Polypropylene-based melt mixed composites with singlewalled carbon nanotubes for thermoelectric applications: switching from p-type to n-type by the addition of polyethylene glycol

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Abstract: The thermoelectric properties of melt-processed conductive nanocomposites consisting of an insulating polypropylene (PP) matrix filled with singlewalled carbon nanotubes (CNTs) and copper oxide (CuO) were evaluated. An easy and cheap route to switch p-type composites into n-type was developed by adding polyethylene glycol (PEG) during melt mixing. At the investigated CNT concentrations of 0.8 wt% and 2 wt% (each above the electrical percolation threshold of ~ 0.1 wt%), and a fixed CuO content of 5 wt%, the PEG addition converted p-type composites (positive Seebeck coefficient (S)) into n-type (negative S). PEG was also found to improve the filler dispersion inside the matrix. Two composites were prepared: P-type polymer/CNT composites with high S (up to 45 μV/K), and n-type composites (with S up to -56 μV/K) through the addition of PEG. Two prototypes with 4 and 49 thermocouples of these p- and n-type composites were fabricated, and delivered an output voltage of 21 mV and 110 mV, respectively, at a temperature gradient of 70 K.

1. Introduction

A thermoelectric generator (TEG) is an energy harvesting device that can convert waste heat directly into electricity. It consists of multiple p-type and n-type thermoelectric (TE) materials that are connected electrically in series and thermally in parallel.

The performance of a TE material is evaluated by a dimensionless figure of merit ZT ($ZT=\sigma S^2T/\kappa$), where σ is the electrical conductivity, S is the Seebeck coefficient, κ is the thermal conductivity and the numerator σS^2 is defined as the power factor [1]. Depending on the dominant charge carrier type, the Seebeck coefficient can be positive (holes, p-type) or negative (electrons, n-type). For room temperature applications, semiconductors (e.g. bulk bismuth telluride (Bi_2Te_3) alloys), are widely used as TE materials due to their high power factors [2]. However, it is difficult to reduce the high thermal conductivity of these materials (e.g. Bi_2Te_3 has a κ of 1.2 W/(m·K)) to a value lower than 1 W/(m·K) so that their ZT is still around 1. The toxicity and scarcity of employed component (e.g. Te) are of concern. Their rigidity and high production cost limit semiconductor based TE materials to niche applications [3].

On the contrary, organic materials are flexible and contain abundant atoms (mostly C, H, O) [4]. Polymers are widely available, can be easily processed into different shapes and have much lower cost. In addition, pure polymers in general have intrinsic low thermal conductivity ranging from 0.1 to 0.6 W/(m·K) [5], which is one of the desired TE parameters. They can be processed either in the solution or melt state, both of which could be scaled up for mass fabrication. In comparison, melt processing is more environmental friendly as it does not require the use of solvents and enables the production of larger amounts of material.

Two general concepts are introduced for polymer-based TE applications as well for p- and n-type materials: (a) use of intrinsically conductive polymers (ICPs) and (b) use of conductive polymer composites (CPCs) consisting of an insulating/conducting (ICP) polymer matrix and conductive and/or semiconductor fillers. As ICPs are in most cases not meltable, they have to be processed in solution.

Among the ICP materials, based on their high electrical conductivity, solution processed poly(3,4-ethylenedioxythiophene) (PEDOT) and polyaniline (PANI) have been intensively studied as **p-type** TE materials [6, 7]. PEDOT-Tos, where Tos represents the counter-ion tosylate, has been shown to display a high power factor (up to 324 µW/(m·K^2)), and the Seebeck coefficient of this material was increased up to few hundreds of µV/K through a chemical doping of the polymer structure [6]. A multilayer thin film of solution processed polyaniline, graphene and doublewalled carbon nanotubes, as a p-type material, exhibited a high power factor up to 1825 µW/(m·K^2) which is comparable to that of semiconductors [7].

In contrast, **n-type polymer**-based materials are rarely studied, mostly due to their low air stability and poor TE properties. Nevertheless, n-type organic materials are crucial to fabricate completely organic and flexible TEGs. **Powder-pressed n-type** ICPs, poly(K_x(Ni-1,1,2,2-ethenetetrathiolate)s) (poly(Ni-ett)s) were reported with a stable high power factor of 66 μW/(m·K^2) at room temperature [8]. However, these polymers are neither soluble nor processed in the melt state. **Solution processed n-type** poly(Ni-ett)s were therefore developed, but much lower power factors of ~ 0.02 and 4.7x10^{-4} μW/(m·K^2) were reported [9, 10]. The highest power factor at room temperature for solution processed n-type ICPs was reported for self-dopable perylene diimides (PDI); the power factor of this material reached a value of 1.4 μW/(m·K^2) [11]. However, this polymer had to be stored inside a protected atmosphere to obtain this value.

To fabricate **n-type TE materials based on composites**, conductive fillers like carbon nanotubes (CNTs) can be added to polymers to enhance their electrical conductivity while maintaining a low thermal conductivity (0.1-2 W/(m·K) [12]). Nevertheless, most as-produced CNTs are p-type conductors due to oxygen impurities [13]. When these p-type CNTs are taken to fabricate n-type composites, n-type polymer matrices are required to obtain an n-type characteristic. N-type polymers, such as polyethyleneimine (PEI) (an ion conducting polymer) and poly(fluorene-alt-benzothiadiazole) (a conjugated polyelectrolyte) have been used with common p-type CNTs to produce n-type composites that displayed power factors of ~ 10 μW/(m·K^2) [14-17] and ~ 18 μW/(m·K^2) [18], respectively. Common p-type CNTs have been treated with nitrogen or salt/crown ether to produce n-type CNTs [13, 19]. Composites with these n-type CNTs showed power factors of 0.01 μW/(m·K^2) with electrically conductive poly(3-hexylthiophene) (P3HT) (filled with 80 wt% n-type nitrogen converted CNTs) [19] and 7 μW/(m·K^2) with rubber (filled with 30 wt% n-type salt/crown ether converted CNTs) [13, supp. inf.] as matrices. Air stability is a challenging issue for these n-type materials. The negative Seebeck coefficients of PEI-doped CNT composites turned into positive value after 18 days [15] or 10 hours [13] of exposure to air. The corresponding electrical conductivity also decreased [15]. Additional treatment could improve the stability of these n-type composites, for instance, a treatment with strong reducing agent $NaBH_4$ and lamination improved the air stability of n-type PEI doped CNT composites [15].

For the production of effective TEGs, the usage of compatible p- and n-type materials – preferably with the same base materials – is desirable as this can avoid problems caused by different thermal expansion coefficients as well as corrosion effects [20]. For instance, Mai et al. developed solution-processed p- and n-type composites by varying the concentration of p-type CNT in n-type conjugated polyelectrolytes, of which power factors of 4 $\mu W/(m \cdot K^2)$ were measured for the p-type composites (filled with 60 wt% CNTs) and 17.8 $\mu W/(m \cdot K^2)$ for the n-type composites (filled with 50 wt% CNTs) [18]. Montgomery et al. fabricated a solution-processed p-type TE material with a power factor of 1.48 $\mu W/(m \cdot K^2)$ based on polyvinylidene fluoride (PVDF) and 20 wt% p-type CNTs [16]. After spray coating of PEI, this p-type material was then converted into n-type and showed a power factor of 1.47 $\mu W/(m \cdot K^2)$ [16]. Dörling et al. demonstrated a UV radiation induced switching phenomenon of p-type (~ 26 µV/K) to n-type (~ -6 µV/K) for solution-processed P3HT composite filled with 30 wt% n-type CNTs [19]. A corresponding module (composed of 5 p/n thermocouples) delivered an output voltage of 12 mV at 70 K temperature difference [19].

All n-type polymer based TE materials described before were fabricated using solvent-based methods. These techniques, including roll to roll printing, are still practiced on the laboratory scale and need large amount of solvents for processing.

Despite of the advantage of **melt mixing versus solution mixing**, there are only few papers focusing on melt mixed composites based on insulating polymers with conductive fillers. There is only limited work on melt mixed p-type composites, and no articles could be found reporting n-type composites obtained by melt mixing. One reason for this is that both the electrical conductivity and Seebeck coefficient achieved for such polymer composites are still very low [21-24]. Antar et al. developed melt mixed p-type composites with poly (lactic acid) (PLA), multiwalled CNTs (MWCNTs) and expanded graphite (eGR), with a maximum Seebeck coefficient of ~18 µV/K for PLA filled with 10-30 vol% eGR [21]. Melt mixed p-type composites based on polycarbonate (PC) and 2.5 wt% MWCNTs were reported by Liebscher et al. with Seebeck coefficients lower than 14 µV/K [22,23]. Melt mixed PVDF composites filled with up to 8 wt% MWCNTs also showed low Seebeck coefficient of maximum 10 µV/K [24]. After foaming these PVDF/CNT composites, a slight reduction in the Seebeck coefficient and reduction of the electrical conductivity were found. However, when using 5-15 vol% graphene nano-platelets (GNPs), Seebeck coefficients of ~°28 µV/K were reached and the corresponding composite with 15 vol% GNP designed with foam structure demonstrated significantly improved Seebeck coefficients up to 58 µV/K but the electrical conductivity was extremely low (< 10^{-8} S/cm) [24]. Our previous work has shown that a melt mixed composite based on polypropylene (PP), 0.8 wt% singlewalled CNTs and 5 wt% copper oxide exhibits a Seebeck coefficient up to 45°µV/K [25].

Considering the compatibility of p- and n-type materials required for TEG construction and the lack of investigation in melt mixed n-type polymer-based TE materials, the focus of this contribution is to develop melt mixed both p- and n-type polymer composites from the same base materials. For these proposed melt mixed p- and n-type composites, polypropylene (PP), a widely used thermoplastic in industry, is utilized as the polymer matrix. Commercial singlewalled CNTs (p-type) were selected to build up an electrical network inside the insulating polymer matrix. The co-addition of p-type semiconductor CuO was used to increase the electrical conductivity and Seebeck coefficient of p-type composites [25]. These p-type composites (filled with CNT/CuO) were then switched into n-type simply by the addition of a processing additive, polyethylene glycol (PEG), during composite preparation. In previous work the addition of PEG was shown to improve the filler dispersion during melt processing [26]. Furthermore, two prototypes were fabricated as a proof of concept, to show the feasibility of using melt mixing technique to develop both p- and n-type polymer-based composites.

2. Experimental

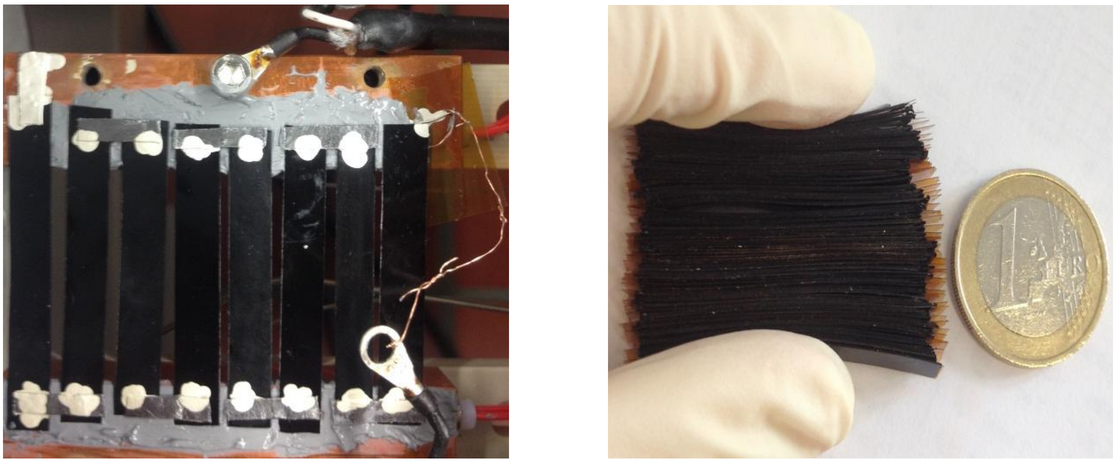
2.1 Materials and composite preparation

PP granules (Moplen HP400R, LyondellBasell Industries) were mechanically milled into a powder with a diameter less than 1 mm and melt mixed with singlewalled CNTs (purity > 75%, Tuball^{TM}, OCSiAl Ltd., plasma oxidized by the supplier) to prepare PP/CNT composites. Based on previous investigations [25] where the influence of a CuO addition (2 - 10 wt%) was studied, a content of 5 wt% CuO was selected which resulted in an optimized power factor at both CNT loadings. Thus, at both CNT contents, CuO powder (< 5 µm, purity > 97%, Riedel de Haën, now Sigma Aldrich, SEM image compare [25]) at 5 wt% was added simultaneously with PP and CNT to prepare PP/CNT/CuO composites. To produce n-type composites, PEG (M_n 10,000 g/mol, flakes, Sigma Aldrich) was added together with CNTs, CuO and PP to prepare PP/CNT/CuO/PEG composites. Therefore, for samples with 0.8 wt% CNTs, the ratios of PEG to CNTs of 1:1 (0.8 wt% PEG), 2:1 (1.6 wt% PEG), 3:1 (2.4 wt% PEG), 4:1 (3.2 wt% PEG), 5:1(4 wt% PEG) and 6:1 (4.8 wt% PEG) were studied. Based on the results on 0.8 wt% CNTs, at 2 wt% CNT loading only the PEG:CNT ratios of 5:1 (10% PEG) and 4:1 (8 wt% PEG) were prepared. The appropriate amounts of PEG, CNT, PP and CuO were put into a glass vial and dried overnight inside a vacuum oven at 80°C. Before melt mixing, the glass vial was shaken to distribute the components. A conical twin-screw microcompounder (Xplore MC 15, The Netherlands) with a capacity of 15 ccm was used for the melt mixing with mixing conditions fixed to a melt temperature of 210°C, a rotation speed of 250 rpm, and a mixing time of 5 min. The extruded strand was cut in granule sized pieces and compression molded at 210°C under a pressure of 50 kN into circular plates with a diameter of 60 mm and a thickness of 0.3 mm using a press PW 40 EH (Paul Otto Weber GmbH, Germany). The sample plates were cooled with a minichiller set to -6°C for 90 s. These mixing and compression molding conditions were selected in order to be comparable to previous studies [25, 27]. Rectangular samples were manually cut and used for characterization of electrical conductivity, Seebeck coefficient and Hall Effect. For thermal conductivity characterization, plates with a diameter of 15 mm and a thickness of 2 mm (based on the instrument's requirements) were compression molded under the same compression molding conditions. In the nomenclature the numbers represent the weight percentage of the used filler/additive with respect to the whole composite. For instance, PP-xCNT-yCuO-zPEG represents a composite having x wt% CNTs, y wt% CuO and z wt% PEG.

2.2 Prototype fabrication

Strips with a dimension of 40 mm × 5 mm × 0.3 mm were cut from the selected pressed plates of both p- and n-type composites (PP-2CNT-5CuO for p-type and PP-2CNT-5CuO-10PEG for n-type). For one prototype, named as module 1, 8 strips (4 strips of each p- and n-type materials) were mounted on two isolated copper blocks with an electrically insulating but thermally conducting paste (GC-Extreme Thermal Compound, GELID solutions) homogenously spread on top of the copper block (see Figure 1a). These p- and n-type materials were connected electrically in series and thermally in parallel, of which the electrical connections are realized using silver paste and graphite foil. Two ends of module 1 (with 4 p/n thermocouples) were then connected by copper wire to a multimeter Keithley DMM 2001 for the voltage measurement.

For the other prototype, named as module 2 (with 49 thermocouples shown in Figure 1b), p- and n-type materials were connected together by pressing the connections at 120°C, which is above the melting temperature of PP (in a design similar to the structure reported by Hewitt [28]). Polyamide films were then inserted in between p/n materials as the insulation layer. This prototype was then mounted to the copper block as shown in Figure 1a to measure the output voltages at different temperature gradients.



(a) (b)

Figure 1 The demonstration of (a) thermoelectric module 1 with 4 thermocouples and (b) module 2 with 49 thermocouples

2.3 Material characterization

To characterize the electrical volume conductivity (σ) of samples containing 0.8 wt% CNTs, a 2-electrode test fixture combined with a Keithley electrometer E6517A was used. As samples with 2 wt% CNTs have lower electrical resistance, a 4-electrode test fixture combined with Keithley multimeter DMM 2000 was used to eliminate the effects of contact resistance. The Seebeck coefficient (S) at room temperature was determined using the IPM-SRX-900K platform (Fraunhofer IPM, Germany). The Hall effect measurements were carried out on a IPM-HT-Hall-900K SYSTEM (Fraunhofer IPM, Germany). The values represent mean values (including standard deviation) of 8 measurements. The thermal conductivity (κ) through the sample thickness of 3 samples was measured based on the laser flash principle and carried out using a Netzsch LFA 447 Nano Flash (Netzsch equipment manufacturing GmbH, Selb, Germany). With this method, specific heat (C_p) and thermal diffusivity (α) are characterized to give the thermal conductivity (κ) of samples. The needed sample density (ρ) was determined using a buoyancy method.

The state of the macro-dispersion of the fillers in the composites was studied by the transmission light microscope using software ImageJ version 1.43o. The area ratio A (%) of the area of filler agglomerates (concerning both, CNT and CuO) related to the total area of the images was calculated. Thin sections with a thickness of 5 µm were cut from extruded strands using a Leica RM 2155 microtome (Leica Microsystems GmbH, Germany). Only agglomerates with diameters > 1µm were regarded and 17 cuts were investigated to give the area ratio for each sample. Scanning electron microscopy (SEM) observations of cryo-fractured composite surfaces were performed using a Gemini 1530 microscope.

2.4 Thermoelectric module characterization

The temperature gradient was controlled by the embedded sensors inside the two copper blocks (see Figure 1a). The thermally conducting but electrically insulating paste used between the module and the copper heating block insures homogenous heat conduction. The temperature of one copper block (cold side) was kept at 40°C while the other copper block (hot side) was gradually heated up to a maximum temperature of 110°C to create temperature gradients of 10 K, 20 K, 30 K, 40 K, 50 K, 60 K and 70 K. The generated thermoelectric voltage at the corresponding temperature gradient was measured by the multimeter Keithley DMM 2001.

3. Results and discussion

3.1. Electrical and thermoelectrical characterization of PP based composites

The previous work on PP composites filled with this type of singlewalled CNTs indicated the electrical percolation threshold to be below 0.1 wt% [25, 27]. Thus, the selected CNT contents of 0.8 and 2.0 wt% are above the percolation threshold and are able to build up an effective charge transport inside the composite. These CNT-filled composites are p-type with positive Seebeck coefficient as the used CNTs are p-type fillers (see Table 1). As the Seebeck coefficient is inversely proportional to the carrier concentration (n), while the electrical conductivity is directly proportional to the carrier concentration, increasing the CNT concentration typically results in a reduction in the Seebeck coefficient and an increase in the electrical conductivity [25], as shown e.g. for solution prepared PVDF/CNT composites by Hewitt et al [29]. In our study, electrical conductivity increases slightly when increasing the CNT content from 0.8 to 2.0 wt%, however, the Seebeck coefficient is not reduced but at the same level. At both CNT contents, the addition of p-type filler CuO (5 wt%) injects more charge carriers into composites, slightly increasing the electrical conductivity (see Table 1). Due to the large effective mass of carriers from CuO [30], the carrier mobility (μ) of the composites was greatly reduced. Only a slight increase in the Seebeck coefficient is observed for the composites despite the large Seebeck coefficient of CuO (430 μV/K) [31], whereas the rise is more pronounced (increase by ca. 11 μV/K) in the composite with the lower CNT loading. This low effect is possibly due to the inverse proportionality of Seebeck coefficient to the carrier concentration [32] and the limited amount of CuO.

Table 1 Electrical properties of PP based composites filled with CNTs and CuO (σ electrical conductivity, S Seebeck coefficient, σS^2 power factor, n carrier concentration, μ carrier mobility).

Material	σ [S/cm]	S [μV/K]	σS^2 $[\mu W/(m\cdot K^2)]$	Carrier type	n $[cm^{-3}]$	μ $[cm^2/(V\cdot s)]$
PP-0.8CNT	$1.6\text{x}10^{-3}\pm 6\text{x}10^{-4}$	34.1±4.2	$1.8\text{x}10^{-4}$	p	$3.40\text{x}10^{13}$	$8.50\text{x}10^{2}$
PP-2CNT	$7.9\text{x}10^{-2}\pm 3\text{x}10^{-3}$	35.6±8.0	$1.0\text{x}10^{-2}$	p	$4.99\text{x}10^{15}$	$4.11\text{x}10^{2}$
PP-0.8CNT-5CuO	$3.8\text{x}10^{-3}\pm 8\text{x}10^{-4}$	45.0±11.3	$7.7\text{x}10^{-4}$	p	$2.49\text{x}10^{16}$	7.6
PP-2CNT-5CuO	$1.7\text{x}10^{-1}\pm 3\text{x}10^{-2}$	36.8±1.0	$2.3\text{x}10^{-2}$	p	$7.83\text{x}10^{16}$	8.8

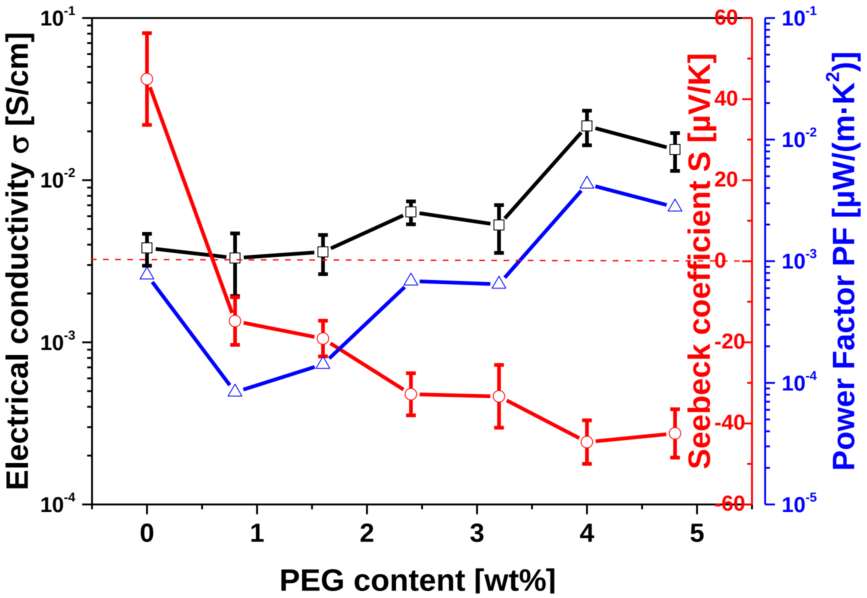


Figure 2 The influence of PEG content on the TE properties for melt mixed composites with fixed CNT (0.8 wt%) and CuO (5 wt%) concentration.

With the co-addition of PEG with 0.8 wt% CNTs and 5 wt% CuO, the electrical conductivity increased starting at 2.5 wt% PEG addition and reached a maximum value at 4 wt% PEG. This p-type composite was turned into n-type, as evidenced by the negative Seebeck coefficient observed with only 0.8 wt% PEG. Further addition of PEG resulted in higher negative Seebeck coefficient (Figure 2). Within the studied PEG concentration range, the Seebeck coefficient was switched from 45 µV/K for the sample without PEG to -44.6 µV/K with 4 wt% PEG addition. This value was changed to -26.4 µV/K after exposure to air for 8 months, and the electrical conductivity remained relative constant (see Figure 3). This material is more stable than the n-type PEI-doped CNT composite reported in [15] (-34 µV/K was turned into 10 µV/K after 18 days exposure to air).

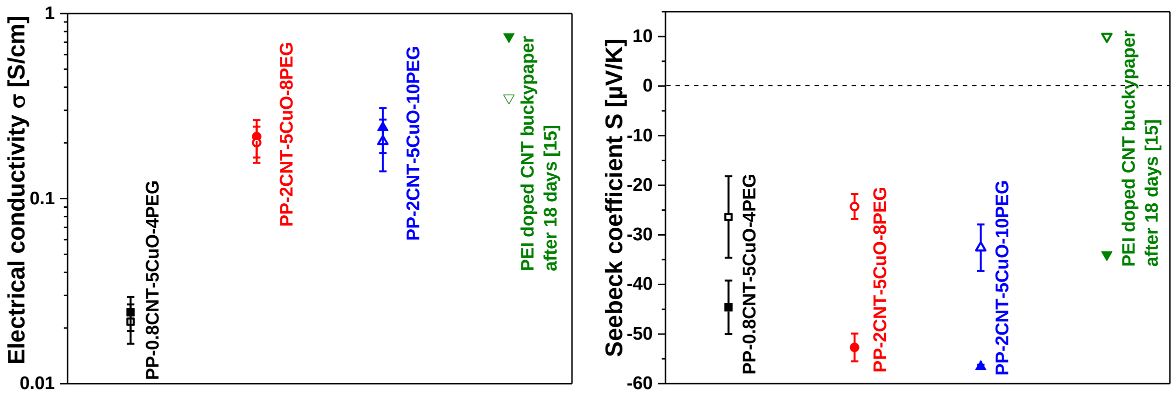
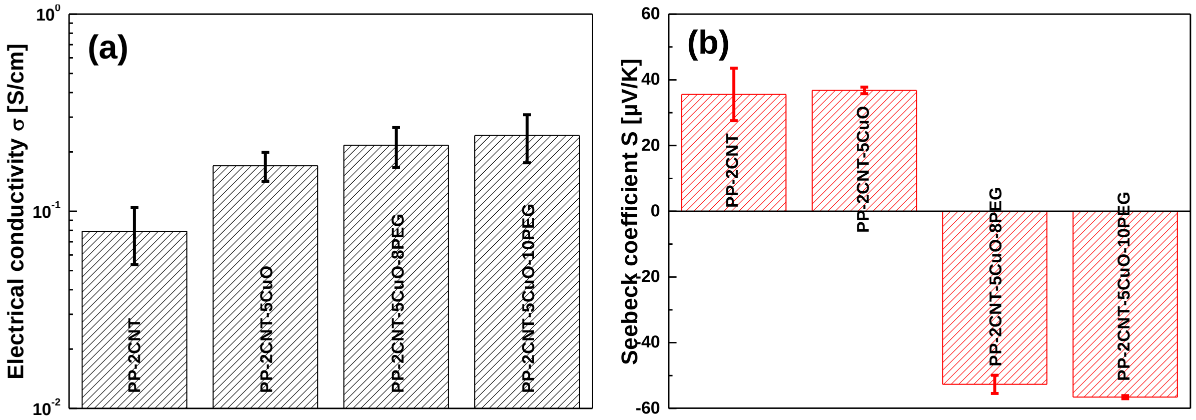


Figure 3 Change in the electrical conductivity σ and Seebeck coefficient S of composites after air exposure for 8 months compared to literature values on PEI-doped CNT buckypaper [15]. Close symbols: as-prepared samples; open symbols: air-exposed samples after 8 months.



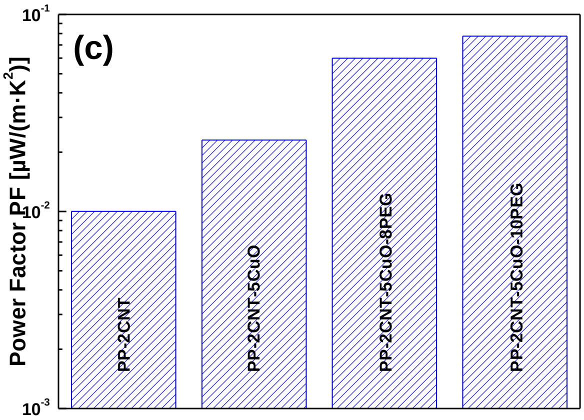


Figure 4 The influence of PEG content on the TE properties for melt mixed composites with fixed CNT (2 wt%) and CuO (5 wt%) concentration.

Similar switching behavior by PEG addition is observed for the composite with 2 wt% CNTs (Figure 4) and 5 wt% CuO. In the composites without PEG, electrical conductivity and Seebeck coefficient at 2 wt% are only slightly higher than that of the composite with 0.8 wt% CNT (compare Table 1) indicating that both concentrations are in the plateau region of the percolation curve. For PP-2CNT-5CuO the Seebeck coefficient is changed from 36.8 µV/K into -56.6 µV/K for PP-2CNT-CuO-10PEG. As a PEG:CNT ratio of 5:1 was found to be the best at 0.8 wt%, this ratio was also applied for composites with 2 wt% CNTs. In addition, 8 wt% PEG (PEG:CNT=4:1) was tested to prove the n-doping induced by PEG. The Seebeck coefficient of the composite depends on the PEG content, as was seen for the composites with 0.8 wt% CNTs. The achieved highest power factor in this work is 7.8x10^{-2} µW/(m·K^2) for PP-2CNT-5CuO-10PEG, which is comparable to solution processed n-type semiconducting polymers (~ 0.1 µW/(m·K^2) [33]). The Hall effect measurements (Table 2) further confirm that PEG is an effective dopant for switch p-type composites into n-type. Also the PEG-doped composites with negative Seebeck coefficient at 2 wt% CNT remain as n-type after air exposure for 8 months (see Figure 3). This is the first time that PEG is proven as an n-type dopant. A plausible mechanism of n-type doping was proposed by Nonoguchi et al.[34]: electron dopants inject electrons to compensate the holes e.g. from CNTs. Above a certain concentration, the Seebeck coefficient is changed into negative value. In this work, the amount of PEG used with respect to the content of CNT and CuO is above the critical concentration, causing all the composites prepared to show a negative Seebeck coefficient. Despite of the inclusion of high thermal conducting CNTs and CuO, all p-type composites and PEG converted n-type composites demonstrate low thermal conductivity of ~ 0.5 W/(m·K) (see Table 3).

Table 2 Hall effect properties of PEG converted n-type composites (n carrier concentration, μ carrier mobility).

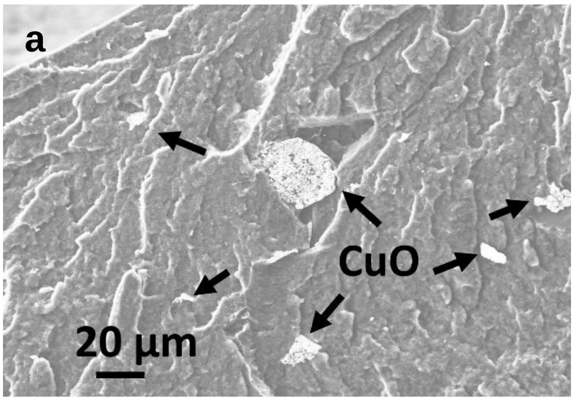
Material	Carrier type	n [cm^{-3}]	μ [$cm^2/(V\cdot s)$]
PP-0.8CNT-5CuO-4PEG	n	4×10^{17}	2.14
PP-2CNT-5CuO-10PEG	n	1.1×10^{19}	0.22

Table 3 Measured properties for the determination of the bulk thermal conductivity of samples (ρ sample density, C_p specific heat, α thermal diffusivity, κ thermal conductivity).

Sample	ρ [g/cm^3]	c_p [$J/(g\cdot K)$]	α [mm^2/s]	κ [$W/(m\cdot K)$]
PP-0.8CNT	0.86±0.02	1.70±0.07	0.26±0.02	0.37±0.02
PP-2CNT	0.91±0.01	1.66±0.07	0.34±0.03	0.51±0.03
PP-0.8CNT-5CuO	0.92±0.00	1.62±0.04	0.27±0.02	0.40±0.02
PP-2CNT-5CuO	0.93±0.02	1.54±0.10	0.32±0.01	0.47±0.02
PP-0.8CNT-5CuO-4PEG	0.94±.02	1.75±0.01	0.25±0.01	0.40±0.02
PP-2CNT-5CuO-10PEG	0.97±0.01	1.65±0.05	0.30±0.02	0.48±0.02

3.2. Morphological characterization

The SEM image Figure 5a depicts the morphology of a cryo-fractured composite without PEG, and reveals that the CuO particles are partially larger as indicated by the supplier. The remaining particles show sizes up to 30 μm, however also smaller particles can be seen. At higher magnifications (Fig. 5b-d) it can be observed that the CNTs are well dispersed inside the PP matrix. At the fractured surfaces at both CNT loadings, a network-like structure can be identified. In the PEG-modified composites no significant changes in CNT dispersion at microscale are observed, however, due to the immiscibility between PEG (hydrophilic) and PP (hydrophobic) the PEG component can be identified as CNT-free areas appearing as holes (see Fig 5c and 5e). This morphology is similar to that reported on PEG-modified melt mixed LLDPE/multiwalled CNT composites [26].



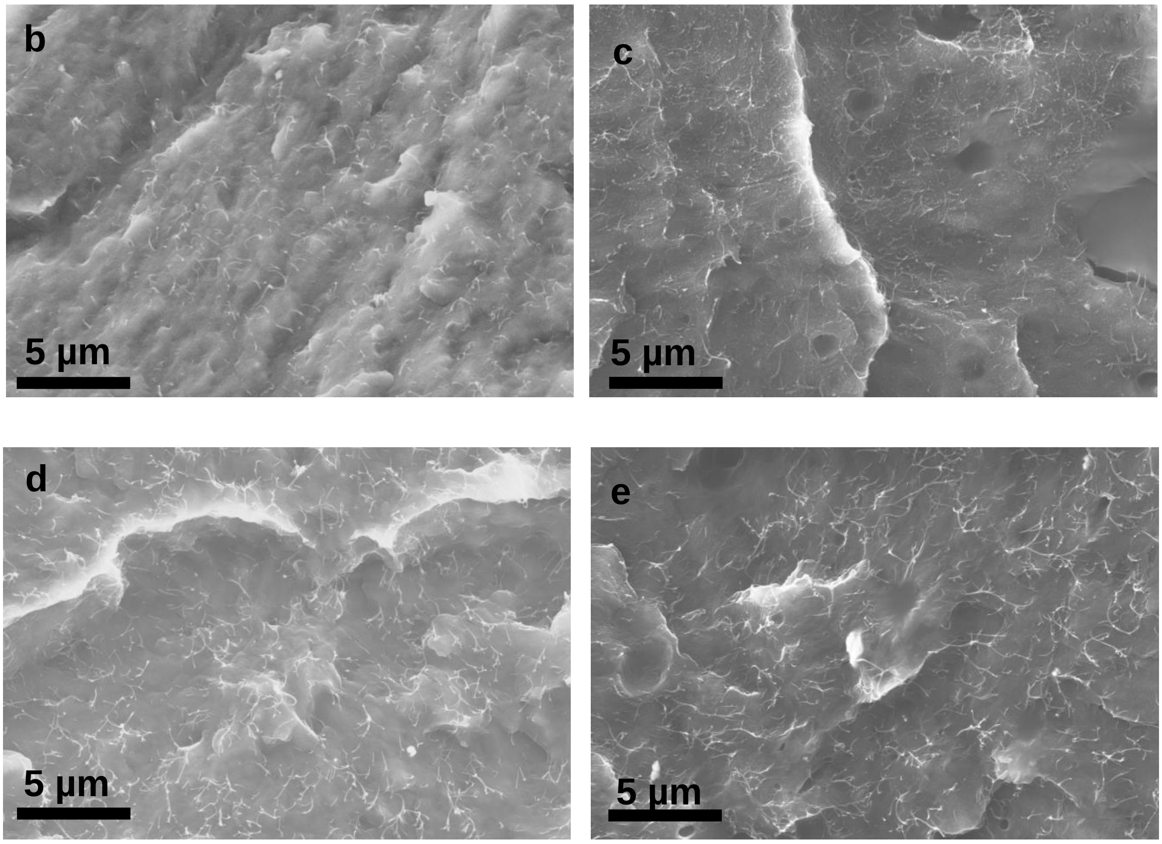


Figure 5 Composite morphology as observed by scanning electron microscopy (a) PP-2CNT-5CuO showing the CuO inclusions and CNT networks in (b) PP-0.8CNT-5CuO, (c) PP-0.8CNT-5CuO-4PEG, (d) PP-2CNT-5CuO, (e) PP-2CNT-5CuO-10PEG.

During melt mixing of these PEG containing PP composites, PEG flakes melt first due to their lower melting point (T_m: ~ 63°C for PEG; T_m: 140°C-163°C for PP). The soft PEG melt infiltrates initial filler agglomerates, reduces the agglomerate strength and prevents filler compaction induced by the rotating screws during mixing. After the melting of the PP granules, the fillers are then transferred from the PEG into the PP matrix. For this process, it has been shown that the processing conditions, PEG molecular weight and filler properties determine the transfer rate [26]. Nevertheless, it is difficult to distinguish whether the fillers are located inside the PEG regions from SEM images. The CNTs employed have hydrophilic groups coming from plasma oxidation, onto which PEG could absorb. CuO powder is also hydrophilic. It is reasonable to assume that some CNTs and (small sized) CuO powder are still located inside the PEG regions.

On the macro-scale, the reduced agglomerate area ratio (A) and smaller particles observed using light microscopy in the 5 µm thin section (Figure 6) confirms the dispersing effect of PEG addition during melt mixing of the composites as well without and with CuO addition. This improved dispersion may be a reason for the conductivity increase when adding PEG to the composites with 0.8 and 2.0 wt% CNTs (compare Figs. 2 and 4a).

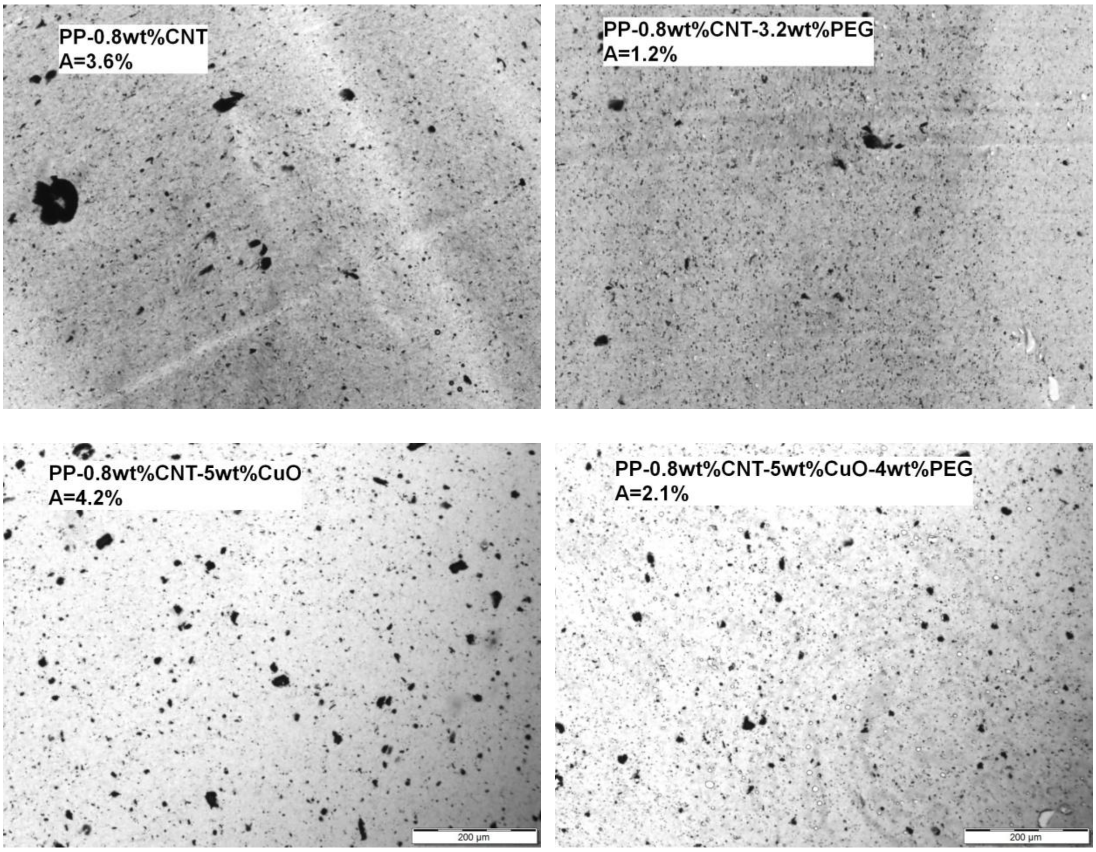


Figure 6 Characteristic light microscope images (section thickness 5µm) illustrating the reduced agglomerate area (A) with PEG addition during melt mixing.

3.3. Thermocouple Prototypes based on p- and n-type melt mixed PP-CNT composites

As a proof of concept, prototypes with 4 thermocouples and 49 thermocouples were built up from compression molded flexible composites, as seen in Figure 7. In these prototypes, PP-2CNT-CuO is used as the p-type and PP-2CNT-5CuO-10PEG is used as the n-type. The prototype (module 1) with 4 thermocouples has a resistance of ~ 16°kΩ. With a temperature difference of 70 K, module 1 gave an output voltage of ~21 mV. The other prototype (module 2) with 49 thermocouples delivered an output voltage of 110 mV at a70 K temperature gradient. A high resistance of around 500 MΩ was observed for module 2, which is due to the high contact resistance of the connections which were formed by applying pressure to the materials at 120°C. Further optimization could reduce the contact resistance between the p- and n-type materials. After several cyclic tests, no deterioration of the performance was observed for either module. As PEG is locked inside the composite, no surface migration of PEG was observed during the measurements up to 110°C.

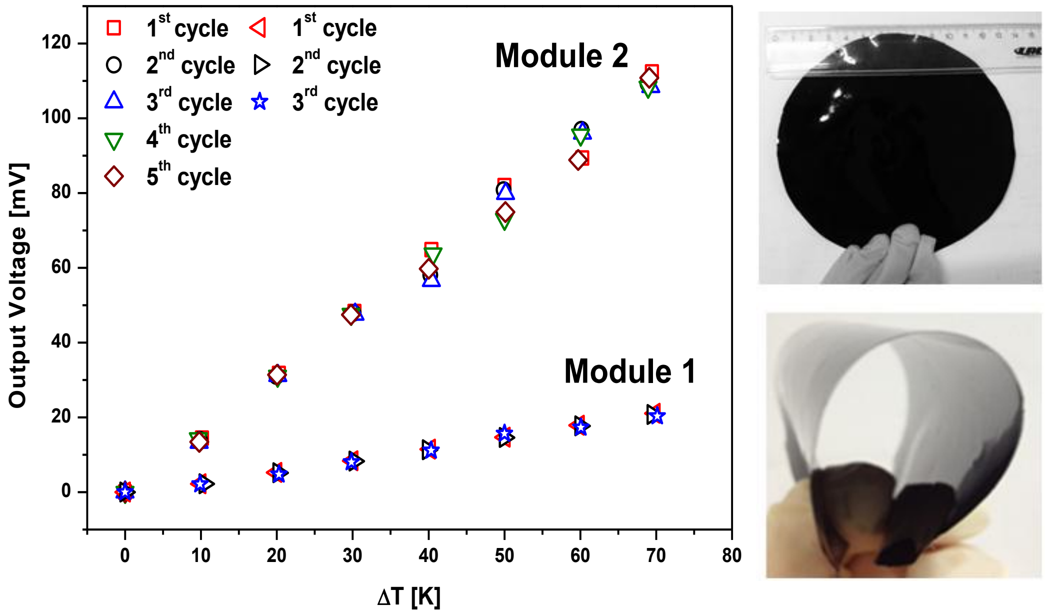


Figure 7 Thermoelectric output voltage versus ΔT for the prototype thermoelectric modules with the cold side temperature fixed at 40°C and the hot side temperature was gradually heated up to 110°C. The flexibility of the films is shown.

4. Conclusions

Our work demonstrates for the first time the feasibility of using a melt mixing technique to fabricate both n-type and p-type polymer composites from the same base materials. For this, PP with singlewalled CNTs and CuO was used to fabricate p-type composites. The addition of certain amount of PEG simultaneously switches p-type composites into n-type and improves the filler dispersion. With the addition of PEG, the Seebeck coefficient of the composite with 2.0 wt% CNTs was changed from 36.8 µV/K to -56.6 µV/K when 10 wt% PEG was added. A high power factor reaching values up to 7.8×10^{-2} $\mu W/(m\cdot K^2)$ was recorded for the n-type composite filled with only 2 wt% CNTs, 5 wt% CuO, 10 wt% PEG (cf. 2.3×10^{-2} $\mu W/(m\cdot K^2)$ for its p-type counterpart). These n-type composites remain with negative Seebeck coefficient after being exposed to air for 8 months. As a proof of concept, prototypes with 4 and 49 thermocouples were built and delivered thermoelectric voltages of 21 mV and 110°mV at a temperature gradient of 70 K.

In summary, this work shows a new strategy to fabricate n-type polymer/CNT composites from a solvent-free melt mixing technique that can be easily scaled up using current industrial techniques for mass production.

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***Highlights**

- Compatible p- and n-type melt mixed composites prepared with same base material
- Polypropylene composites with singlewalled carbon nanotubes at 0.8 and 2.0 wt%
- PEG addition during melt mixing switches p-type CNT composites into n-type
- PEG increases electrical conductivity due to the better dispersion of fillers
- TEG prototypes with output voltages of 21 mV (4 p/n) and 110 mV (49 p/n) @ ΔT= 70 K

***Graphical Abstract**