M. Culebras, C.M. Gomez, A. Cantarero

Materials Science Institute, University of Valencia,
Valencia, 46071, Spain

THERMOELECTRIC MATERIALS BASED ON POLY (3, 4-ETHYLENDIOXYTHIOPHENE)

Poly (3, 4-ethylenedioxythiophene) with several counterions was investigated for thermoelectric applications. Polystyrene sulfonate, tosylate, and perchlorate were used as counterions. Thermal, optical and thermoelectric characterization have been made on poly (3, 4-ethylenedioxythiophene) based polymers. Very high conductive poly (3, 4-ethylenedioxythiophene):ClO_4, was synthesized by electrochemical deposition. Its high conductivity (750 S/cm) indicates that this polymer can be the starting point for new high performance thermoelectric materials.

Key words: conducting polymers, energy, organic semiconductors, thermoelectric.

Introduction

During the last decade many investigations have been focused on the development of energy recovery devices, due to high energy demand in today's society. Therefore, it is important to use the energy losses, such as heat, and produce energy. Thermoelectric materials have recently attracted attention for its potential as power generation [1], cooling [2] and thermal detection [3], so thermoelectric materials can convert waste energy into electricity. Efficient thermoelectric materials are of great interest in industrial, automotive and aerospace applications. The efficiency of a thermoelectric material is measured by a factor known as figure of merit, ZT:

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

where σ is the electrical conductivity, S the Seebeck coefficient and κ the thermal conductivity. According to equation (1), the maximum efficiency will be attained when the material has high electrical conductivity and low thermal conductivity. If the thermal conductivity is similar in different samples, the power factor PF ($PF = \sigma S^2$) is often used to compare the relative efficiency. The maximum efficiency of a thermoelectric material is achieved for a given temperature range, so that a thermoelectric material could be very efficient for low temperatures, however, if the material is subjected to high temperatures, the efficiency can decrease significantly, and vice versa. Traditionally, inorganic materials, such as $PbTe$ [4, 5] and Bi_2Te_3 [6, 7, 8], have been used for thermoelectric applications. These inorganic compounds have several drawbacks, such as high cost of production, toxicity and scarcity of materials. For this reason, many efforts have been devoted to the search for new efficient thermoelectric materials during the last years.

Organic conducting polymers, such as polyaniline (PANI) [9], polythiophene (PTH) [10], poly (3, 4-ethylenedioxythiophene): poly (styrenesulfonate) (PEDOT:PSS) [11] and polycarbazoles (PC) [12] have a great potential for thermoelectric applications. These organic materials offer more advantages than inorganic compounds when used for thermoelectric applications, such as chemical modification easier manipulation, abundance, low cost of raw materials, low thermal conductivity (0.2 W/mK for PEDOT:PSS) and good mechanical properties. But, on the contrary, the global thermoelectric efficiency is reduced. The polyanion, PSS, can be replaced by small anions, such as tosylate or perchlorate to increase the conductivity by preventing the excess of insulating phase.

In this work, we use as base polymer PEDOT with several counter ions, that is, polystyrene sulfonate (PSS), tosylate (Tos), and perchlorate (ClO_4). Chemical and physical properties, as solubility and electrical conductivity, are strongly dependent on the counterion employed. The objective of this work is to compare thermoelectric properties of the three polymers, PEDOT:PSS, PEDOT: Tos and PEDOT: ClO_4, as a function of the counterion used.

1. Experimental

1.1. Materials

PEDOT:PSS solution (1.3 wt.% in water) with a ratio of PEDOT to PSS of 38.5 to 61.5 %, ethylenedioxythiophene 97 % (EDOT), iron (III) *P*-toluensulfonate hexahydrate, lithium perchlorate 99 %, nitric acid (HNO_3) and hydrochloric acid (HCl) were purchased from Sigma-Aldrich Co. acetonitrile, butanoland tetrahydrofurane were obtained from Fisher Scientific.

1.2. Preparation of PEDOT:PSS

The commercial solution of PEDOT:PSS was precipitated in tetrahydrofurane. The suspension was filtered and dried at 100 °C in vacuum for 5 h. Finally, the powder obtained was used to make a thin pellet (100 µm thickness).

1.3. Preparation of PEDOT:Tos

Iron tosylate, FeTos, was added to the EDOT (1 wt.%) solution in butanol (molar ratio 1:1.5). The solution was deposited on a glass substrate at 100 °C. The polymer obtained was washed several times with water and ethanol, then it was filtered and dried at 100 °C in vacuum for 5 h. Finally, the powder obtained was used to make a thin pellet (100 µm thickness).

1.4. Preparation of PEDOT:ClO_4

The preparation of PEDOT:ClO_4 films was performed in a three electrode cell [13, 14] from a solution formed by 0.1 M of $LiClO_4$ in acetonitrile (ACN) with EDOT monomer (10^{-2} M). Gold coated glass as a working electrode, platinum grid as a counter electrode and an $Ag/AgCl$ as reference electrode were used into the cell. A Keithley 2400 was used as a potentiostat. After the necessary connections were made, a current of –3 mA was applied to the electrolytic cell and the desired amounts of PEDOT were coated onto the working electrode. PEDOT coated gold glass was washed with ACN to remove the monomer and oligomeric species from the surface. Then the gold layer was removed using acid solution (HNO_3:HCl ratio 1:3) and finally the film (110 – 120 nm) was washed several times with water.

1.5. Characterization

The van der Pauw method has been used to determine the electrical conductivity [15] of the samples. The electrical conductivity is obtained from two four-point resistance measurements. For the first resistance measurement a current I_{AC} is driven from two contacts, named A and C, and the potential difference V_{BD} between the other two contacts, B and D, is measured, giving $R_1 = V_{BD}/I_{AC}$.

The second resistance, $R_2 = V_{AB}/I_{CD}$, is obtained by driving a current from C to D and measuring the voltage between A and B. A Keithley 2400 current source was used as driving source and voltmeter. The conductivity of the sample can be obtained by solving the van der Pauw equation:

$$e^{-\pi d R_1 \sigma} + e^{-\pi d R_2 \sigma} = 1 \tag{2}$$

where d is the sample thickness.

A home-made setup has been used to measure the Seebeck coefficient. Temperature differences are generated between two points of the sample and the associated potential difference has been measured. A Lakeshore 336 temperature controller has been employed to control the temperature and a Keithley 2750 Multimeter/Switch System to record the potential difference. The Seebeck coefficient is determined as the ratio between the electrical potential, ΔV, and the temperature difference, ΔT:

$$S = \frac{\Delta V}{\Delta T} \tag{3}$$

The linearity of the $\Delta V/\Delta T$ ratio has been checked.

The Raman spectroscopy analysis was carried out in a Jobin Yvon T64000 spectrophotometer with macro and micro input. The excitation source was a laser Spectrum 70 capable of producing several lasers lines through the visible range. The excitation wavelength was 514.16 nm, the signal was recorded in a range of 1200 cm^{-1} to 1800 cm^{-1} with acquisition time of 100 seconds. Two scans were performed in order to eliminate peaks originated from cosmic rays.

Differential scanning calorimetry (DSC) was performed on a TA instruments DSC Q-20 calibrated with indium and sapphire. The samples were subjected to two scans in the range of –90 to 220 °C at a heating rate of 20 °C/min.

2. Results and discussion

Typical polyanion such as polystyrene sulphonic acid, PSS, of PEDOT has been replaced by small anions such as tosylate and perchlorate to study changes on thermoelectric properties. PSS is a polymeric anion, Tos is an organic anion and perchlorate is an inorganic anion. Figure 1 shows the molecular structures of PEDOT, PSS, Tos and perchlorate.

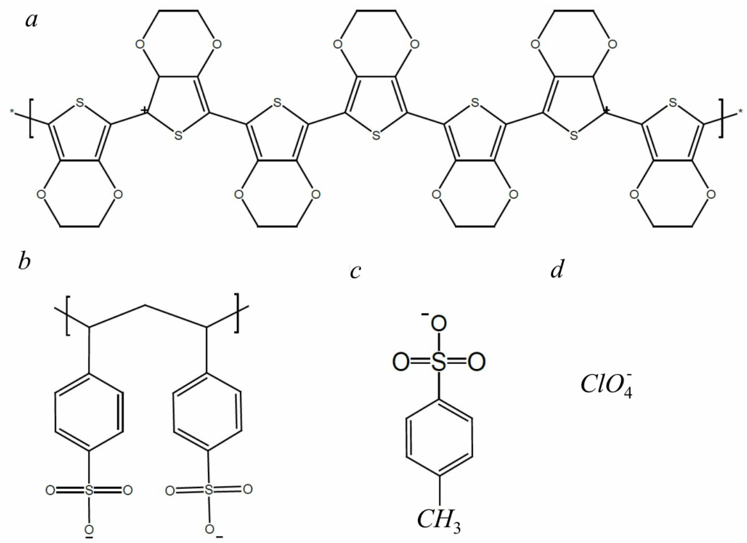

Fig. 1. Molecular structures of: a) PEDOT, b) PSS, c) Tos and d) perchlorate.

In order to characterize the thermal properties, DSC was used. It is important to know how these materials behave under a certain range of temperatures since the physical state is important for thermoelectric applications. Figure 2 shows the DSC curves of PEDOT:PSS, PEDOT:Tos and PEDOT:ClO_4 with no indication of a well-defined glass transition temperature. In the first DSC scan an endothermic peak around 100 – 110 °C is observed in all cases related to the melting of the PEDOT crystals [16]. No presence of free water in the samples is revealed by the absence of a peak near 0 °C. No peaks were observed during a second temperature scan indicating that the sample did not have enough time to re-crystallize during the quick cooling. The PEDOT chains tend to form crystals during the synthesis or during slow cooling if there is enough time to reorganize themselves.

Similar curves are observed for PEDOT:Tos and PEDOT:PSS but in the case of PEDOT:ClO_4 the heat flow increases from 140 °C possibly due to a degradation process.

In order to detect the characteristic vibration modes of PEDOT, the Raman analysis has been made in all the samples. Figure 3 shows the Raman spectra of the three samples. Different bands have been detected: around 1360 cm^{-1} the $C_\beta - C_\beta$ stretching, around 1440 cm^{-1} the symmetric stretching $C_\alpha = C_\beta(-O)$ and the asymmetric tension band $C = C$ splitted into two bands with peaks at 1506 cm^{-1} and 1568 cm^{-1}. Table 1 summarizes the vibration modes observed in all spectra [17, 18].

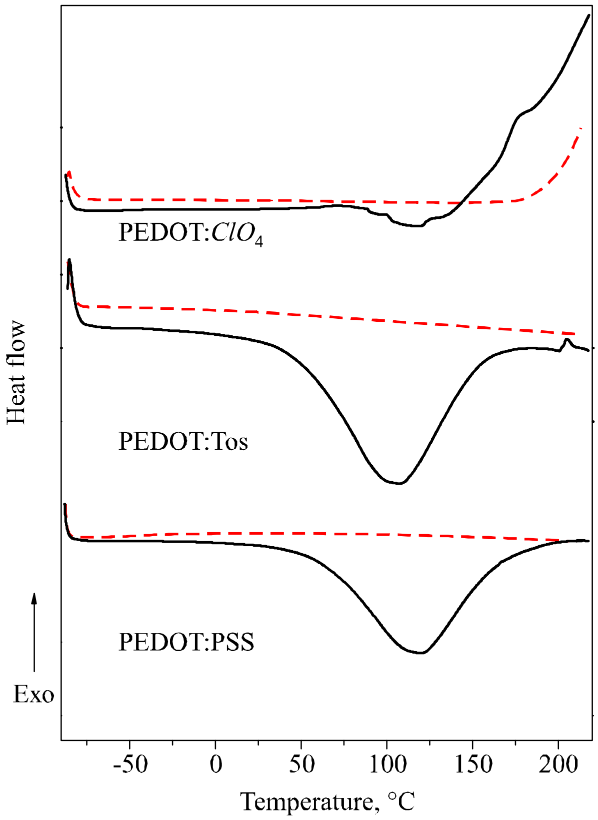

Fig. 2. DSC of PEDOT:PSS, PEDOT:Tos and PEDOT:ClO_4 (black line is the first scan and dash red line is the second scan).

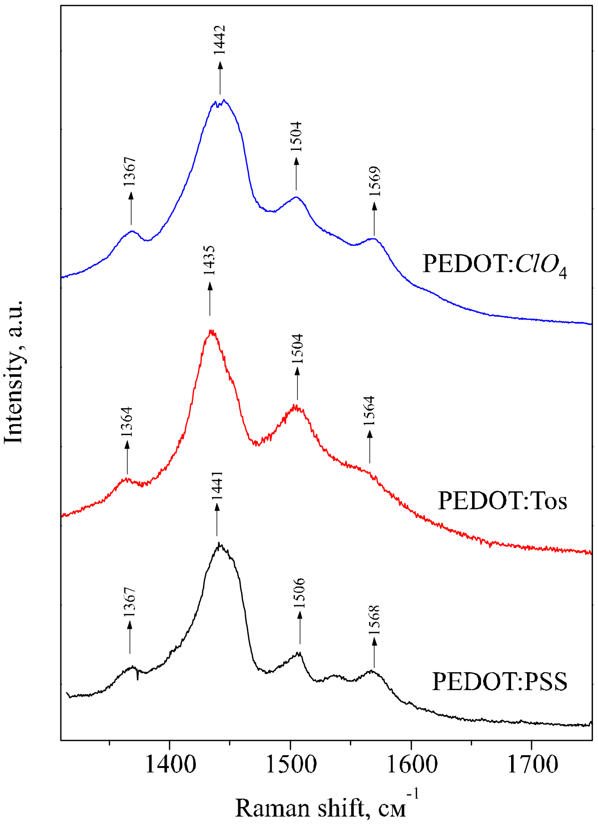

Fig. 3. Raman spectra of PEDOT:PSS, PEDOT:Tos and PEDOT:ClO_4.

No significant differences have been detected among the different samples; the vibrations correspond to the polymer backbone that in the three types of samples is the same, PEDOT.

Table 1

Vibration modes of PEDOT:PSS, PEDOT:Tos and PEDOT:ClO$_4$

PEDOT:PSS		PEDOT:Tos		PEDOT:ClO_4	
Raman shift (cm^{-1})	Assignation	Raman shift (cm^{-1})	Assignation	Raman shift (cm^{-1})	Assignation
1367	$C_\beta - C_\beta$ – str	1364	$C_\beta - C_\beta$ – str	1367	$C_\beta - C_\beta$ – str
1441	sym $C_\alpha = C_\beta(-O)$ str	1435	sym $C_\alpha = C_\beta(-O)$ str	1442	sym $C_\alpha = C_\beta(-O)$ str
1506/1568	asym $C = C$ str	1504/1564	asym $C = C$ str	1504/1569	asym $C = C$ str

Electrical conductivity was measured at 298 K, because it is the representative temperature for room temperature applications. Table 2 compiles the values of electric conductivity, the Seebeck coefficient, power factor (PF) and figure of merit (*ZT*) for PEDOT:PSS, PEDOT:Tos and PEDOT:ClO_4 systems. The electric conductivity data obtained by the van der Pauw method are: 0.16, 1.53 and 753 S/cm for PEDOT:PSS, PEDOT:Tos and PEDOT:ClO_4, respectively.The very high conductivity of PEDOT:ClO$_4$ is possibly due to the electrochemical synthesis that induces structural order and polymer chains longer than the oxidative synthesis. The Seebeck coefficient values obtained as a function of the type of counterion are: 8.7, 13.2 and 9.31 μV/K for PEDOT:PSS, PEDOT:Tos and PEDOT:ClO_4, respectively. The Seebeck coefficient is relatively constant with the type of counterion. The power factor, $PF = S^2T\sigma$ has been calculated in order to compare the relative efficiency of these materials, with values of 1.2×10^{-3}, 2.6×10^{-2} and 6.52 μW/mK^2 for PEDOT:PSS, PEDOT:Tos and PEDOT:ClO_4, respectively. The best value has been obtained for PEDOT:ClO_4 due to its high electrical conductivity. To compare with other inorganic materials studied in the bibliography, the *ZT* value has been calculated by assuming a coherent value of the thermal conductivity. In this work, we assume a value of 0.2 W/mK for the thermal conductivity, that is the value reported for PEDOT:PSS by several authors [19, 20]. A good value of $ZT = 0.01$ was obtained for PEDOT:ClO_4 in this paper. The comparison with other conductive polymers gives values of *ZT* of 7.9×10^{-5} for polyaniline doped with HCl [21] or of $0.01 - 2.3 \times 10^{-3}$ in the case of polythieno [3, 2-*b*] thiophene [22] indicating that improved *ZT* values have been obtained in this paper. However, when comparing with similar systems, we find in the literature values of *ZT* of 0.04 for PEDOT:PSS [23] and 0.25 for PEDOT:Tos [24]. Probably, the discrepancy between actual values and the ones obtained by Bubnova et al [23, 24] relies on the fact that different ways of sample processing are utilized, that is, pressed pellets against thin films.

Table 2

Electrical conductivity, Seebeck coefficient, Power Factor and ZT assuming 0.2 W/mK for thermal conductivity, of PEDOT:PSS, PEDOT:Tos and PEDOT:ClO$_4$ at 298 K

Sample	σ (S/cm)	*S* (μv/K)	PF (μW/mK^2)	*ZT*
PEDOT:PSS	0.16	8.70	1.2×10^{-3}	2×10^{-6}
PEDOT:Tos	1.53	13.20	2.6×10^{-2}	4×10^{-5}
PEDOT:ClO_4	753.00	9.31	6.52	1×10^{-2}

Conclusion

PEDOT with several counterions have been prepared by oxidative and electrochemical synthesis. DSC analysis indicates the presence of endothermic peaks due to a partial crystalline structure. Electrical conductivity strongly depends on the counterion, while the Seebeck coefficient does not significantly. Thermoelectric power of these systems is dominated by the electrical conductivity. Although the best *ZT* value obtained in this work was 100 times lower than the best inorganic materials, PEDOT:ClO_4 can be the starting point for new high performance thermoelectric composites.

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