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Preparation and thermoelectric properties of polythiophene/multiwalled carbon nanotube composites

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ABSTRACT

Different polythiophene (PTh)/multiwall carbon nanotube (MWNT) composites with 30 wt.% and 50 wt.% MWNT were prepared by mechanical ball milling, solution mixing and in situ composite, respectively. The composites prepared by solution mixing showed the best thermoelectric properties among these methods. Therefore, the morphology, internal structure and thermal stability of the composites by solution mixing were evaluated by SEM, XRD, FTIR and TGA. The results showed that the MWNT were uniformly dispersed in the polymer matrix and the composite materials exhibited good thermal stability under 200 °C. The effect of MWNT content in the composites on thermoelectric properties, such as electrical conductivity, Seebeck coefficient and thermal conductivity were investigated. With increasing MWNT content, the Seebeck coefficient slightly fluctuates, varying from 27.7 to 22.7 μV/K, and the thermal conductivity slightly increases, but the electrical conductivity increases remarkably, and thus leads to enhance the figure of merit (ZT) obviously. The highest ZT of 8.71×10^{-4} at 120 °C was found in the composite with 80 wt.% MWNT.

1. Introduction

Thermoelectric systems are very promising in harvesting electricity from waste heat or heat sources with small temperature gradients relative to environmental temperature [1]. Compared with the conventional systems, the thermoelectric devices offer good reliability, reduced operational noise levels and long-term, maintenance-free operation owing to the absence of moving parts and their simple leg-type structure. These advantages have greatly promoted the fundamental research in the field of thermoelectric (TE) materials [2–4]. For the past four decades, most investigations for TE materials focused on inorganic compounds, such as bismuth telluride [5], skutterudites [6] and half-Heusler alloys [7]. However, the relatively high cost and poor process ability of the inorganic semiconductor TE materials are impeding their spreading applications to many new TE systems.

Conducting polymers, such as polyaniline (PANI), polypyrrole (PPY), polythiophene (PTh) and its derivatives, are another type of candidates for thermoelectric (TE) materials due to their lightweight, good environmental stability, non-toxicity, low synthetic cost, flexibility to be integrated into various forms, and much lower thermal conductivity [8]. However, compared with inorganic TE materials, polymer TE materials have been given less attention due to low ZT, which comes from the low electrical conductivity as well as low Seebeck coefficient [9]. In this regard, it is important to explore new types of materials.

Conductive polymer/inorganic composites with low cost and easy to process could be potentially used as thermoelectric (TE) materials if the ZT value can be improved. Feng and Ellis [10] have proposed a phonon-blocking and electron-conducting model in which polymers with very high Seebeck coefficient at their non-doped states were blended with highly electrical conducting nano-size species. With an even higher conductivity, the proposed composites hold promise to have a ZT value greater than 4. Recently, more and more attention was paid to the polymer/inorganic composites [11]. The polyaniline/Bismuth composites by ball milling showed high Seebeck coefficient [12]. Polyaniline/graphite composites with 50 wt.% graphite prepared by ball milling showed the ZT of 1.37×10^{-3} at 393 K [13]. The PEDOT:PSS/Bi_2Te_3 composites prepared by ball milling obtained high power factor (47 $\mu W/mK^2$) [14]. The PEDOT:PSS/expanded graphite composites prepared by solution mixing method, exhibited high power factor of about 5 $\mu W/mK^2$ [15]. Hewitt et al. [16] studied the TE properties of PVDF/MWNT composites prepared by solution mixing. The increase of ZT by a factor of 100 was achieved utilizing the poor thermal conductivity of the polymer and the good electrical conductivity of the nanotubes. By in situ composite method, Zhao et al. prepared graphite oxide/ordered polyaniline composites [17], and the maximum thermoelectric figure of merit ZT was up to 4.86×10^{-4}. Poly(3-hexylthiophene)/MWNT composites [18] and poly(3-hexylthiophene)/graphene nanosheet composites [19]

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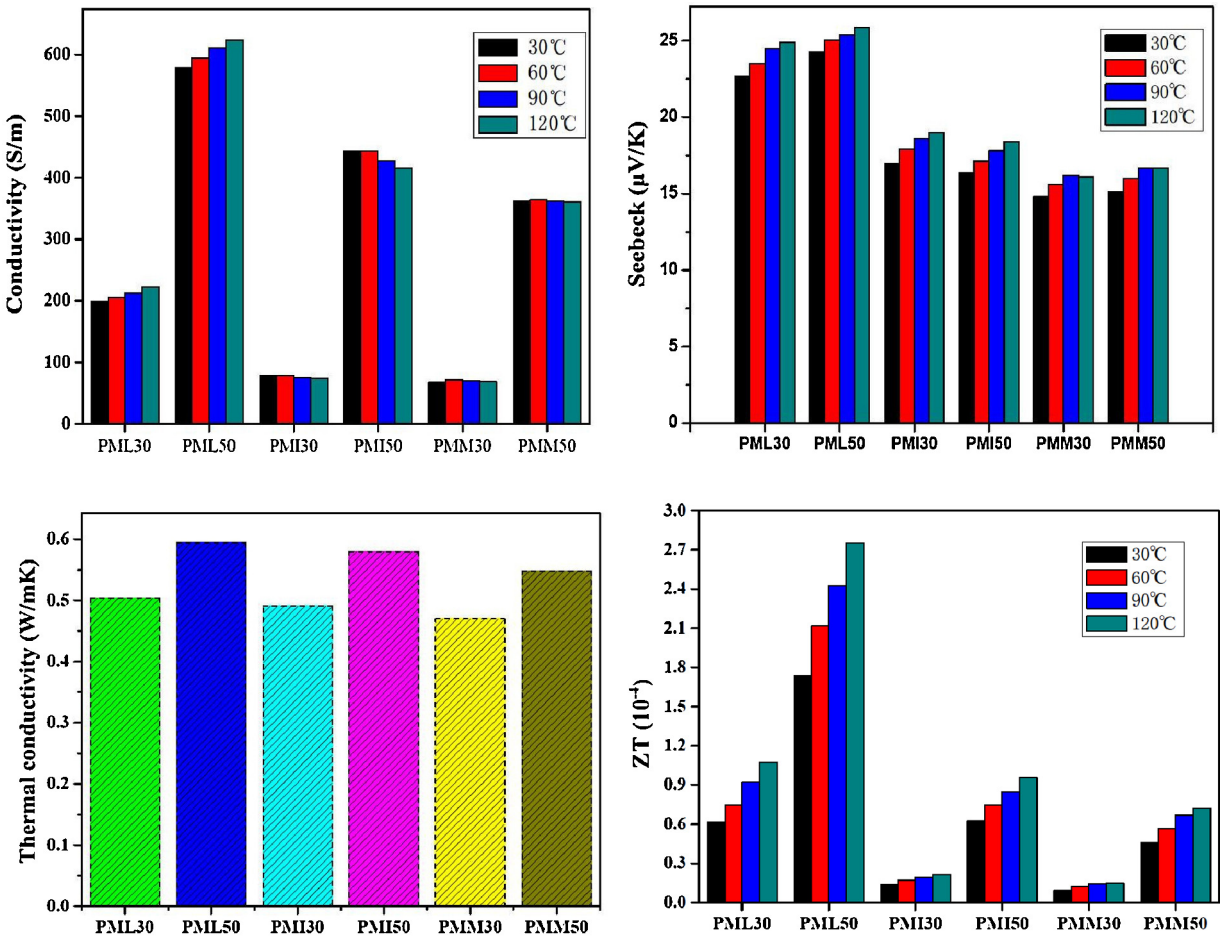

Fig. 1. Electrical conductivity, Seebeck coefficient, thermal conductivity and ZT value of PTh/MWNT composites prepared by different methods.

were also prepared by in situ composite in Cai's group exhibited good thermoelectric properties.

Although a lot of reported results for thermoelectric composites were prepared by different methods, it is difficult to conclude which method is best for the best thermoelectric property of the composites. In this work, we prepared PTh/MWNT composites with 30% and 50% MWNT by mechanical ball milling, solution mixing and in situ composite, respectively and studied their thermoelectric properties. The composites prepared by solution mixing showed the best thermoelectric properties among these methods. Therefore, the effect of MWNT content on thermoelectric properties of the composites prepared by solution mixing was investigated in detail.

2. Experiment

2.1. Materials

The commercial MWNT (diameter = 40–60 nm, length = 5–15 μm) was purchased from Shenzhen Nanotech Port Co., Ltd, and was used after purification by concentrated nitric acid (68%, AR grade) in a procedure similar to reference [20]. The thiophene monomer (99%), anhydrous irons (III)-chloride (CP), and anhydrous chloroform (AR) were purchased from Aladdin, Sinopharm Chemical Reagent Co., Ltd, and Shanghai Shenxiang Chemical Reagent Co., Ltd, respectively. Anhydrous chloroform was dried by 4 Å molecular sieves overnight. Other react agents were used as received without further purification.

2.2. Preparation of PTh

The PTh powder was chemically polymerized through the oxidation of the monomer by $FeCl_3$ in anhydrous chloroform solutions. 60.8 g (0.375 mol) anhydrous $FeCl_3$ was added to a 500 ml flask which contained 250 ml dried $CHCl_3$. The mixture was vigorously stirred for 1 h with constant N_2 bubbling. Then 12 ml (0.15 mol) thiophene monomer in 50 ml anhydrous $CHCl_3$ was added dropwise to the above mixture over a period of 2 h, at a molar ratio of $FeCl_3$:thiophene = 2.5:1. The reaction mixture was stirred at room temperature for another 24 h under N_2 atmosphere, and then poured into a large quantity of methanol and filtered with a Bucher funnel. The product was washed thoroughly with methanol to remove iron ion contamination until the filtrated fluid was colorless. The brick-red product was dried at 60 °C for 24 h under vacuum. The yield of PTh was 9.52 g (79.3%).

2.3. Preparation of PTh/MWNT composites

2.3.1. Preparation of PTh/MWNT composites by ball milling

Powders of PTh and purified MWNT were blended with 30% and 50% MWNT. Then the mixtures were milled in a cylindrical steel jar of 250 ml with 5 steel balls of 10 mm and 5 steel balls of 5 mm in diameter at a rotation speed of 270 rpm for 10 h. The sample was collected for further testing.

2.3.2. Preparation of PTh/MWNT composites by solution mixing

To promote the mixing during the milling, the PTh powders and purified MWNT with 10, 20, 30, 40, 50, 60, 70, 80 and 90 wt.%