with SWCNTs of the type Tuball from OCSiAl Ltd. The incorporation of the nanotubes was done by melt mixing using a small-scale twin-screw compounder of the type Xplore 15ccm. In addition, copper oxide (CuO) from Sigma Aldrich was used as a TE filler. In addition, the ionic liquid (IL) 1-methyl-3-octylimidazolium tetrafluoroborate (purity >97%, HPLC, Sigma Aldrich) was applied. For switching p- to n-type behaviour, polyethylene glycol (PEG) flakes (Sigma Aldrich,  $M_n$  10,000 g/mol) were used. The morphology of the composites was studied scanning electron microscopy (Zeiss UltraPlus) on cryofractures. To measure electrical conductivity a 4-electrode test fixture combined with a Keithley electrometer E6517A or Keithley multimeter DMM2000 was used and the Seebeck coefficient at room temperature was determined using a measurement platform SRX (designed and developed by Fraunhofer IPM Freiburg, Germany).

## 3 RESULTS

### 3.1 P-type composite development

For the selected SWCNTs, electrical percolation for charge transport occurs already at 0.1 wt% CNTs. The measured conductivities are already high enough to measure the Seebeck effect starting at 0.75 wt% SWCNTs.

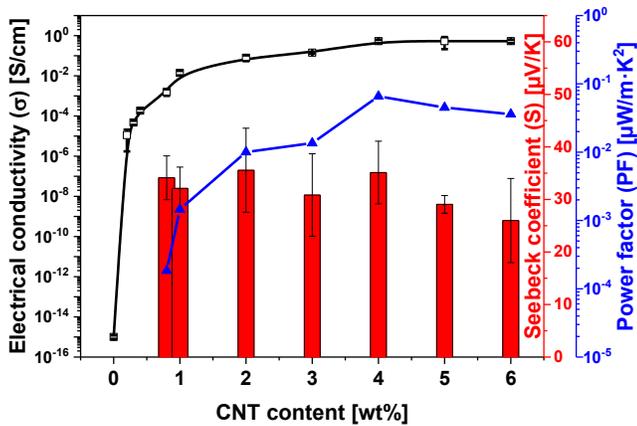


Figure 2: Dependence of TE properties on SWCNT content for melt mixed PP based composites, adapted from [20].

Whereas conductivity show an increasing tendency with SWCNT content, the maximum S value of 35  $\mu\text{V/K}$  was achieved at 4 wt% loading, followed by a decreasing tendency at higher loadings (Fig. 2). Thus, an optimized power factor of  $6.6 \times 10^{-2} \mu\text{W}/(\text{m} \cdot \text{K}^2)$  is obtained at 4 wt% [20]. The addition of CuO at a fixed SWCNT content, here 2 wt%, slightly increases the electrical conductivity and Seebeck coefficient and achieves best values of power factor at 5 wt% SWCNT (Fig. 3). In composites with 0.8 wt% SWCNTs the value of 34.1  $\mu\text{V/K}$  could be enhanced to 45  $\mu\text{V/K}$  after addition of 5 wt% CuO [20].

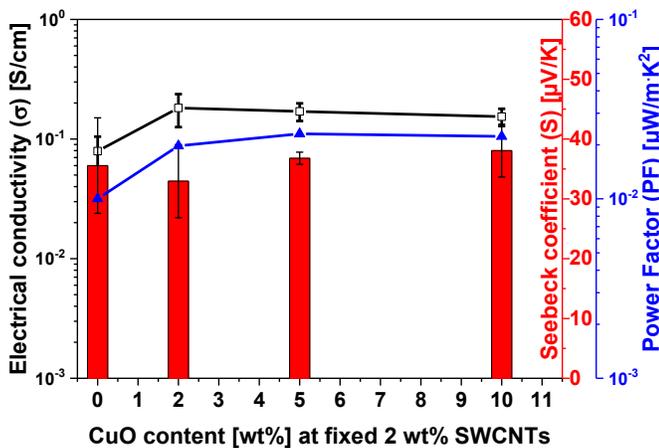


Figure 3: TE properties vs. CuO content PP/2 wt% SWCNT, adapted from [20].

When the selected ionic liquid (2 wt%) was used in combination with 2 wt% SWCNTs, an increase in Seebeck coefficient towards 63.8  $\mu\text{V/K}$  was achieved [21]. This corresponds to a power factor of  $0.26 \mu\text{W}/(\text{m} \cdot \text{K}^2)$  and a ZT (@RT) of  $1.6 \times 10^{-4}$  (thermal conductivity 0.51  $\text{W}/(\text{m} \cdot \text{K})$ ).

Morphological studies revealed quite good SWCNT dispersion in the PP matrix and showed small IL inclusions, as IL and PP are not miscible (Figure 4).

Changes in the melt-mixing conditions (variation of rotation speed and mixing temperature) did not show significant influences on the TE properties [21].

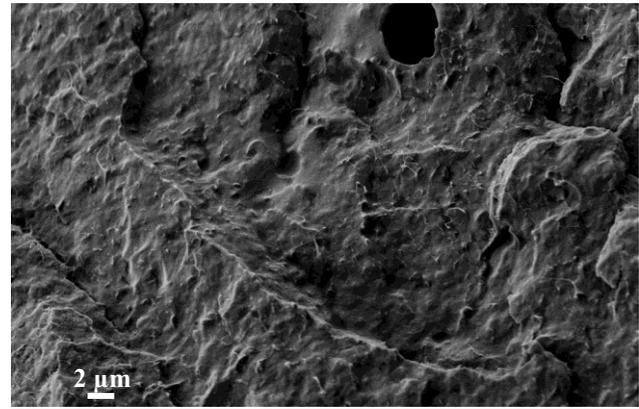


Figure 4: SEM cryofracture of PP filled with 2 wt% SWCNT and 2 wt% IL

### 3.2 N-type composites

Among the diverse possibilities to achieve n-type materials, we used the way of using special processing additives during the melt mixing, i.e. polyethylene glycol (PEG). In this procedure doping of the nanotubes could be achieved resulting in negative Seebeck coefficients [22]. Already the ratio SWCNT:PEG = 1:1 resulted in this switch of the behaviour. Similar results as shown in Figure 5 for PP with 0.8 wt% SWCNTs were also obtained for composites with 2 wt% SWCNTs. The use of the optimized ratio of SWCNT:PEG = 1:5 resulted in the composites with 2 wt% SWCNTs in a Seebeck coefficient of  $-56 \mu\text{V/K}$  and a power factor of  $7.8 \times 10^{-2} \mu\text{W}/(\text{m} \cdot \text{K}^2)$ .

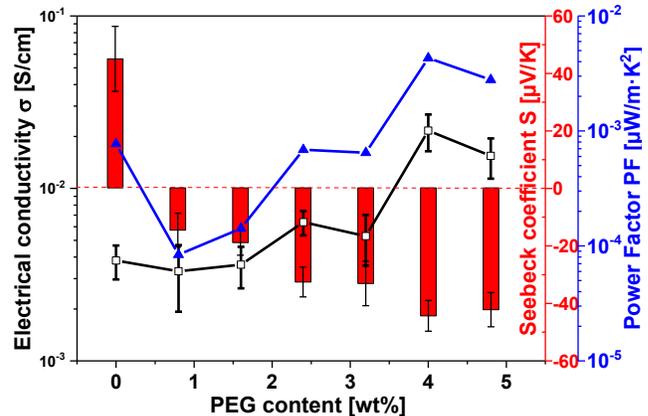


Figure 5: Dependence of TE properties on PEG content for PP/0.8 wt% SWCNT/5 wt% CuO, adapted from [22].

### 3.3 Thermoelectric generator modules

To construct demonstrators, finally two melt-mixed composites were selected: p-type PP/2wt% SWCNT composite with 5 wt% CuO (with S up to 45  $\mu\text{V/K}$ ) and n-type composite (with S up to  $-56 \mu\text{V/K}$ ) using the same composition and 10 wt% PEG. The two prototypes with 4 and 49 thermocouples of these p- and n-type composites delivered output voltages of 21 mV and 110 mV, respectively, at a temperature gradient of 70 K [22].

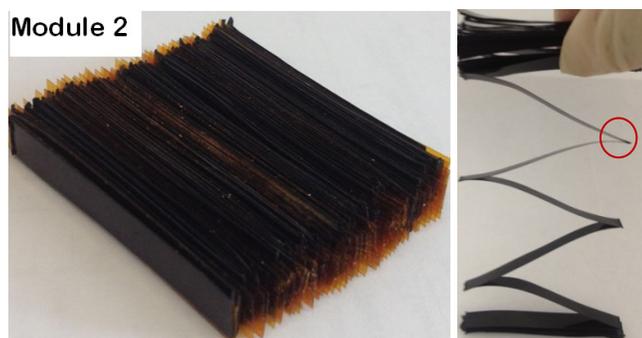


Figure 6: TEG module with 49 thermocouples made from strips of melt mixed PP-SWCNT composites.

#### 4 SUMMARY

Even if the values achieved for the power factor are still far below those of traditional TE materials and ICP like PEDOT:PSS, such composites may be suitable if only low thermopower is required, like to enable the function of sensors. Especially the recovery of heat from pipes or tubes transporting hot media (below 120°C) can be imagined. The main drawback at the moment is the comparatively low electrical conductivity of polymer based composites, which may be increased by using for example branched nanotubes having already a network structure. The Seebeck coefficients of the CPCs are partially comparable to those reported for ICPs.

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