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Influence of the MWCNT surface functionalization on the thermoelectric properties of melt-mixed polycarbonate composites

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ABSTRACT

The thermoelectric properties of conductive polymer composites consisting of a polycarbonate (PC) matrix loaded with different kinds of commercially available multi-walled carbon nanotubes (MWCNTs) have been examined. The PC/MWCNT composites were prepared by melt-mixing using a small-scale compounder. Unfunctionalized, as well as carboxyl (–COOH) and hydroxyl (–OH) modified MWCNTs were incorporated into the PC matrix at a constant amount of 2.5 wt.%, which is a concentration above the electrical percolation threshold. The amount of MWCNTs was kept low to understand the fundamental aspects of the physical properties and their correlation to the composite morphology. The results suggest that different functional groups on the surface of MWCNTs can have an impact on the thermoelectric values and the conductivity of the composites, measured at room temperature. The highest Seebeck coefficient (*S*) was found for the composite containing carboxyl functionalized MWCNTs (11.3 μV/K). In specific, an increase of the Seebeck coefficient was found with an increased oxygen content of MWCNTs. It is believed that these thermoelectric figure of merit values are still too low for commercial applications; however, they can be enhanced by increasing the amount of conducting fillers and improvement of dispersion in the polymer matrix.

1. Introduction

Nowadays, there is a huge concern regarding the finite supply of fossil fuels. Thermoelectric materials are one potentially alternative resource, specifically for thermal energy harvesting (such as waste heat), due to their ability to generate voltage upon exposure to temperature gradients relative to the environmental temperature. This so-called thermoelectric or Seebeck effect is described by the thermoelectric power (TEP), or thermopower, or Seebeck coefficient (*S*), which is the direct solid state conversion of thermal energy to electricity [1]. The thermoelectric power is defined as:

$$S = \frac{\Delta V}{\Delta T} \qquad (1)$$

where ΔV is the electric potential difference (or the generated thermovoltage) created by a temperature gradient, ΔT, to which the material is exposed. The Seebeck coefficient is used for the calculation of the power factor (*PF*; $PF = \sigma \times S^2$, σ is the electrical conductivity), a well-known entity for comparing the efficiency of different thermoelectric materials. The dimensionless thermoelectric figure of merit (*ZT*; $ZT = \frac{\sigma \times S^2}{\kappa} T$, κ is the thermal conductivity and T the absolute temperature) is also used as a common measure to determine the materials' energy conversion efficiency [2,3]. The Seebeck coefficient is an intrinsic property of the materials related to their electronic properties and independent of their geometry [4]. Moreover, it is positive for p-type semi-conductors and negative for the n-type ones. Taking into account the previous equation of the thermoelectric figure of merit, it can be easily realized that for an efficient thermoelectric material, high electrical conductivity and high Seebeck coefficient, as well as low thermal conductivity are generally required. The low thermal conductivity is necessary so that the temperature gradient can be sustained within the material's structure and induces the generation of charge carriers. Traditional thermoelectric materials are made from low band gap semiconductors like Bi_2Te_3, PbTe, etc. However, they are expensive to mass production, often toxic and consist of rare and expensive elements [3].

Recently, polymer based thermoelectrics have been reported and investigated both theoretically [5] as well as experimentally [6,7]. In addition, carbon nanotubes (CNTs) have shown promising

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thermoelectric behavior which has been found to be related to the level of doping [8,9] as well as the dopant nature [10–14]. Accordingly, several studies exist in which polymer/CNT composites have been utilized for the thermal energy harvesting [3,5,15–18]. Especially CNT-based polymer composites are of particular interest due to their low thermal conductivity, potentially high electrical conductivity, ease of production, relatively low cost, flexibility and high specific properties. The CNT networks in a polymer matrix have the ability to allow electron transport by tunneling, when junctions are separated by an insulating polymer film (even of some nm thick). At the same time, phonon scattering at the CNT–polymer–CNT interfaces will prevent their effective transmission through the composite resulting in low thermal conductivity values. Therefore, it can be concluded that polymer/CNT composites should fulfill well the demands for an efficient thermoelectric material taking into account the previous formula of the thermoelectric figure of merit. In almost all of the corresponding studies, polymer/CNT composites have been fabricated by means of solution mixing techniques which are known not to be easy in terms of up-scaling. Relatively high filler loadings ($\gg$50 wt.%) can be realized [18], which result in quite high electrical conductivities [19–23], while power factors being in the range of $\sim$140 μW/mK^{-2} have been reported for single-walled carbon nanotubes (SWCNTs) in poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) matrix [24]. However, such high filler loadings may result also in a significant increase of thermal conductivity [17,25,26]. One often reported approach for thermoelectric CNT-polymer composites is using electrically conductive matrix polymers, such as polyaniline (PANI) [21,23,24,27], polythiophene (PT), and PEDOT [19,24]. Their use can result in polymer composites with electrical conductivities up to 4×10^5 S/m as reported by Moriarty et al. [24]. Doping of the SWCNTs by using e.g. polyethyleneimine (PEI) or hexafluoroacetone [28,29] resulted in Seebeck coefficients up to -50 μV/K. Furthermore, Seebeck coefficients between 10 and 30 μV/K were reported for polythiophene/multi-walled carbon nanotube (MWCNT) and PANI/graphite composites [16,27].

Hewitt et al. showed Seebeck coefficients of MWCNT buckypapers between 11 and 19 μV/K, and also discussed the dependence of the Seebeck coefficient on the MWCNT acid treatment procedure [30]. It was shown that acids with an oxygen content, such as sulfuric acid (H_2SO_4) and nitric acid (HNO_3), cause an increase of the Seebeck coefficient. For acids without oxygen, such as hydrochloric acid (HCl), no influence was shown. In addition, the duration of treatment, and the molarity of the acid exhibited a significant influence as well. Just recently, it has been reported that different dopants can change drastically the thermoelectric behavior of SWCNTs [14]. For composites of SWCNTs and PC prepared by solvent mixing, it was shown that by increasing the SWCNT content (up to 30% mass concentration), the electrical conductivity increases to approximately 1000 S/m [28]. Additionally, the Seebeck coefficient reached the value of 60 μV/K and was found to be only slightly dependent on the SWCNT content. Furthermore, Seebeck coefficients up to 10 μV/K were reported for expanded graphite and PC, which could be slightly improved up to 12 μV/K by using additional polymers (PEDOT and PSS) [31]. In CNT based composites, polymers having electron rich functional groups, like PVA and PEI, have been found to act as n-doping to the incorporated SWCNTs, what resulted in coefficients up to -21.5 μV/K [29]. Studies using other preparation methods apart from solvent mixing are rare in literature. Antar et al. reported about melt-mixed composites of polylactide (PLA)/MWCNTs and expanded graphite [26]. In this study, high filling levels of up to 30 wt.% resulted in electrical conductivities of about 4000 S/m. However, a strongly increased thermal conductivity to 5.5 W/m K^{-1} was also reported. The Seebeck coefficient reached a maximum of 17 μV/K for composites with expanded graphite and about 9 μV/K for MWCNT composites. Beside this study, almost no work is reported about the thermoelectric behavior of polymer/CNT composites prepared by melt-mixing. In our previous work, it could be shown that for melt-mixed PC/MWCNT composites an increasing filler content results in an increase of the thermoelectric figure of merit due to high electrical conductivity and low remaining thermal conductivity [32].

In this study, a special focus is given on the influence of the functional groups of the MWCNTs on the thermoelectric properties of the resulting polycarbonate based polymer composites. The filler loading was kept at a low level to understand the relation between the physical properties and the morphology of the polymer composites. The electrical and thermal conductivity, as well as the Seebeck coefficient of the composites were determined and discussed in detail. Furthermore, the morphology of the composites was characterized and taken into account for the evaluation of the physical properties.

2. Experimental

2.1. Materials

The polycarbonate type Makrolon® PC 2205 (Bayer MaterialScience, Leverkusen, Germany) with a density of 1.2 kg/m^3 and a melt volume rate (MVR) of 34 cm^3/10 min was used as the polymer matrix. Three different commercially available MWCNTs, namely Nanocyl™ NC3150, NC3151 and NC3153 were obtained from Nanocyl S. A. (Sambreville, Belgium). All MWCNT grades were produced via catalytic chemical vapor deposition processes (CCVD), and have purity higher than 95%. The NC3150 grade is reported as unfunctionalized MWCNTs (u-MWCNT), while the NC3151 and NC3153 were functionalized with carboxyl (MWCNT–COOH) and hydroxyl (MWCNT–OH) groups, respectively.

2.2. Sample preparation

For the compounding, a DSM Xplore 15 micro compounder (Geleen, Netherlands) with conical twin-screws was used. Prior to compounding, drying of both components was carried out at 100 °C under vacuum overnight. The mixing process was performed at 300 °C under a constant rotation speed of 150 rpm for a time period of 5 min. Preliminary thermogravimetric analysis (TGA) of MWCNTs, a known technique to characterize carbon nanotubes with respect to the different structural forms and the existence of reactive side-wall functional groups [33], has shown that the processing temperature slightly affected the MWCNT functional groups (data given in ESI). As reference, the unfunctionalized MWCNTs (u-MWCNTs) were used. In order to compare different functionalizations of MWCNTs, MWCNT–COOH and MWCNT–OH have been utilized. The amount of MWCNTs introduced in the PC matrix was kept constant at 2.5 wt.%. Hereafter, the PC composites containing u-MWCNTs, MWCNT–COOH and MWCNT–OH are denoted as PC/u-MWCNT, PC/MWCNT–COOH and PC/MWCNT–OH, respectively. To obtain samples for defined electrical conductivity measurements, the extruded strands were cut into short pieces and pressed under vacuum at 300 °C into circular plates of 25 mm diameter and 0.8 mm thickness using a Weber press (PW 20, Paul Otto Weber; Remshalden, Germany). The compression molding temperature corresponded to the mixing temperature while the pressure was set for all samples at 17.5 kN. Subsequently, the temperature control was stopped, and the cooling process started. For the thermal conductivity measurements, different disk geometry was required. For this purpose, the compression molding device of the Weber press (PW 40, Paul Otto Weber; Remshalden, Germany) was used, while the pressure was