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Thermoelectric Properties of Flexible Polyvinyl Alcohol/Poly (3,4-Ethylenedioxy thiophene)/Titanium Carbide Ternary Composites

Volkan UGRASKAN *[1]

Abstract

The thermoelectric (TE) characteristics of polyvinyl alcohol/poly (3,4-ethylenedioxy thiophene)/titanium carbide (PVA/PEDOT/TiC) composites were explored in this work. The composite films with varying TiC weight ratios were made using the solvent casting process. The homogeneous distribution of TiC particles in the composite structure was revealed by SEM micrographs. The presence of TiC particles in the crystallinity of PVA/PEDOT was revealed by XRD patterns. The electrostatic interactions in the composite structure were revealed by FTIR-ATR studies. The electrical conductivity of PVA/PEDOT rose from 0.06 S/cm to 1.15 S/cm with the contribution of 5% TiC, while the Seebeck coefficient increased from 3.9 μV/K to 98.8 μV/K with the contribution of 1% TiC, according to TE studies. The composite samples exhibited a maximum power factor of 0.72 $\mu W/mK^2$, which is 10^4 times greater compared to PVA/PEDOT.

Keywords: Thermoelectric, polymer, composite, polyvinyl alcohol, PEDOT:PSS, titanium carbide

1. INTRODUCTION

The demand for energy has grown in direct proportion to the development of industrial applications and the growing human population [1]. Researchers have focused on ecologically friendly and sustainable energy sources. Given its environmental friendliness, silent operation, and long operational life, thermoelectric power production, which converts heat directly into electricity, has become an intriguing technology [2].

The performance of TE materials correlates with a dimensionless figure of merit;

$$ZT=\sigma S^2 T/\kappa \tag{1}$$

where S is the Seebeck coefficient, σ is electrical conductivity, κ is thermal conductivity, and T is absolute temperature. An efficient TE material should, in theory, have high σ, a low S, and low κ [3].

Inorganic-based materials including semiconductors, skutterudites, tellurides, and different oxides have received the most attention in TE research. These materials have a high TE efficiency, however, their expensive cost, element scarcity, low mechanical flexibility, and severe toxicity restrict their uses [4, 5].

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Flexible TE (FTE) materials have emerged as intriguing alternatives because of their conformability, which allows for effective interaction with curved heat sources, maximizing heat harvesting [6]. Organic TE materials that are naturally flexible are great candidates for FTE devices. Stiff inorganic TE materials are additionally feasible to create flexible TE devices by combining them with adaptable substrates or deformable interconnectors. Flexible organic/inorganic composites/hybrids open up new avenues for the fabrication of flexible thermoelectric devices [7].

Conductive polymers offer tremendous promise for usage in TE applications due to their tunable σ, low density, nontoxic properties, abundance, simplicity of application, and low thermal conductivity [8]. However, due to the poor σ of these polymers, doping or secondary doping methods can be used. Furthermore, one of the most popular ways is the in-situ or ex-situ preparation of conductive polymer-based composites with suitable organic/inorganic components. The introduction of inorganic-based TE materials or carbon-based materials in this technique improves TE capabilities by boosting energy-filtering effects inside the flexible polymer structure [6]. Because the κ of conductive polymers are weak and comparable, power factor ($PF = \sigma S^2$) is usually used to indicate their TE properties [9].

PEDOT:PSS, which has garnered plenty of attention, is made up of exceptionally conducting and hydrophobic PEDOT chains and insulating and hydrophilic PSS chains [10]. Since the substantial amount of conjugation and outstanding planarity in PEDOT:PSS backbones, it has better TE features compared to other conducting polymers [11].

Even though PEDOT:PSS/inorganic composites have greater TE characteristics, mechanical elasticity is restricted because of inorganic TE materials' intrinsic brittleness. A safe method is to use stretchy polymers such as polyvinyl alcohol (PVA), which may drastically enhance elongation at break [12]. There are several studies on the TE properties of PVA/PEDOT composites reported in the literature [12-16]. However, to the the author’s knowledge, there are no studies reported on the TE properties of PVA/PEDOT/TiC composites. TiC has a high melting temperature, a high degree of toughness, and excellent thermal and chemical stability, and σ, and is cost-effective. According to Ozturk et al., the contribution of TiC to PPy enhanced σ from 0.8 S/cm to 160.2 S/cm, while the *PF* rose from 0.0115 μW/mK^2 to 1.732 μW/mK^2 [17]. In this work, the TE properties of the TiC-filled PVA/PEDOT:PSS ternary composites were investigated.

2. MATERIALS AND METHODS

2.1. Materials

Table 1 and 2 list all of the substances and instruments used in this work.

Table 1 The substances used in this work

Chemicals	Source
Polyvinyl alcohol (Mw ~47,000)	Sigma Aldrich
3,4-ethylenedioxythiophene (EDOT) (97%)	Acros Chemicals
Poly(sodium 4-styrenesulfonate) (PSS) (Mw ~70,000)	Merck
Ammonium persulfate (≥98.0%)	Merck
Titanium carbide (99.99%, particle size: <1 μm)	Nanokar Nanotechnology

Table 2 The instruments used in this work

Instruments	**Model**
FTIR-ATR	Nicolet IS10 Thermo FTIR
UV-vis	Shimadzu UV2600
SEM	Zeiss EVO LS10
XRD	Panalytical Empyrean
Electrical conductivity	Entek Electronic, FPP 470
Seebeck coefficient	Entek Electronic

2.2. Synthesis of PEDOT:PSS

The PEDOT:PSS synthesis was carried out precisely as reported in the literature [19]. 1 g of PSS was dissolved in 80 mL of distilled water in the first phase. The solution was then treated with 3.51 mmol of EDOT. To polymerization was started with gently addition of 20 mL aqueous solution containing 7 mmol APS. For 16 h, the reaction was performed at room temperature.

2.3. Preparation of PVA/PEDOT:PSS/TiC Ternary Composites

First, in 10 mL of water, 0.1 g of ethylene glycol and 1 g of PVA were dissolved. The medium was then combined with 10 mL of the synthesized PEDOT:PSS solution. Finally, TiC was added to the medium at 1%, 3%, 5%, 7%, and 10% by mass in contrast with PVA, and composites were formed following homogenization. The composite solutions were poured onto the glass substrate using the solvent casting process and vacuum dried at 60 °C. The polymer solution obtained was filtered after the reaction.

3. CONCLUSIONS AND DISCUSSION

XRD patterns of PVA/PEDOT and the composite were shown in Fig. 1. The diffraction pattern of PVA/PEDOT revealed two peaks at 2Θ=19.4° and 40.8°, indicating the semi-crystalline structure of PVA. This might be owing to the occurrence of substantial intramolecular hydrogen bonding in individual PVA monomer units and intermolecular H-bonding between them [18]. The addition of PEDOT:PSS exhibited no impact on PVA crystallinity, which might be attributed to its weak crystalline structure. Furthermore, the strong peaks found in the diffraction pattern of the composite indicated the crystalline structure of TiC and confirmed the existence of TiC in the composite.

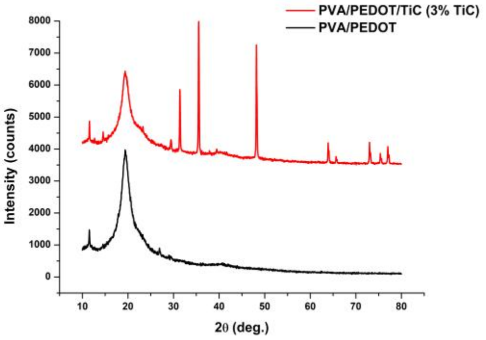

Figure 1 XRD patterns of PVA/PEDOT and the composite

SEM micrographs of PVA/PEDOT and the composite were shown in Fig. 2. In the micrograph of PVA/PEDOT, homogeneously dispersed PEDOT particles were observed in the PVA. The homogeneous distribution of the particles has been realized in the insulating PVA in such a way as to reduce the free area in order to provide σ [19]. In the micrograph of the composite, it was determined that the TiC particles were dispersed within the composite structure without a significant agglomeration, contributing to the electrical properties of the PEDOT molecules.

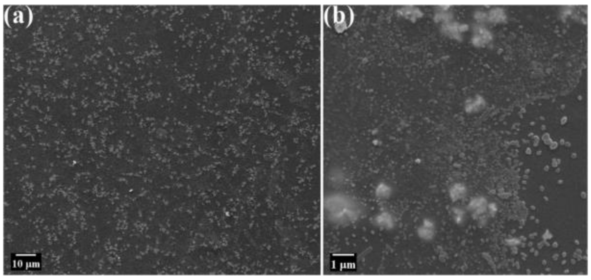

Figure 2 (a) SEM micrographs of PVA/PEDOT and (b) the composite

Fig. 3 depicted the FTIR-ATR spectra of PVA/PEDOT and the composite. In the spectrum of PVA/PEDOT, the peaks observed at 3207 cm^{-1}, 1430 cm^{-1}, and 1030 cm^{-1} correspond to O-H stretchings, CH–OH bending vibrations and C–O stretching vibrations of PVA. The peaks observed at 1517 cm^{-1} and 1301 cm^{-1} were associated with C=C and C–C stretching vibrations of the thiophene ring whereas the peaks at 1166 cm^{-1} and 1124 cm^{-1} confirmed the presence of a sulfonic acid group. Additionally, the stretching vibration C–S bond in the thiophene rings were obtained at 962 cm^{-1}, and 880 cm^{-1} [20, 21].

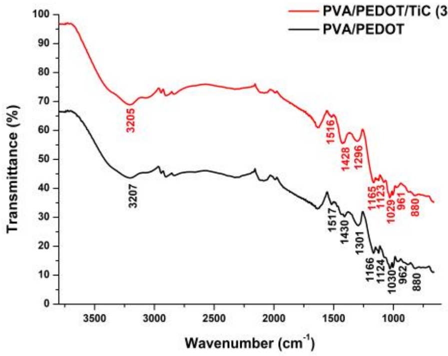

Figure 3 FTIR-ATR spectra of PVA/PEDOT and the composite

When the composite's spectrum was analyzed, it was discovered that it possessed a spectrum similar to PVA/PEDOT, with certain peaks shifting to lower wavenumbers. This might be attributed to a rise in electron density in the composite structure, as shown by the change in electron density [22, 23].

UV-vis spectra of the samples were illustrated in Fig. 4. The absorbance peaks of neutral, polaron and bipolaron species are located in the PEDOT structure at 1200 nm, 900 nm, and 600 nm, respectively. When the spectra of the samples were investigated, peaks of polaron species were identified around 900 nm. The absence of a particular peak at 600 nm, on the other hand, indicates that the neutral parts are not dominant [24, 25]. Furthermore, the peaks detected at around 225 nm exhibit π-π* transitions, whereas the increased intensity of the composite peaks is related to an increase in the π-π* transition as a result of TiC addition.

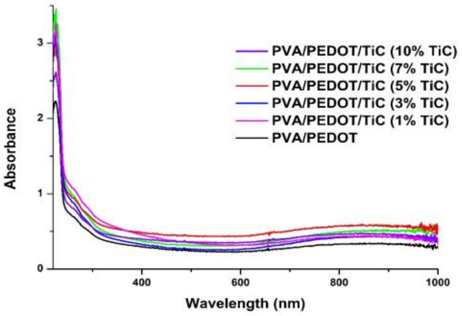

Figure 4 UV-vis spectra of the samples

The TE properties of the samples were given in Fig. 5. The σ measurements were conducted at 298 K. S measurements were performed with the cold and hot ends of the samples at 298 K-308 K. The σ and S values of PVA/PEDOT were found as 0.06 S/cm and 3.9 μV/K, respectively. The σ of the composites was determined to increase up to 5% TiC by mass, following that the σ values remained constant. The sample containing 5% TiC yielded the highest σ value of 1.15 S/cm. The rise in σ values is due to an increase in crystallinity caused by the rearranging of the PEDOT:PSS interfacial layers as a result of TiC addition [26, 27]. Furthermore, as seen in the FTIR-ATR study, the addition of TiC increases charge carrier density, which is another contributor to the increase in σ.

According to the S measurements, the largest S of the samples was 98.8 μV/K. The inclusion of TiC may induce the filtration of low-energy carriers while conveying high-energy carriers in the PEDOT:PSS structure, which is also known as the energy-filtering effect [28]. The PF values of the samples were calculated using the equation of $PF= \sigma S^2$. Because the PF is equal to the square of the S and the σ, the composite containing 3% TiC exhibited the greatest PF of 0.72 $\mu W/mK^2$.These findings show that TiC size has a substantial impact on the TE performance of the composite films.

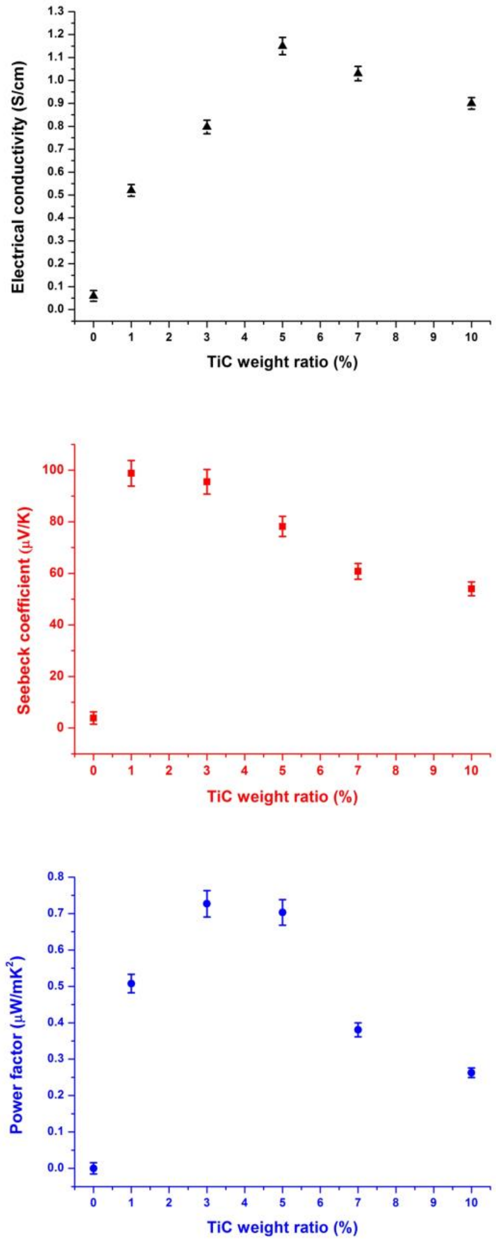

Figure 5 TE properties of the samples

4. CONCLUSION

In the present study, the TE properties of PVA/PEDOT/TiC composites were investigated. The composite films containing different weight ratios of TiC were prepared by solvent casting method and their characteristics were determined using SEM, XRD, FTIR-ATR, and UV-vis analyses. SEM micrographs showed the homogenous distribution of TiC particles in the composite structure. XRD patterns indicated the contribution of TiC particles in the crystallinity of PVA/PEDOT. FTIR-ATR analyses showed the electrostatic interactions in the composite structure. From TE analyses, it was obtained that the σ of PVA/PEDOT increased from 0.06 S/cm up to 1.15 S/cm with the addition of 5% TiC while the S increased from 3.9 μV/K 98.8 μV/K with the addition 1% TiC. The highest PF of the composite samples was obtained 0.72 μW/mK^2 which is 10^4 times higher compared to PVA/PEDOT.

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The Declaration of Conflict of Interest/ Common Interest

No conflict of interest or common interest has been declared by the authors.

The Declaration of Ethics Committee Approval

This study does not require ethics committee permission or any special permission.

The Declaration of Research and Publication Ethics

The authors of the paper declare that they comply with the scientific, ethical and quotation rules of SAUJS in all processes of the paper and that they do not make any falsification on the data collected. In addition, they declare that Sakarya University Journal of Science and its editorial board have no responsibility for any ethical violations that may be encountered, and that this study has not been evaluated in any academic publication environment other than Sakarya University Journal of Science.

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