

Thermoelectric Properties of *ex-situ* PTH/PEDOT Composites

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Abstract

A thermoelectric material can convert temperature difference into electrical potential difference. Today, intensive researches are being carried out in order to use flexible, non-toxic and inexpensive conductive polymers instead of hard, hard-to-shape, expensive and toxic semiconductor metals used as thermoelectric materials. Among the conductive polymers investigated for this purpose, poly(3,4-ethylenedioxythiophene) (PEDOT) is the most promising. However, its thermoelectric properties alone are not sufficient. Thermoelectric properties can be increased by incorporating nanoparticles in inorganic, organic or polymeric structures into conductive polymers. In this study firstly, PTh was synthesized with and without magnetic field by oxidative polymerization in aqueous media in the presence of poly(sulfonic acid diphenyl aniline). Secondly, PEDOT was synthesized with and without magnetic field in aqueous media by oxidative polymerization. Then, *ex-situ* PTH/PEDOT composites were obtained with different ratios of PTh/PEDOT. Particle sizes of polymers were measured and their FTIR and UV-vis. spectra were taken. Seebeck coefficient and electrical conductivity were measured from thin films of polymers. Power factor values were calculated. It was found that the Seebeck coefficients of PTh and *ex-situ* PTH/PEDOT composites increased with magnetic field. The highest Seebeck coefficient and power factor of PEDOTs were obtained from PEDOT synthesized without magnetic field as 1683.3 $\mu\text{V}/\text{K}$ and 98.2 $\mu\text{W}/\text{mK}^2$, respectively. The highest Seebeck coefficient and power factor of *ex-situ* PTh/PEDOT composites were obtained from (PTh/PEDOT3)m synthesized with magnetic field as 400 $\mu\text{V}/\text{K}$ and 0.1 $\mu\text{W}/\text{mK}^2$, respectively.

Keywords

Poly(sulfonic acid diphenyl aniline);
Poly(3,4-ethylenedioxythiophene);
Seebeck coefficient;
Thermoelectric

Ex-situ PTH/PEDOT Kompozitlerinin Termoelektrik Özellikleri

Öz

Bir termoelektrik malzeme, sıcaklık farkını elektriksel potansiyel farkına dönüştürebilir. Günümüzde termoelektrik malzeme olarak kullanılan sert, şekillendirilmesi zor, pahalı ve toksik yarı iletken metallere yerine esnek, toksik olmayan ve ucuz iletken polimerlerin kullanılması için yoğun araştırmalar yapılmaktadır. Bu amaçla araştırılan iletken polimerler arasında poli(3,4-etilendioksitiyofen) (PEDOT) en umut verici olanıdır. Ancak termoelektrik özellikleri tek başına yeterli değildir. Termoelektrik özellikler inorganik, organik veya polimerik yapılarıdaki nanopartikülleri iletken polimerlere ekleyerek artırılabilir. Bu çalışmada ilk olarak PTh, poli(sülfonik asit difenil anilin) varlığında, manyetik alanlı ve manyetik alansız sulu ortamda oksidatif polimerizasyon ile sentezlendi. İkinci olarak, PEDOT, oksidatif polimerizasyon yoluyla, manyetik alanlı ve manyetik alansız sulu ortamda sentezlendi. Daha sonra, farklı PTh/PEDOT oranları ile *ex-situ* PTH/PEDOT kompozitleri elde edildi. Polimerlerin partikül büyüklükleri ölçülmüş ve FTIR ve UV-vis. spektrumları alındı. Polimerlerin ince filmlerinden Seebeck katsayısı ve elektriksel iletkenlik ölçüldü. Güç faktörü değerleri hesaplandı. PTh ve *ex-situ* PTH/PEDOT kompozitlerinin Seebeck katsayılarının manyetik alanla arttığı bulundu. PEDOT'ların en yüksek Seebeck katsayısı ve güç faktörü sırasıyla, 1683,3 $\mu\text{V}/\text{K}$ ve 98,2 $\mu\text{W}/\text{mK}^2$ olarak manyetik alan olmadan sentezlenen PEDOT'tan elde edildi. *Ex-situ* PTh/PEDOT kompozitlerin en yüksek Seebeck katsayısı ve güç faktörü sırasıyla, 400 $\mu\text{V}/\text{K}$ ve 0.1 $\mu\text{W}/\text{mK}^2$ olarak manyetik alanla sentezlenen (PTh/PEDOT3)m'den elde edildi.

Anahtar kelimeler

Poli(sülfonik asit difenil anilin);
Poli(3,4-etilendioksitiyofen);
Seebeck katsayısı;
Termoelektrik

1. Introduction

A thermoelectric (TE) material is a semiconductor material where voltage occurs at the ends with the heat difference occurring between two surfaces or when current is passed over it, one surface heats while the other surface cools depending on the direction of the current. The TE materials are used as generators which can generate electricity from waste heat sources. TE generators have important advantages such as long operating life, no moving parts (Dubey and Leclerc 2011), noise-free operation, use of solid state technologies in energy conversion, easy maintenance and portable (Yang *et al.* 2008, Atik and Kayabaşı 2009, Pichanusakorn and Bandaru 2010, Aswal *et al.* 2010). Since the efficiency of the TE materials used limits the efficiency of these generators, the use of TE generators is now limited to very small applications. Figure of merit (ZT) refers to the efficiency of a TE material. $ZT = S^2\sigma T/\kappa$, where T, σ , κ and S are absolute temperature, electrical, thermal conductivity, and Seebeck coefficient respectively. The TE efficiency of a material increases with the high electrical conductivity (σ) and Seebeck coefficient (S) of this material. The thermal conductivity of this material (κ) must be small, for the high TE efficiency of a material (Du *et al.* 2012). Although the TE properties of the semiconductor metals and alloys used today are good, they cannot be used widely because of their high costs, difficult preparation and heavy metal pollution. Therefore, there is a great need to develop non-toxic, abundant raw materials, easy production process and elasticity organic TE materials instead of inorganic semiconductors (Yue and Xu 2012). In recent years, interest in polymers and their composites has increased and they are being studied for a wide range of applications (Hünér *et al.* 2018).

Conductive polymers (CPs) are also being investigated as thermoelectric materials and their TE properties are tried to be developed (Han *et al.* 2014, Wei *et al.* 2015, Russ *et al.* 2016, Crispin 2012, Kroon *et al.* 2016, Bahk *et al.* 2015). To date, the most studied CPs for producing polymeric TE materials are polyaniline (PANI), polythiophene

(PTH) and poly(3,4-ethylenedioxythiophene) (PEDOT). Since the thermal conductivity of the polymers is close to each other and not much changed by the added additives, the TE properties are compared by the parameters defined by PF ($= S^2\sigma$) where PF is power factor, S is Seebeck coefficient, σ is electrical conductivity (Bharti *et al.* 2018). In order to increase the TE efficiency of CPs, studies such as doping process, nanostructure formation (Bahk *et al.* 2015, Chen *et al.* 2015), preparation of nanoparticle containing nanocomposites (Aswal *et al.* 2016) have been carried out, but the increase provided by these methods is not sufficient.

The Seebeck coefficients of the undoped conductive polymers are relatively high, but when they are doped, their electrical conductivity increases and the Seebeck coefficients are reduced. Therefore, charge carrier concentration should be optimized. Due to the quantum restriction in nanostructured (especially 1-dimensional) conductive polymers and the change in the number of energy levels of electrons, the changes in conductivity and counter-Seebeck coefficient can be prevented (Dresselhaus *et al.* 2007). Low thermal conductivity in 1-dimensional stacked conductive polymers due to interface-phonon scattering, high Seebeck coefficient is expected due to high electrical conductivity and increased energy levels near the conductivity band due to the highly oriented polymer chains (Kuchibhatla *et al.* 2007, Wang *et al.* 2011). Another reason for the increase of the Seebeck coefficient is the elimination of the low speed charge carriers at the nanoparticle polymer interface.

On the other hand, when the molar mass is increased and the polymer chains are more oriented, the electrical conductivity is expected to rise as the electron mobility will increase. It has been shown that the molar mass has higher and more oriented chains, when synthesized under magnetic field (MF) in conventional polymers (Turro 1983). Block copolymers, liquid crystals and polyelectrolytes are self-directing materials. It is also expected to direct the polymer chains formed during the conductive polymer synthesis.

It is understood from the studies in the literature that the charge carrier mobility should be increased in order to increase the PF value of a polymeric material. It is clear that the way to increase mobility is to keep the polymer chains as long and oriented as possible. Because in such chains, charge carriers can move faster. In the literature studies, it is seen that when the conventional polymers are synthesized under magnetic field, chain lengths increase. Therefore, in this study, it is aimed to prepare PTh and then PEDOT under magnetic field as well as to prepare PTh and PEDOT blends under magnetic field in order to prepare a thermoelectric material with high PF value. Self-regulating poly(sulphonic acid diphenyl aniline (PSDA) was added to the reaction medium during PTh synthesis to obtain more regular polymer chains.

2. Material and Method

2.1 Materials

3, 4-Ethylenedioxythiophene (EDOT), thiophene (Th), copper(II) nitrate, poly(styrene sulfonic acid) (PSSA) were supplied from Alfa Aesar. Hydrogen peroxide (35%) were also obtained from Merck. PSDA, which was previously synthesized in our laboratory, was used as a router in PTh synthesis. In all experiments deionized water was used.

2.2 Synthesis of PTh nanoparticles

The $\text{Cu}(\text{NO}_3)_2$ (0.04 g) and deionized water (50ml) were added to the reaction vessel. PSDA synthesized by $\text{Cu}(\text{NO}_3)_2/\text{H}_2\text{O}_2$ was also added in the medium at a rate of 2% as the router. After stirring thoroughly for 30 minutes, the thiophene monomer (0.168 g) and H_2O_2 (35%, 0.9 g) were added to the reaction vessel. Stirring was continued at 50 °C for about 5 hours with a mechanical stirrer. The resulting polymer was purified by dialysis for 4 days. Then the purified polymer was dried at room temperature. This polymer synthesized without magnetic field is called as PTh. The same reaction was also performed under the flux density of 4.6 kGauss and this polymer is called as (PTh)m.

2.3 Synthesis of PEDOT particles

PEDOT particles were synthesized as in the literature (Ahmed and Karaman 2018). The PSSA (1.76 g) and deionized water (10 ml) were added to the reaction vessel and stirred for 1.5 hours with mechanical stirrer. At the same time, EDOT monomer (0.11 g) and deionized water (10 ml) were added to a beaker and stirred for 1.5 hours with mechanical stirrer. And then EDOT mixture was added dropwise to the reaction vessel and after 1 hour $\text{Cu}(\text{NO}_3)_2$ (0.007 g) and H_2O_2 (0.52 g) were added and the mixture was stirred for 24 hours with mechanical stirrer. This polymer was called PEDOT. The same synthesis was done under magnetic field and the resulting polymer was called (PEDOT)m.

2.4 Ex-situ PTh/Pedot composites

The composites were obtained *ex-situ* by mixing different ratios (PTh/PEDOT 1:2, 1:1, 2:1) from synthesized PThs and PEDOTs. In addition, PThs synthesized under magnetic field were mixed *ex-situ* with different ratios of PEDOTs synthesized under magnetic field and composites were obtained. The codes and definitions given to composites prepared *ex-situ* are given in Table 1.

2.5 Characterization

The FTIR-ATR (SENSOR27, Bruker Optic GmbH, fourier transform infrared spectroscopy) was used for polymer characterization. Diluted aqueous solutions of the synthesized polymers were prepared and the adsorption spectra in quartz cuvettes were taken by Shimadzu brand A109351 05066 model UV mini-1240 UV-vis spectrophotometer (The absorbance values were obtained as a result of the calculation made by the device using logarithms according to the "e" base). Seebeck coefficients were measured from thin films of synthesized polymers on microscope glass by ENTEK (SC 001). The electrical conductivity was measured using four probe technique by ENTEK FPP 470 at room temperature. The particle sizes were determined by dynamic light scattering (DLS, Brookhaven 90Plus Particle Size Analyzer).

3. Results and Discussion

PTh was synthesized in the presence of PSDA. The same synthesis was done under MF. PEDOT was synthesized with and without MF. PTh and PEDOT synthesized under MF were matched to obtain ex situ composites by mixing them at different ratios. In addition, PTh and PEDOT synthesized without MF were matched and mixed in certain proportions to obtain *ex-situ* composites. The structure of PThs and PEDOTs were characterized by UV and FTIR-ATR, and particle size was measured by DLS. Thin films of polymers and composites were cast on glass substrate. Electrical conductivity and Seebeck coefficient were measured from thin films. Power factors were calculated. The codes and definitions given to the synthesized polymers and the prepared composites are given in table 1.

Table 1. The codes and definitions given to the synthesized polymers and the prepared composites.

| Sample | MF | PSDA | PTh | PEDOT |
|---------------|----|------|-----|-------|
| PTh | - | + | + | - |
| (PTh)m | + | + | + | - |
| PEDOT | - | - | - | + |
| (PEDOT)m | + | - | - | + |
| PTh/PEDOT1 | - | + | 2 | 1 |
| PTh/PEDOT2 | - | + | 1 | 1 |
| PTh/PEDOT3 | - | + | 1 | 2 |
| (PTh/PEDOT1)m | + | + | 2 | 1 |
| (PTh/PEDOT2)m | + | + | 1 | 1 |
| (PTh/PEDOT3)m | + | + | 1 | 2 |

UV-vis. spectra of PTh, (PTh)m, PEDOT and (PEDOT)m prepared at the same concentration are given in Figure 1a, b. It is seen from the UV-vis. spectra (Fig. 1a) that (PTh)m synthesized under MF absorb slightly more in the 400-600 nm region. The fact that the color of (PTh)m is darker than PTh also supports this result. The peak in the 350-400 nm range is due to the π - π^* transition absorption (Yildiz *et al.* 2008, Aydemir *et al.* 2008). The slight red shift in the maximum absorption of the π - π^* transition indicates that the conjugation length in the polymer chain increases slightly. In our previous study (Huner and Karaman 2018), the absorption of PThs synthesized with the same formulation without PSDA was much lower than in

figure 2, which can be attributed to PSDA. The free carrier tail between 550 and 600 nm indicates the long conjugation and the conductivity (Ram *et al.* 2005, Kim *et al.* 2000) of PEDOTs (Figure 1b). The lower conductivity band around 600 nm in (PEDOT)m synthesized under MF indicates that the conductivity of (PEDOT)m is lower than PEDOT, the conductivity decreased from 0.35 to 0.19 S/cm.

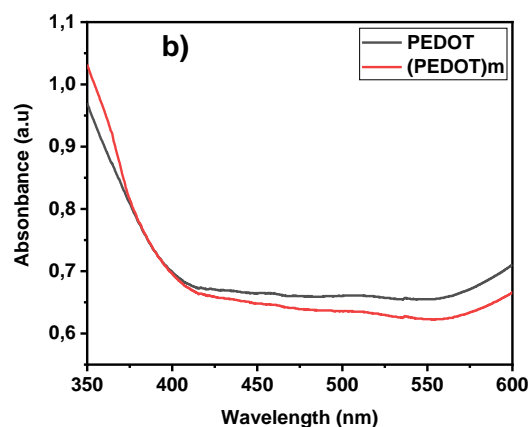
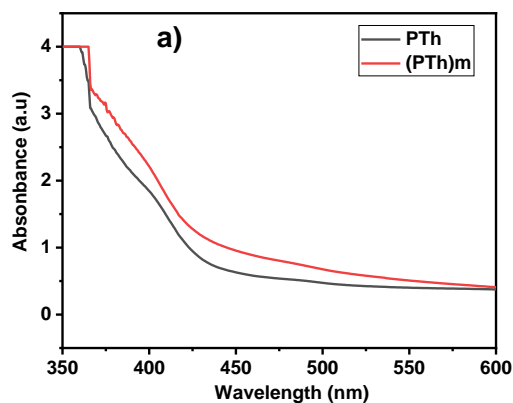


Figure 1. The UV-vis. spectra of synthesized polymers a) PTh, (PTh)m b) PEDOT, (PEDOT)m.

FTIR spectra of PThs are given in Figure 2. The peaks seen at approximately 625, 750, 1032, 1120, 1440 and 1600 cm^{-1} are characteristic peaks of the groups in the structure of the PTh (Jeon *et al.* 2010, Lee *et al.* 2009, Majid *et al.* 2009, Huner and Karaman 2018). In comparison of the spectra of PTh and (PTh)m, it can be seen that the peak positions do not change with MF, but the intensity of the peaks is slightly decreased. It was also observed that the intensity of the peaks of C-H out

of plane bending of the thiophene ring at 750 cm^{-1} and the stretching vibration of C=O at 1420 cm^{-1} decreased in (PTh)m synthesized under MF. In the FTIR spectra, the effect of PSDA could not be seen since it was thought that the peaks of PTh covered the PSDA peaks.

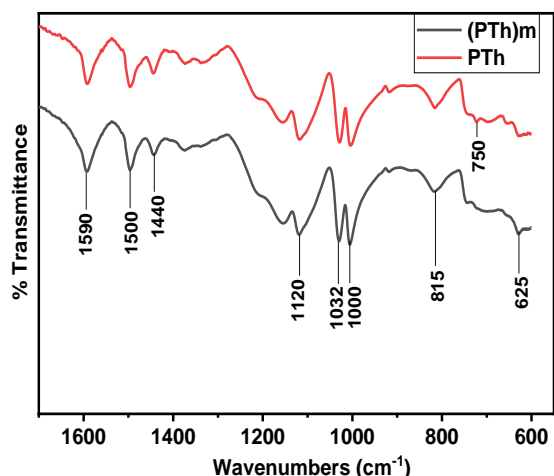


Figure 2. The FTIR Spectra of PTh and (PTh)m.

Particle sizes of the aqueous PEDOT, PTh particles synthesized in the presence of PSDA and their particles synthesized under MF were given in Table 2. The particle size of PTh particles are almost 3 times greater than (PTh)m particles synthesized under MF. The particle size of (PEDOT)m samples synthesized under MF are almost 1.5 times greater than PEDOT particles. The magnetic field decreased the particle size for PTh while increased it for PEDOT. In our previous study (Huner and Karaman 2018), the magnetic field did not change the PTH particle size much, here the change is attributable to the presence of PSDA.

Table 2. Particle sizes of the aqueous PEDOT, PTh particles synthesized in the presence of PSDA and their particles synthesized under MF.

| Sample | R_H (nm) | Polydispersity |
|----------|------------|----------------|
| PTh | 745 | 0,370 |
| (PTh)m | 275 | 0,312 |
| PEDOT | 75 | 0,670 |
| (PEDOT)m | 126 | 0,051 |

Seebeck coefficient and electrical conductivity of PTh, PEDOT and their *ex-situ* composites with and without MF were given in Figure 3. Samples were measured 3 times and averaged. Seebeck coefficient is given with error bar.

The Seebeck coefficient of PTh did not change considerably with MF, while the Seebeck coefficient of PEDOT decreased (~2.5 times). The highest Seebeck coefficient for PThs is $14.3\text{ }\mu\text{V/K}$ obtained from (PTh)m and this value is smaller than $23\text{ }\mu\text{V/K}$, which is the Seebeck coefficient of PTh obtained on ITO substrate by electrolytic polymerization in the literature (Hiraishi *et al.* 2009). The highest Seebeck coefficient for PEDOTs is $1683.3\text{ }\mu\text{V/K}$ obtained from PEDOT synthesized without MF and this value is higher than $12.4\text{ }\mu\text{V/K}$, which is the Seebeck coefficient of obtained from commercial-undoped PEDOT:PSS in the literature (Tsai *et al.* 2011). The Seebeck coefficient of *ex-situ* PTH/PEDOT composites synthesized without MF is about 133.3 , 213.3 and $305\text{ }\mu\text{V/K}$ for PTH/PEDOT ratio 2:1, 1:1, 1:2, respectively. The Seebeck coefficient of *ex-situ* PTH/PEDOT composites synthesized with MF are about 150 , 343.3 and $400\text{ }\mu\text{V/K}$ for PTH/PEDOT ratio 2:1, 1:1, 1:2, respectively. MF increased the Seebeck coefficient of composites. Seebeck coefficient increased as the amount of PEDOT increased in *ex-situ* PTH/PEDOT composites with and without MF. However, the Seebeck coefficient of composites is still lower than the value of PEDOT. Seebeck coefficient of *ex-situ* PTH/PEDOT composites have greater than PThs. The Seebeck coefficients of composites with MF (for PTH/PEDOT ratio: 2:1, 1:1, 1:2) are about 10 , 24 and 28 times greater than PTh with MF ($\sim 14.3\text{ }\mu\text{V/K}$), respectively. The highest Seebeck coefficient of *ex-situ* PTH/PEDOT was obtained as $400\text{ }\mu\text{V/K}$, for the *ex-situ* (PTh/PEDOT3)m (PTh/PEDOT ratio 1:2) synthesized with MF. This value is 12.5 times greater than the value of $32\text{ }\mu\text{V/K}$ (Lee, Kim and Kim 2014) reported in the literature and approximately 35.7 times greater than the $11.2\text{ }\mu\text{V/K}$ (Shi *et al.* 2013) value of PEDOT:PSS/PTh obtained by electropolymerization.

The conductivity values of PTH samples synthesized in the presence of PSDA were about 10 times higher than that of (PTh)_m synthesized under MF in the presence of PSDA. The conductivity of PTH obtained with MF and without MF in an aqueous medium is 0.001 and 0.0001 S/cm, respectively, while PTH obtained in an aqueous medium is not conductive in the literature (Jeon *et al.* 2010). Conductivity for PEDOT synthesized without MF is 0.346 S/cm, while for PEDOT synthesized with MF, it is 0.191 S/cm. These values are considerably higher than the values 10^{-5} - 10^{-6} (Liu *et al.* 2012) and 10^{-3} - 10^{-4} S/cm (Nardes and Kemerink 2008, Xia and Ouyang 2012, Nardes *et al.* 2008) found for PEDOT:PSS in the literature. The conductivity of *ex-situ* PTH/PEDOT composites synthesized without MF is about 0.0015, 0.011 and 0.005 S/cm for PTh/PEDOT ratio 2:1, 1:1, 1:2, respectively. Electrical conductivities of *ex-situ* PTH/PEDOT composites synthesized with MF are about 0.0018, 0.008 and 0.0069 S/cm for PTh/PEDOT ratio 2:1, 1:1, 1:2, respectively. It is well known that MF increases the rate of polymerization reactions proceeding by radical mechanism by forming longer-lived triplet products faster (Steiner *et al.* 1989). It is also known that polymers synthesized under MF have high molecular weight and therefore cannot adapt to the crystal structure of the chains (Kimura 2003). It is expected that the electrical conductivity will increase with high molecular weight. Therefore, it can be said that unlike Pth and PEDOT, their composites in MF, with increased electrical conductivity with MF, have a higher molecular weight and contain less or no crystalline phase. In the literature, cationic PTh and PEDOT:PSS composites (Worfolk *et al.* 2012, Rider *et al.* 2010) have been obtained, but their conductivity and thermoelectric properties have not been investigated. The conductivity of *ex-situ* PTH/PEDOT was found lower than the conductivity of *in-situ* PTH/PEDOT nanocomposites reported as 17.6 S/cm by Lee *et al.*, which *in-situ* PTH/PEDOT was synthesized by two-step oxidative polymerization (Lee *et al.* 2014).

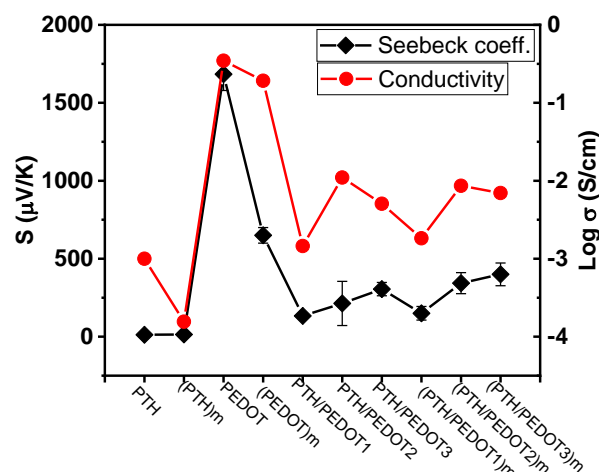


Figure 3. Seebeck coefficients (S) and logarithms of electrical conductivities (σ) of the films of PTH and PEDOT nanoparticles synthesized with/without magnetic field, and their *ex-situ* composites.

The power factors calculated from the Seebeck coefficients and electrical conductivity of PThs, PEDOTs and their *ex-situ* composites are given in Figure 4. The values of PF were also given on a logarithmic scale in the graph since the differences are very large. The PFs of PThs synthesized with and without MF are about 3.2×10^{-6} and 1.44×10^{-5} $\mu\text{W}/\text{mK}^2$, respectively. The PFs of PEDOTs synthesized with and without MF are about 8.1 and 98.2 $\mu\text{W}/\text{mK}^2$, respectively. PTh/PEDOT ratios varied from 2:1 to 2:1 of *ex-situ* PTh/PEDOT composites with MF, while PF values increased from 0.004 to 0.111 $\mu\text{W}/\text{mK}^2$. The highest power factor value obtained from PEDOT synthesized without MF is ~ 98.2 $\mu\text{W}/\text{mK}^2$ and this value is 13.4 times higher than 7.3 $\mu\text{W}/\text{mK}^2$ (Lee *et al.* 2014) in the literature. The highest PF of *ex-situ* PTh/PEDOT was obtained from (PTh/PEDOT₃)_m composite (PTh/PEDOT ratio 1:2) as 0.11 $\mu\text{W}/\text{mK}^2$. This value is ~ 10 times lower than the value of 1.57 $\mu\text{W}/\text{mK}^2$ (Shi *et al.* 2013) reported in the literature.

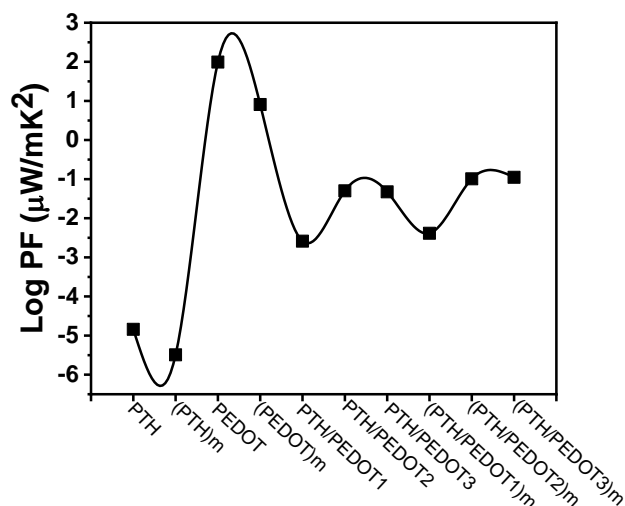


Figure 4. Logarithms of PF of the films of PTh and PEDOT nanoparticles synthesized with/without magnetic field, and their *ex-situ* composites.

4. Conclusions

In this study, PTh and PEDOT were successfully synthesized by oxidative polymerization, with and without MF. Then, *ex situ* PTh/PEDOT composites were obtained with different PTh/PEDOT ratios. The particle size of PTh decreased with MF, while PEDOT's increased. While the particle size of PTh synthesized without PSDA did not change much with MF, PSDA used in this study changed the particle size of PTh with MF. Seebeck coefficients of PTh and PTh/PEDOT composites were seen to increase with magnetic field. The electrical conductivity of PTh/PEDOT composites did not change much with the magnetic field, but decreased for PEDOT and PTh. Power factors of *ex-situ* PTh/PEDOT composites increased with magnetic field. In this study, the Seebeck coefficient values 1638.3 and 400 obtained for PEDOT and (PTh/PEDOT₃)_m composite, respectively, are much higher than the Seebeck coefficient of PEDOT and PTh/PEDOT obtained by different methods in the literature.

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