THE USE OF BENZOYL PEROXIDE AS AN INITIATOR TO PREPARE PANI AND CNT/PANI FOR THERMOELECTRIC APPLICATIONS

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Abstract

Organic thermoelectric (TE) materials combine TE conversion with flexibility, and could facilitate development of self-sustainable wearable electronic devices. In these systems, organic TE materials-based flexible TE generators could generate power from the temperature differences between human body and ambient environment for non-stop operation of self-sustainable wearable electronics without the necessity of external recharging. Among various organic TE materials, polyaniline (PANI) and especially the carbon nanotube (CNT)/PANI composites are receiving special interest for such applications due mainly to the excellent $\pi-\pi$ stacking between CNTs and PANI that provide simultaneous enhancement of electrical conductivity and Seebeck coefficient. As it is known, chemical oxidative polymerization of aniline in the presence and absence of CNTs is the most common procedure to prepare CNT/PANI and PANI in the TE field, and the most common initiator in aforementioned reaction is ammonium persulfate (APS). However, the structure of APS is actually rather different than PANI. Alternatively, we propose in the present work to use benzoyl peroxide (BPO) as an initiator to prepare PANI and CNT/PANI for TE applications. Because, unlike APS, phenyl rings of BPO might help to realize structural coherency, and hence the resultant samples might exhibit better thermoelectric power factor. To check the validity of this idea, we prepared PANI and CNT/PANI by using BPO as an initiator, and compared their TE properties with the samples that prepared traditionally by using APS as an initiator. For the BPO-synthesized samples, the polymerization reactions were performed by inverted emulsion polymerization since BPO is not soluble in water. The TE properties were determined by Linseis LSR-3/800 Seebeck coefficient and electrical resistance measurement system. Strikingly, we report that BPO-synthesized samples exhibited both higher electrical conductivity and Seebeck coefficient, providing a significant enhancement in power factor as compared to APS-synthesized PANI and CNT/PANI.

Keywords: Thermoelectric, polyaniline, carbon nanotube, benzoyl peroxide, emulsion polymerization

1. INTRODUCTION

Conducting polymers receive a considerable interest for room temperature thermoelectric (TE) applications. Particularly, their flexible characteristics and non-toxicity make them ideal candidates for wearable electronics [1-4]. Among various organic TE materials, polyaniline (PANI) and its composites with carbon nanotubes (CNT) are widely studied owing to the ease in synthesis of PANI and its low cost as well as the $\pi-\pi$ stacking that could arise upon wrapping it around CNTs [5-11].

In the field, the most common procedure to prepare PANI and CNT/PANI as TE materials involves chemical oxidative polymerization of aniline in the absence and presence of CNTs by using ammonium persulfate (APS) as an initiator. For APS-synthesized PANI, electrical conductivity and Seebeck coefficient values of about 50-300 S/cm and 8-15 μV/K were usually reported in previous studies depending on the synthesis and redoping conditions [2,3,12-17]. Particularly, previous reports suggest that synthesis temperature and redoping

conditions are the two influential parameters regarding the electrical transport properties of resultant PANI [10, 18-21]. On the other hand, it is worth mentioning that looking to the molecular structures of PANI and APS, there is actually no structural coherency. In this context, instead of APS, use of benzoyl peroxide (BPO), which is regarded as a thermal initiator, might provide better TE properties since BPO has better structural coherency with PANI owing to its phenyl rings. On the other hand, there are no previous reports on the TE performance of BPO-synthesized PANI and CNT/PANI.

Accordingly, the present work involves preparation of PANI and multiwalled carbon nanotube (MWNT)/PANI composite by using BPO as an initiator, and investigation of their TE properties. Since BPO is not soluble in water, the synthesis reactions were carried out by inverted emulstion polymerization. Following the polymerization reactions, the samples were dedoped, and then redoped with CSA in m-cresol medium. In addition, the effect of the synthesis temperature on the TE performance was also studied with BPO-PANI, considering that BPO is a thermal initiator unlike APS, and synthesis temperature is known to be one of the influential factors regarding the resultant electrical conductivity of PANI. Further, APS-PANI was also synthesized at same conditions with BPO but through chemical oxidative polymerization for a better comparion. Strikingly, BPO-PANI provided 15-fold improvement in electrical conductivity together with a 1.3-fold enhancement in Seebeck coefficient as compared to APS-PANI. The highest electrical conductivity, Seebeck coefficient and TE power factor values were realized in 0°C-synthesized BPO-PANI as 455 S/cm, 14.4 μV/K, and 9.43 μW/mK^2, respectively.

2.   EXPERIMENTAL

2.1   Materials

Aniline (ANI) (≥99.5%) was purchased from Sigma Aldrich, and pre-distilled before use. BPO (for synthesis), APS (≥98.0%), Sodium dodecyl sulfate (SDS) (>99%), MWNT (>90%, diameter: 110 – 170 nm), CSA (98%), m-cresol (for synthesis), ammonium hydroxide solution (puriss.), and acetone (EMSURE) were also purchased from Sigma Aldrich, but used as-received. Chloroform was purchased from Isolab, and used as-received. Deionized (DI) water was used throughout the experiments.

2.2   Preparation of APS-PANI, BPO-PANI, and MWNT/BPO-PANI

For BPO-PANI, 0.006 moles of BPO was dissolved in chloroform and 0.006 moles of SDS was dissolved in water. Separately, 0.003 moles of ANI was dissolved in water and 0.006 moles of CSA was mixed with ANI-water for 30 min. The SDS-water mixture was added to BPO-chloroform, and then, CSA-ANI-water was introduced to the reactor to initiate the polymerization reactions. The reactions were performed for 24 hr at various temperatures. Following the reactions, the polymers were precipitated in acetone at room temperature, filtered, and dried at vacuum oven. The dedoping was carried out in ammonium hydroxide solution at room temperature overnight. For APS-PANI, dedoped polymers were prepared with similar conditions and equimolar feed compositions to the preparation of BPO-PANI. Only exception is that APS was dissolved in water instead of chloroform, and SDS was not introduced at all for the synthesis of APS-PANI. Regarding MWNT/BPO-PANI composites, the synthesis procedure was similar with the BPO/PANI. Only difference is that MWNT was dispersed in water by using a Bandelin HD2070 homogenizer prior to its introduction to the reactor. The weight percentage of the MWNT in MWNT/BPO-PANI composite was calculated to be 31% following the dedoping. All samples were redoped at the same conditions (2:1 ANI:CSA molar ratio, in m-cresol) for 24 hr, and they were prepared on soda lime glass by drop casting.

2.3   Characterization

Fourier transform infrared (FT-IR) spectroscopy was performed on a Bruker Tensor II FT-IR spectrometer from KBr pellets to verify the synthesis of the polymers. The thermoelectric properties of the redoped samples were

determined at room temperature on a Linseis LSR-3/800 Seebeck coefficient/electrical resistance measurement system with a minimum temperature gradient between the probes of 2 °C in all measurements. A stylus profilometer was used to determine the thickness, which was used in the calculation of electrical conductivity.

3.   RESULTS & DISCUSSION

FT-IR spectroscopy was performed on dedoped polymers to comment on the molecular structures and to confirm the succesful synthesis of the polymers as shown in **Figure 1** and **Figure 2**. As can be seen in **Figure 1**, both the FT-IR spectrum of APS-PANI and BPO-PANI exhibited characteristic bands and peaks of PANI [15, 22-25]. Particularly, the characteristic peaks at about 1580 and 1490 cm^{-1} in **Figure 1** and **Figure 2** could be ascribed to the quinonoid (Q) ring-stretching and benzenoid (B) ring-stretching, respectively, and these characteristic peaks are important to verify preparation of PANI in the emeraldine form [15]. As it is known, PANI has three oxidation states, and only the emeraldine state becomes conducting upon protonation. In the FT-IR spectrum of emeraldine, the intensity the Q ring-stretching should be similar to the intensity of B ring-stretching, which was evident in both **Figure 1** and **Figure 2**, hence, confirming succesful synthesis of PANI in the emeraldine form through both chemical oxidative polymerization with APS and via inverted emulsion polymerization with BPO [15, 22-25]. As it is known, BPO is a thermal initiator and it might perform much better at higher temperatures in terms of reaction yield. In this context, we studied the synthesis of BPO-PANI at various temperatures as well, and the FT-IR spectra of the resultant polymers were shown in **Figure 2** after the dedoping step. As can be seen in **Figure 2**, a significant deviation was not detected in the spectra of different temperature-synthesized polymers, and hence it might be thought that reaction temperature does not have a significant effect on the overall molecular structure. Still, we detected a significant deviation regarding the monomer conversions as listed in **Table 1**. One thing is that the monomer conversion with APS was found to be relatively lower than one could normally expect. This was ascribed to the use of CSA during the polymerization reactions instead of the commonly used HCl. Another point is that monomer conversions were found to be decreasing with lowering the reaction temperature for the synthesis of BPO-PANI via inverted emulsion polymerization. Regarding MWNT/PANI, the synthesis was carried out at 55 °C, and a monomer conversion of 88% was recorded. This is similar to the monomer conversion in the synthesis of BPO-PANI at the same reaction conditions as could be expected.
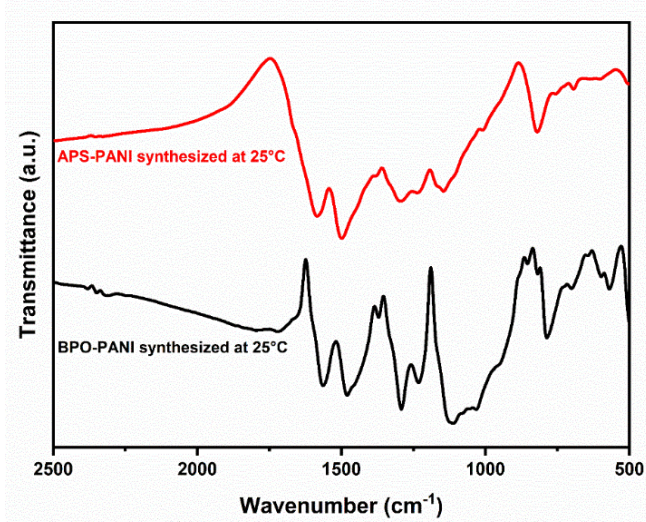

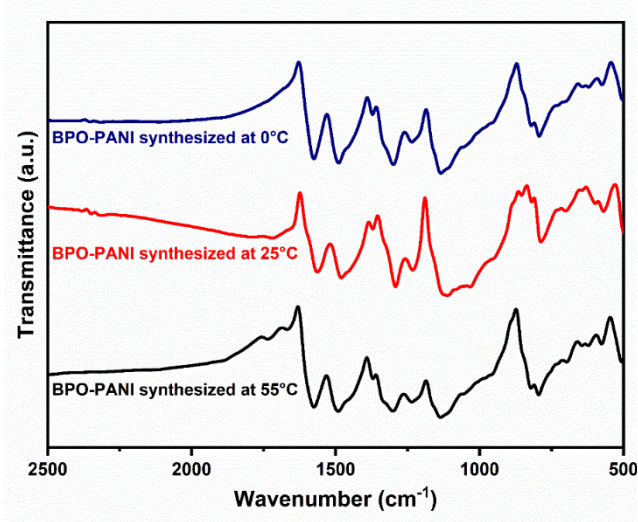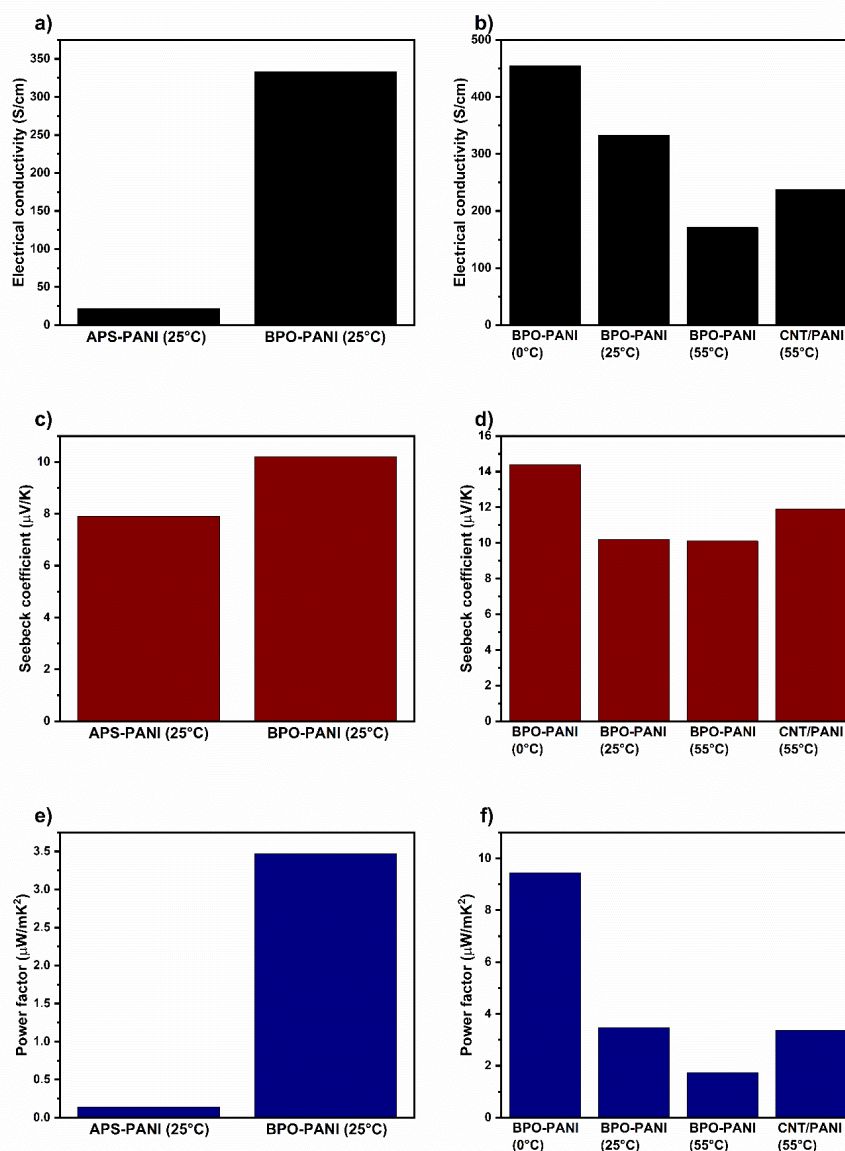**Figure 1** FT-IR spectrum of APS- and BPO-PANI

Figure 2 FT-IR spectra of BPO-PANI that polymerized at different temperatures

Table 1 Monomer conversions at various reaction conditions

Sample	Initiator	Polymerization temperature (°C)	Monomer conversion (%)
APS-PANI	APS	25	64
BPO-PANI	BPO	25	85
BPO-PANI	BPO	55	91
BPO-PANI	BPO	0	20
MWNT/PANI	BPO	55	88

Figure 3 TE properties of APS-PANI, BPO-PANI, and MWNT/PANI: electrical conductivity (a and b), Seebeck coefficient (c and d), and power factor (e and f)

The TE properties of APS-PANI, BPO-PANI, and MWNT-PANI were shown in **Figure 3**. Strikingly, we report that particularly the electrical conductivity of BPO-PANI was found to be higher than that of APS-PANI. This result supports our initial claim that BPO might be a more suitable initiator in terms of reaching a better electrical transport properties in the resultant PANI due to its structural coherency with PANI. Regarding Seebeck

coefficient, again an improvement though a limited one, was realized as compared to APS-PANI as can be seen in **Figure 3c**. The simultaneous enhancement in electrical conductivity and Seebeck coefficient might imply that carrier mobility was particularly improved by using BPO as an initiator instead of APS. Regarding the effect of temperature, we report that although the monomer conversions increase with increasing polymerization temperature (**Table 1**), the TE properties, particularly the electrical conductivity values, were actually found to be improving with decreasing temperature as illustrated in **Figure 3b** and **Figure 3d**. In this context, the overall TE power factor of 0 °C-synthesized BPO-PANI was actually higher than even MWNT/PANI that prepared at 55 °C (**Figure 3f**). This is very interesting as such an observation suggests that the choice of reaction temperature seems to be more influential than even introduction of MWNT, although preparation of CNT/PANI composites is a common approach in PANI-based TE materials.

4.   CONCLUSION

In the present work, the use of BPO was studied to prepare PANI as a TE material. Also, the effect of reaction temperature on the monomer conversion and resultant TE properties were investigated. The results show that PANI that synthesized at 25 °C via inverted emulsion polymerization by using BPO as an initiator exhibited an electrical conductivity of about 333 S/cm, which is about 15-fold higher than that of the PANI that prepared at similar conditions but through chemical oxidative polymerization by using APS as an initiator. In addition, BPO-PANI that synthesized at 25 °C was found to be providing a Seebeck coefficient of about 10.2 μV/K, which is slightly higher than the Seebeck coefficient of APS-PANI. The simultaneous enhancement in conductivity and Seebeck coefficient might be due to a possible improvement of carrier mobility in the BPO-PANI as compared to APS-PANI. Regarding the effect of temperature, we report that despite monomer conversions were decreasing with a decrease in synthesis temperature, the TE properties, particularly the electrical conductivity, improved significantly with such a decrease. Overall, the highest TE power factor was reached in 0 °C-synthesized BPO-PANI as 9.4 μW/mK^2, which was interestingly even higher than the MWNT/PANI that synthesized at 55 °C, and hence further highlighting the importance of reaction temperature on the resultant charge transport properties.

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