Synthesis and characterization of poly(ethylene thiosuccinate) (PETS) with succinic anhydride and 1,2-ethanedithiol monomers as supercapacitor electrode materials

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Abstract

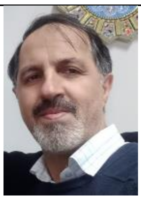
Sulfur, as a mineral element, plays an important role in the synthesis of organic compounds and polymer chemistry. Due to its reactivity, it produces a wide range of compounds with specific functional groups that have diverse physical and chemical properties. Polythioesters are a group of polymers with a sulfur-containing functional group that, unlike polyesters, has been less studied.

Polythioesters usually have high melting points and thermal stability, and low solubility in organic solvents.However, the reaction temperature, type of monomers, and polymerization methods affect the specific properties of the product. Various methods for synthesizing these polymers have been mentioned in the literature, but the use of succinic anhydride monomer has been investigated for the first time in this study for the synthesis of poly(ethylene thiosuccinate) (PETS) as polythioester in the presence of 1,2-ethanedithiol monomer without the presence of a catalyst. Identification of the polymer by FT-IR, ^{1}HNMR and EDAX analyses confirm its successful synthesis. Also, the melting point and glass transition temperature of the polymer by DSC analysis are 142 and 88, respectively. FE-SEM images show amorphous morphology for the polymer. Cyclic voltammetry (CV), galvanostatic charge-discharge (GCD), and electrochemical impedance spectroscopy (EIS) techniques were investigated for neat PETS and its nanocomposite with multi-walled carbon nanotubes and nickel(II) cobalt hexacyanoferrate (PETS/MWCNT + 5% Ni_2CoHCF).

1.Introduction

The thioester bond is a common functional group, especially in biological molecules, that has interesting properties and serves as a key component in biological systems. Unlike thioesters, esters are stabilized by resonance structures. The non-bonding pair of electrons on the oxygen atom attached to the carbonyl group resonates with the double bond electrons of the carbonyl group, forming a partial double bond that prevents rotation about the C-O single bond [1]. A similar resonance structure can be considered for thioesters, however, this resonance structure does not have much effect on the stability of thioesters because the overlap of the sulfur p3 orbitals with the carbon p2 orbitals is weak. Therefore, thioesters are very electrophilic and are more susceptible to attack by nucleophiles [2]. This makes them excellent acyl transfer agents, which nature has exploited. As acetyl-CoA acts as an acetylating reagent in the metabolism of cellular components such as peptides, fatty acids, terpenes, porphyrins, and lipids. In addition, the thiolate and thiol anions are good leaving groups due to their high polarizability and low degree of dipole [3]. The replacement of sulfur atoms with oxygen atoms in the polymer chain of polythioesters enhances their electrical, mechanical, optical, and thermal characteristics, in addition to their chemical resistance [4]. The chemical synthesis of polythioesters was first reported in 1951. However, the relatively complex and inefficient processes that require toxic and very expensive reagents are not suitable for commercialization [5]. In general, the synthesis of polythioesters is carried out by 1) addition polymerization of dithiol acids to non conjugatediolefins, 2) condensation reactions of dithiols with diacids or their derivatives such as diacid chlorides [6], 3) addition polymerization of bicyclic thioethers (e.g., tyranes) with active diacid derivatives [7], 4) ring-opening polymerization [8], and 5) microbial synthesis [9-11]. The first studies on the synthesis of polythioesters, carried out in the 1950s, were carried out using aliphatic dithiols and aliphatic or aromatic dichloroacids without solvent or with benzene solvent in the presence of pyridine. The low intrinsic viscosity of the obtained polymers indicates that only polymers with low molecular weight are synthesized. Polymerization using aromatic and aliphatic-aromatic dithiols carried out in the presence of NaOH as a hydrochloride acceptor gives high molecular weight polythioesters [12]. Ring-opening polymerization is another method for the synthesis of polythioesters, which uses specific monomers and was first performed in 1968 by Wise and Overberger [13-14]. The general reaction mechanism in this method is carried out in the presence of cationic and anionic initiators.

In this research, poly(ethylene thiosuccinate) (PETS) was synthesized with succinic anhydride and 1,2-ethanedithiol monomers and its structure was investigated by various methods such as FT-IR and ^{1}HNMR and thermal analysis of



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the polymer by differential scanning calorimetry (DSC). Also, the morphology of the polymer was investigated by FE-SEM analysis.

2.1 Materials succinic anhydride, 1,2-ethanedithiol, triethylamine and N,N- dimethylformamide were purchased from Merck and used without any further purification.

2.2 . Preparation of poly(ethylene thiosuccinate) (PETS)

An appropriate molar amount of succinic anhydride was completely dissolved in dry DMF solvent. Then, 1,2-ethanedithiol was added to the reaction mixture at a molar ratio of 1:1 with succinic anhydride monomer and stirred under an argon atmosphere at room temperature. The reaction mixture was then heated to 80 °C in an oil bath under stirring and argon gas for 24 h until it turned from colorless to yellow. After that, the reaction temperature was increased to 100 °C and the reaction was continued for a certain period of time under the same previous conditions. Then a white precipitate was formed, which was separated by filtration and washed several times with distilled water, then dried in a vacuum oven at 60 °C for 12 hours. The reaction yield was 60%.

3- Results and Discussions

The FT-IR spectrum of PETS polymer is shown in **Fig. 1**. The absorption bands appearing in the range of 3031-2922 cm^{-1} are attributed to the stretching vibrations of aliphatic C-H bonds. The broad absorption band in the range of 2400 cm^{-1} to 3435 cm^{-1} is related to the stretching vibrations of the O-H bond in the possible carboxylic acid present in the polymer chain. The absorption bands due to the stretching vibrations of the S-H bonds remaining at the ends of the PETS chains are observed at 2552 cm^{-1} and 2680 cm^{-1}. The absorption band at 1687 cm^{-1} is assigned to the stretching vibrations of the C=O bonds in the thioester groups. The bands appearing at 1367 cm^{-1} and 1406 cm^{-1} are assigned to the bending vibrations of the C-S bonds in the –S-CH2- and –S-CO- groups. The stretching vibrations of the C-C bonds are observed at 1247-1128 cm^{-1}.

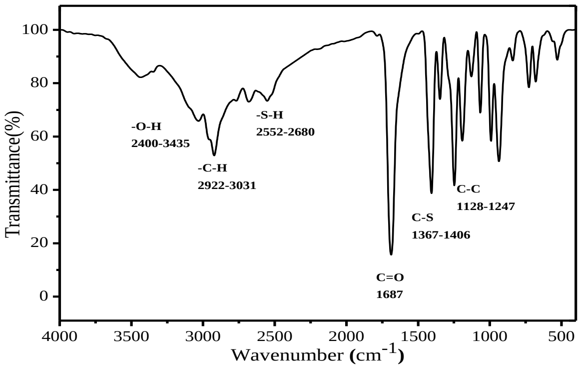


Fig. 1. The FTIR spectrum of PETS

Fig. 2. shows the ^{1}HNMR spectrum of the PETS polymer. This spectrum was taken in CDCl3 solvent. The triplet peak appearing at 2.2 ppm chemical shift is due to the protons of (a) -S- CH2- and the triplet peak at 1.5 ppm is due to the protons of (b) -CO-CH2- carbon. The peak corresponding to the -S-H proton appeared at 1.2 ppm. The peak at 7.25 ppm is related to the deuterated protons in chloroform. Due to the small number of acidic functional groups in the polymer, the probability of the appearance of the absorption peak corresponding to the acidic proton was very low and did not appear.

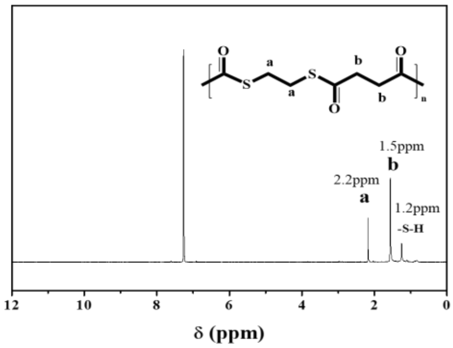


Fig. 2. 1H NMR spectrum of PETSpolymer

Differential scanning calorimetry (DSC) is a method for studying polymers in which important information about the glass transition temperature, melting point, and crystallization temperature is obtained by heating and cooling the material**.** **Fig. 3.** shows the graph of the DSC analysis of the PETS polymer. The results obtained are summarized in **Table 1**. The analysis was performed at a scan rate of 5 °C/min under a nitrogen atmosphere.

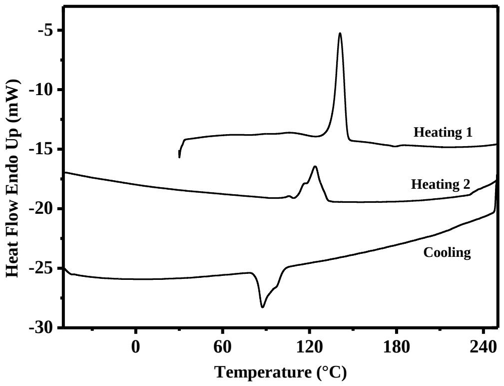


Fig. 3. DSC thermogram of PETS polymer

Table 1

Data extracted from DSC thermograms of PET DTC

T_m (°C)	Melting temperature	142
ΔH_m (J. g^{-1})	Enthalpy of melting	86
T_c (°C)	Crystallization temperature	87
ΔH_c (J. g^{-1})	Enthalpy of crystallization	-47
T_g (°C)	Glass transition temperature	88

Fig. 4. shows FE-SEM images of PETS polymer at 5 and 10 µm scales. The images show an amorphous structure and morphology without distinct particles for the polymer.

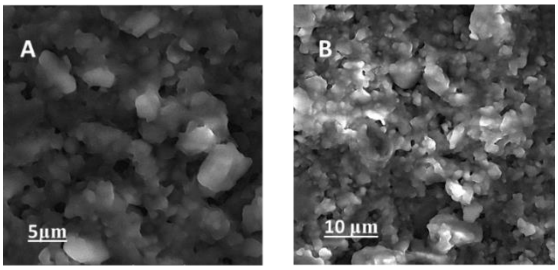
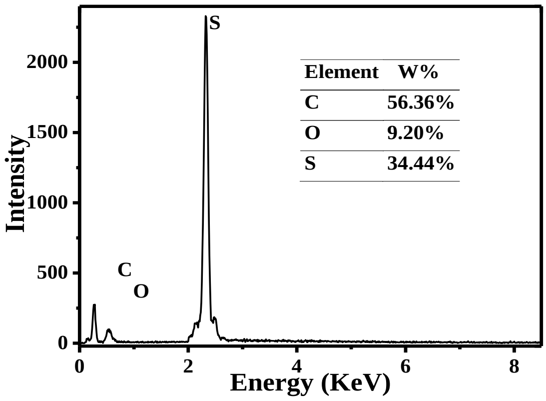


Fig. 4. FE-SEM image of PETS at the scale of 5 and 10 µm.

The EDAX spectrum of the polymer is shown in **Fig. 5**. According to the EDAX spectrum, the presence of C, O, and S atoms confirms the successful synthesis of the polymer.



Element	W%
C	56.36%
O	9.20%
S	34.44%

Fig. 5. EDAX spectrum of PETDTC

Electrochemical measurements

The electrochemical behavior of polymer nanocomposite with multiwall nanotubes at a ratio of 1:1 and the addition of 5% synthesized nickel(II)cobalt hexacyanoferrate Ni_2CoHCF [15] nanoparticles was investigated using cyclic voltammetry (CV), galvanostatic charge-discharge (GCD), and electrochemical impedance spectroscopy (EIS) techniques. Electrochemical behavior of nanocomposite in three-electrode system was used in 0.5 M sodium sulfate as electrolyte. Saturated calomel electrode (SCE) was used as reference electrode and a platinum sheet (1 cm × cm ^{2}) was used as auxiliary electrode. 10% Nafion solution in isopropanol was used as electrode material binder. Fully dispersed electrode material was coated on glassy carbon as working electrode with area of 0.1256 cm 2 in amount of 10 µl. After the solvent evaporated, electrochemical analyses were performed. **Fig. 6.** shows the CV curves of neat PETS polymer and its nanocomposite at different scan rates from 10-80 mV.s $^{-1}$. According to the curves, the current density increases with increasing scan rate and the shape of the curves does not change, indicating the good performance of these electrodes at high scan rates. The CV curve of the PETS in **Fig. 6A-6B** shows an ideal quasi-rectangular shape, which can be attributed to the non-Faradic charge storage mechanism at the interface between the electrode and the electrolyte. In the presence of Ni_2CoHCF nanoparticles (**Fig. 6B**), in addition to improving the current density, oxidation and reduction peaks related to the $Fe^{II/III}$ redox reaction appeared at a potential of near 400 mV. **Fig. 6C-6D** shows the charge-discharge curves of the electrodes at different current densities.

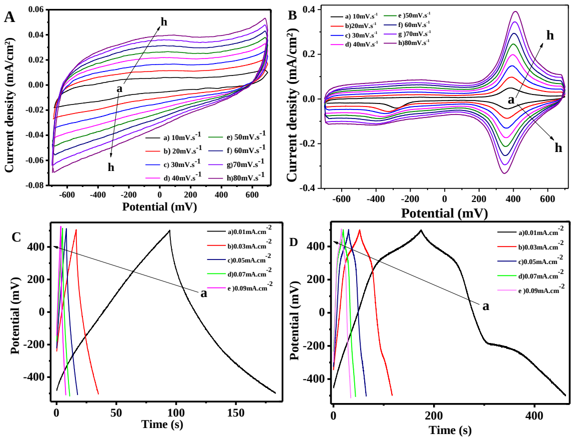


Fig. 6. CV curve of A) PETS B) PETS/MWCNT composite(1:1)+5% Ni_2CoHCF . Charge/discharge curve of D) PETS E) PETS/MWCNT composite(1:1)+5% Ni_2CoHCF .

The general shape of these graphs at different current densities confirms the good behavior of the supercapacitor material over a wide current range in sodium sulfate electrolyte. The charge-discharge curves for the PETS electrode are approximately symmetrical triangle-shaped, indicating the reversibility of the discharge process for the electrode. The nonlinear of the curve for the nanocomposite (**Fig. 6D**) is related to the Faradaic reactions of the Ni_2CoHCF nanoparticles. The long discharge time of the electrode with the nanocomposites compared to the neat polymer electrode indicates its high specific capacity, which is mainly due to the synergistic effects of the Ni_2CoHCF nanoparticles and the carbon nanotubes. Electrochemical impedance spectroscopy technique is used to study the capacitive behavior of electrodes. Charge transfer resistance (R_{ct}) is a parameter obtained by this method and its low value indicates easier charge transfer process in these electrodes. The Nyquist curves for the prepared electrodes are shown in **Fig. 7**. The equivalent circuit in **Fig. 7.** is in perfect agreement with the experimental impedance data. In this circuit, R_1, CPE1, R_2, and W1 are the solution resistance, the electric double layer constant phase element, the charge transfer resistance, and the Warburg element, respectively. The parameters of this equivalent circuit are shown in **Table 2**. According to the obtained data, the Faradaic reaction of Ni2CoHCF nanoparticles in the nanocomposite at the interface of the electrode and electrolyte increased the ionic conductivity and the amount of the CPE element increased, resulting in a decrease in the charge transfer resistance (R2).

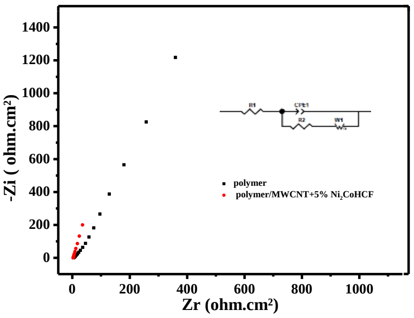


Fig. 5. Nyquist diagram of PETS and its composites as electrode material and equivalent circuit for fitting experimental impedance data of electrodes, Nyquist diagram of equivalent circuit for fitting experimental impedance data of various supercapacitor electrode made by various materials: ☐) PETS ○) PETS/MWCNT+5%Ni_2CoHCF.

Table 2
Equivalent circuit element values with experimental data of impedance diagrams obtained from **Fig. 7.**

Electrode material	**Values of equivalent circuit elements**				
	R1 **(Ω)**	**CPE-T** **($\Omega^{-1}cm^{-2}s^{CPE-P}$)**	**CPE-P**	**R2** **(Ωcm^2)**	**W-R** **($\Omega s^{-0.5}$)**
PETS	0.93	0.001056	0.70	6.98	1269
PETS/MWCNT + 5% Ni_2CoHCF	3.31	0.008426	0.89	4.62	203

4- Conclusions

poly(ethylene thiosuccinate) (PETS) was synthesized with succinic anhydride and 1,2-ethanedithiol monomers and its structure was investigated by FT-IR and ^{1}HNMR. DSC analysis show a glass transition temperature of 88 °C for the polymer. Amorphous morphology is visible based on FE-SEM images for the synthesized polymer. Electrochemical analyses showed improved behavior for the nanocomposite. Also, the Faradaic behavior in the presence of nanoparticles was observed in CV and charge /discharge curves. The charge transfer resistance for the nanocomposite was lower than that of the neat polymer due to the synergistic effect of carbon nanotubes and nanoparticles.

Acknowledgement

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References

[1] Marlier, John F., Emily J. Fogle, Richard L. Redman, Anthony D. Stillman, Matthew A. Denison, and Lori I. Robins, A mechanistic study of thioester hydrolysis with heavy atom kinetic isotope effects. The Journal of organic chemistry, 2015. 80(3): p. 1905-1908.

[2] Yang, W. and D.G. Drueckhammer, Understanding the relative acyl-transfer reactivity of oxoesters and thioesters: computational analysis of transition state delocalization effects. Journal of the American Chemical Society, 2001. 123(44): p. 11004-11009.

[3] Koval', I., Synthesis, structure, and physicochemical characteristics of thiols. Russian journal of organic chemistry, 2005. 41: p. 631-648.

[4] Yue, Tian-Jun, Ming-Chao Zhang, Ge-Ge Gu, Li-Yang Wang, Wei-Min Ren, and Xiao-Bing Lu, Precise synthesis of poly (thioester) s with diverse structures by copolymerization of cyclic thioanhydrides and episulfides mediated by organic ammonium salts. Angewandte Chemie, 2019. 131(2): p. 628-633.

[5] Andree Ben, C. and A. Steinbüchel, Recent developments in non-biodegradable biopolymers: Precursors, production processes, and future perspectives. Applied microbiology and biotechnology, 2019. 103(1): p. 143-157.

[6] You, Nam-Ho, Tomoya Higashihara, Suzuki Yasuo, Shinji Ando, and Mitsuru Ueda, Synthesis of sulfur-containing poly (thioester) s with high refractive indices and high Abbe numbers. Polymer Chemistry, 2010. 1(4): p. 480-484.

[7] Kameyama, A., Y. Kimura, and T. Nishikubo, New synthesis of poly (S-thioester) s by regioselective addition reaction of bis (thiirane) s with diacyl chlorides using quaternary onium salts. Macromolecules, 1997. 30(21): p. 6494-6497.

[8] Ura, Yasuyuki, Mohammad Al-Sayah, Javier Montenegro, John M. Beierle, Luke J. Leman, and M. Reza Ghadiri, Dynamic polythioesters via ring-opening polymerization of 1,4-thiazine-2,5-diones. Organic & biomolecular chemistry, 2009. 7(14): p. 2878-2884.

[9] Suzuki, M., K. Makimura, and S. i. Matsuoka, Thiol-Mediated Controlled Ring-Opening Polymerization of Cysteine-Derived β-Thiolactone and Unique Features of Product Polythioester. Biomacromolecules, 2016. 17(3): p. 1135-1141.

[10] Iwata, S., K. Toshima, and S. Matsumura, Enzyme-catalyzed preparation of aliphatic polyesters containing thioester linkages. Macromolecular rapid communications, 2003. 24(7): p. 467-471.

[11] Lütke-Eversloh, Tina, Andreas Fischer, Uwe Remminghorst, Jumpei Kawada, Robert H. Marchessault, Ansgar Bögershausen, Martin Kalwei, Biosynthesis of novel thermoplastic polythioesters by engineered Escherichia coli. Nature materials, 2002. 1(4): p. 236-240.

[12] Kultys, A., Sulfur‐Containing Polymers. Encyclopedia of polymer science and technology, 2002.

[13] Overberger, C.G. and J.K. Weise, Anionic ring-opening polymerization of thiolactones. Journal of the American Chemical Society, 1968. 90(13): p. 3533-3537.

[14] Purohit, Vishal, Marlena Pieta, Joanna Pietrasik, and Christopher Plummer, Recent advances in the ring-opening polymerization of sulfur-containing monomers. Polymer Chemistry, 2022.

[15] Qiu, Y., Lin, Y., Yang, H., & Wang, L., Ni-doped cobalt hexacyanoferrate microcubes as battery-type electrodes for aqueous electrolyte-based electrochemical supercapacitors. Journal of Alloys and Compounds, 2019. 806: p. 1315-1322.