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All-aromatic SWCNT-Polyetherimide nanocomposites for thermal energy harvesting applications

Lazaros Tzounis [a, b, *], Maruti Hegde [c, 1], Marco Liebscher [b], Theo Dingemans [c, 1], Petra Pötschke [a, **], Alkiviadis S. Paipetis [b], Nikolaos E. Zafeiropoulos [b], Manfred Stamm [a]

[a] Leibniz-Institut für Polymerforschung Dresden e.V., Hohe Str. 6, D-01069 Dresden, Germany
[b] Department of Materials Science & Engineering, University of Ioannina, GR-45110 Ioannina, Greece
[c] Faculty of Aerospace Engineering, Novel Aerospace Materials, Delft University of Technology, Kluyverweg 1, 2629 HS Delft, The Netherlands

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ABSTRACT

The thermoelectric properties of amorphous and semi-crystalline high-performance polyetherimide–SWCNT nanocomposites are reported for the first time. Nanocomposites based on a non-linear polyetherimide (PEI) model system, labeled aBPDA-P3, with 0.6, 4.4 and 10 vol% SWCNTs remained amorphous after the addition of SWCNTs. In contrast, SWCNTs induced crystallization in a linear PEI model system labeled as ODPA-P3. The (thermo)mechanical properties were fully characterized using thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMTA). The electrical conductivity was studied by four-probe measurements and showed higher values for the ODPA-P3 films reaching 20 S/m at 10 vol% of SWCNTs. The thermoelectric performance revealed by Seebeck coefficient (S) measurements showed values of 40 and 55 μV/K for the 0.6 and 4.4 vol% ODPA-P3 SWCNT nanocomposites, while 16 and 47 μV/K for aBPDA-P3 amorphous films. This enhancement has been attributed to SWCNT–induced crystallization in ODPA-P3 matrix. The PEI-SWCNT nanocomposites are ideal candidates as organic flexible films and coatings for large area thermal energy harvesting, where high temperature gradients exist. Potential applications can be envisaged in the aerospace, automotive and micro-electronics sectors.

1. Introduction

Nowadays, there has evolved an increasing demand for alternative energy resources due to the huge issues regarding the finite supply of fossil fuels [1-3]. Alternative energy sources are critical for mitigating environmental degradation due to global carbon dioxide emissions [4]. In the context of green technology, the development of thermoelectric materials and built-in thermoelectric generators (TEGs) are one potential candidate for harvesting thermal energy, due to their ability to generate voltage upon exposure to temperature gradients (Seebeck effect). An ideal thermoelectric (TE) material possesses a high electrical conductivity (σ) combined with high Seebeck coefficient (S) and low thermal conductivity (κ).

Traditional TE materials often consist of low band gap semiconductors e.g. Bi_2Te_3 [5], Bi_2S_3 [6], PbTe [7], etc., however, toxicity and production issues severely limit their widespread application [8] [9]. Therefore, the search for alternative materials capable of functioning as efficient TEGs has spurred TEG research over the past decade. To that end, conjugated polymers such as polyaniline (PANI) [10-12] and polythiophenes [13-17] have been investigated as thermal energy harvester materials. Their low thermal conductivity along with high electrical conductivity facilitated by their conjugated molecular structure enables their application in TEGs. Poly(3,4-ethylenedioxythiophene)/poly(-styrene sulfonate) (PEDOT:PSS; CLEVIOS PH1000) mixed with Bi2Te3 particles have reached power factors ($PF = \sigma \times S^2$, σ is the electric conductivity and S the Seebeck coefficient) in the range of ~130 μW/(m*K^2) [18]. The incorporation of carbon nanotubes (CNTs) may enhance their performance via increased conductivity or molecular orientation effects of the polymer chains. Thereby,

* Corresponding author. Department of Materials Science & Engineering, University of Ioannina, GR-45110 Ioannina, Greece.
** Corresponding author. Leibniz-Institut für Polymerforschung Dresden e.V., Hohe Str. 6, D-01069 Dresden, Germany.
E-mail addresses: ltzounis@cc.uoi.gr (L. Tzounis), poe@ipfdd.de (P. Pötschke).
[1] Current address: University of North Carolina at Chapel Hill, Dept. of Applied Physical Sciences, Murray Hall, 121 South Road, Chapel Hill, NC 27519, United States of America.

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high filler loadings ($\gg$ 50 wt%) can be realized [19], which result in quite high electrical conductivities [20-23]. Namely, electrical conductivities up to 4×10^5 S/m and power factors in the range of ~140 μW/m*K^2 have been reported by Moriarty et al. for single-walled carbon nanotubes (SWCNTs) in a PEDOT:PSS matrix [16]. However, the low thermal and moisture stability of these materials is an impediment to engineering and structural applications.

The introduction of CNTs in engineering non-conductive thermoplastic polymer matrices has resulted in nanocomposites with thermal energy harvesting property, and they have been investigated both theoretically [22], as well as experimentally [24-28]. Polymer nanocomposites are attractive materials due to their ease of production, relatively low cost, flexibility and high specific properties [29-35]. For nanocomposites of SWCNTs in a polycarbonate (PC) matrix prepared by solvent mixing, it has been found that by increasing the SWCNT content (up to 30 wt%), the electrical conductivity increases to approximately 1000 S/m and the Seebeck coefficient reached 60 μV/K showing only a slight dependence on the SWCNT content [36]. CNT-composites with polymers having electron rich functional groups, like PVA and polyethyleneimine, have been found to act as n-doping to the incorporated SWCNTs, and resulted in coefficients up to −21.5 μV/K [37]. Antar et al. reported on melt-mixed composites of Poly(lactic acid) (PLA) with multi-walled carbon nanotubes (MWCNTs) and expanded graphite with high filling levels (up to 30 wt %) resulting in electrical conductivities of ~4000 S/m [38]. The Seebeck coefficient reached a maximum of 17 μV/K for the composites with expanded graphite and ~9 μV/K for MWCNT ones. Research from our group using a series of melt-mixed polycarbonate-MWCNT nanocomposites has shown that an increasing filler content results in an increase of the power factor due to the increase of the electrical conductivity [39-41]. Also, in our recent work the thermoelectric properties of melt processed conductive nanocomposites of polypropylene (PP) matrix filled with single walled carbon nanotubes (2 wt%) and copper oxide (5 wt%) showed that by adding polyethylene glycol (PEG) during melt mixing p-type composites switched into n-type with Seebeck coefficient up to +45 μV/K and 56 μV/K, respectively [28]. Moreover, hierarchical CNT coated fibrous reinforcement structures have been reported also as electrically conductive and thermoelectric elements upon their incorporation in polymer matrices for large scale thermal energy harvesting by structural composites in applications such as aerospace and automotive [42-47].

All polymeric matrices studied so far are based on aliphatic or semi-aromatic backbones. This severely limits their applicability as engineering materials capable of operating in high-temperature environments. In contrast, high performance engineering polymers such as all-aromatic polyimides and poly (ether-imide)s are capable of withstanding high temperatures (>200 °C) and exhibit glass-transition temperatures (Tg) above 200 °C with superlative mechanical properties. The addition of SWCNTs has been shown to improve mechanical and electrical properties of polyimide matrices [48,49]. Importantly, a crystalline polymer interface was found to be crucial for maximizing mechanical reinforcement [50]. Two questions arise: can PEI-SWCNT nanocomposites function as structural and thermoelectric materials and how does the crystalline interfacial polymer affect the thermoelectric properties? Recently, results reported for polypyrrole and P3HT films indicate that crystallinity is a critical parameter for the thermoelectric performance [51,52]. This was reported as well for other organic electronic devices and was attributed to enhanced charge carrier transport properties at higher crystallinities resulting in increased conjugation lengths [53,54]. The generation of thermoelectricity using structural, engineering polymeric materials that are routinely exposed to high temperatures can represent a breakthrough in high performance multifunctional material development.

In this research article, we will demonstrate for the first time that all-aromatic PEI-SWCNT nanocomposite films can be used as thermoelectric structural materials. Two analogous polymer-SWCNT nanocomposites based on two amorphous all-aromatic high-performance PEIs (Fig. 1) having contrasting interfacial polymer morphology have been studied. The nanocomposites of ODPA-P3/SWCNT (10 vol%) representing semi-crystalline nanocomposite reached a maximum power factor of ~1.8 μW/(m*K^2). Our findings showed that the PEI backbone geometry determines whether the polymer is a suitable host for SWCNTs and able to induce crystalline domains. Moreover, we will discuss how these domains affect the electrical and thermoelectric performance. For comparison, SWCNT bucky paper was used as a 100% SWCNT-based reference material without a polymer matrix. Based on all these results, the electrical conductivity and Seebeck coefficient were correlated to the nanocomposite composition and its crystallinity. To the best of our knowledge, this is the first time that SWCNT induced crystallinity in a PEI matrix is demonstrated to improve both the electrical conductivity and the thermoelectric properties of the resulting nanocomposite materials.

2. Experimental section

2.1. Materials and PEI-SWCNT synthesis

HiPCO-type SWCNTs were purchased from Unidym Inc. The SWCNTs contain less than 15% iron catalyst impurity and have an average diameter of 1 nm and average length of 1 μm. 3,3′,4,4′-Oxydiphthalic dianhydride (ODPA) (99.9%) was purchased from TCI Chemical Industry Co. Ltd. (Fig. 1a). 2,3′,3,4′-Biphenyltetracarboxylic dianhydride (aBPDA) (Fig. 1b) was generously donated by UBE Inc. 1,4-Bis[4-(4-aminophenoxy)phenoxy]benzene (P3) was synthesized according to a literature procedure and details could be found elsewhere [55]. Dry NMP (water content <0.005%) was purchased from Acros Organics and used as received. The probe sonicator used was a Cole-Parmer homogenizer with amplitude control, pulse modes, frequency of 20 kHz, and maximum power output of 750 W. A high gain extender probe with a face diameter of 19 mm was used for sonicating samples. A minimum of 20 mL in volume of solvent was sonicated, and a 50 mL flat-bottom flask was used for all high-intensity probe sonication experiments. The bath ultrasonicator used was a Cole-Parmer ultrasonic cleaner with a noted power output of 40 kHz and 110 V and bath volume of 1.5 L. The detailed protocol for the synthesis, as well as the molecular characterization of the aBPDA-P3 and ODPA-P3 can be found in our previously reported study [55]. The bucky paper with a thickness of 100 μm was prepared via vacuum filtration of SWCNT-NMP mixtures and subsequently dried at 100 °C overnight in a vacuum oven.

2.2. Characterization techniques

Molecular weight characterization of the polyamic acid-SWCNT nanocomposites was performed using a Shimadzu Prominence size exclusion chromatography (SEC). The SEC was equipped with 2 Shodex LF-804 columns connected in series and a refractive index detector. *N*-methylpyrrolidone (NMP) with 5 mM of LiBr was used as eluent at a flow rate of 0.5 mL min^{-1} at 60 °C. Molecular weight quantification was performed using 10 polystyrene standards. Molecular weights of polyamic acid-SWCNT solutions were measured at a nominal concentration of ~0.5 mg/mL. The solutions were filtered using a PTFE 0.25 μm filter prior to measurements to ensure removal of most SWCNTs to prevent clogging of the columns.

The dynamic thermal stability of the PEI-SWCNT