Synthesis and characterization a novel polythiourethanes as candidate materials for supercapacitor applications

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Abstract

Sulfur-containing polymers are interesting materials for the next generation of functional materials. These polymers are mainly composed of aliphatic and aromatic copolymers with various functional groups such as phenyl, amine, and N-heterocycles. Polythiourethanes are polymers that contain sulfur and have not been extensively researched regarding their synthesis and applications. The use of various dithiols and diisocyanates is a common method for synthesizing these polymers in theory. In practical, there are certain limitations for synthesis, including the type of catalyst used, the catalyst's percentage, the suitable solubility of the isocyanate monomer, and the low efficiency of the reaction, which pose challenges in the synthesis of polythiourethanes. In this study, a new polythiourethane was synthesized using toluene diisocyanate and 1,2-ethane dithiol. FT-IR, ^{1}HNMR and EDAX analyses were used to confirm the synthesis. The melting point and glass transition temperature for the polymer were obtained 135 and 120 °C, respectively.The FE-SEM images revealed a sheet-like structure for the polymer. The supercapacitive behavior of the neat polymer and its nanocomposites will be investigated by electrochemical analyses of cyclic voltammetry (CV), charge/discharge (GCD) and electrochemical impedance (EIS).

1.Introduction

The incorporation of heteroatoms (such as S and N) into closed polymer structures, as functional groups, can give these materials special properties. These characteristics encompass enhanced thermal and mechanical properties, resulting in greater thermal stability of the polymer [1-3], improved metal adsorption capacity [4-6], self-healing or reprocessing abilities [86-91], as well as crystalline and optical attributes [7-8]. Polythiourethanes are widely recognized heteroatom-containing polymers characterized by the presence of sulfur (S) and nitrogen (N) atoms within their structure. In contrast to their oxygen analogues, polyurethanes, comprehensive research on the synthesis of polythiourethanes remains limited [9-10]. Polythiourethanes are used in optical materials, coatings, and medical technology due to their improved properties such as refractive index, adhesion strength, biocompatibility, and mechanical properties [9-11]. The facile addition of thiols to isocyanates for the synthesis of the thiourethane functional group was reported in 1960 by Dyer and co-workers [12] to produce alkyl thiourethane without side products. The efficiency and absence of by-products have been confirmed for both syntheses of small thiourethane and polythiurethane molecules [13-14]. The kinetics of the base-catalyzed reaction involving primary and secondary thiols with phenyl isocyanate suggest a rapid reaction, whereas the rate is significantly slower in the case of non-aromatic isocyanates. Despite the much higher efficiency of thiol-isocyanate reactions using mild catalysts at low concentrations compared to alcohol-isocyanate reactions, chemists' interest was minimal for almost half a century. Since the late 1980s, the use of amines as catalysts has led to the synthesis of a wide range of polythiourethanes by the reaction of dithiols and diisocyanates for applications as high-refractive index materials. This approach has continued to expand due to the successful industrial and commercial applications that have emerged for optical materials based on polythiourethane [15-16].

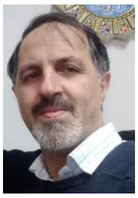
In this research, poly(ethylene 2,4-toluene dithiocarbamate) (PETDTC) was synthesized as a sulfur-containing polymer and its structure was investigated by various methods such as FT-IR and ^{1}HNMR and thermal analysis of the polymer by differential scanning calorimetry (DSC). The morphology of the synthesized polymer was investigated by FE-SEM images.

2.1 Materials Toluene diisocyanate, 1,2-ethanedithiol, triethylamine and acetone were purchased from Merck and used without any further purification.

2.2- . Preparation of poly(ethylene 2,4-toluene dithiocarbamate)(PETDTC)

To synthesize polythiourethane, toluene diisocyanate was stirred in acetone solvent until a clear solution was obtained. Then, the second monomer, ethane dithiol, was added to the solution in a molar ratio of 1 to 1 with the initial monomer. In this reaction, triethylamine was used as a catalyst. The reaction mixture was placed under argon gas for an appropriate time and under stirring conditions until the reaction was complete. The obtained precipitate was dried in a vacuum after washing several times at 60 ° C. The reaction yield was 54%.

3- Results and Discussions



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PETDTC identification was done by FT-IR, ^{1}HNMR and DSC analysis. **Fig. 1** shows FT-IR analysis. The absorption band associated with the stretching vibrations of the aromatic -C-H bonds in the ring and the –N-H bond of the amide group appeared at 3070 and 3274 cm^{-1}, respectively, while the stretching vibrations of the aliphatic -C-H bonds were observed in the range of 2927-2954 cm^{-1}.The peaks associated with the stretching vibrations of the carbonyl group are noted at 1711 and 1643 cm^{-1}, respectively. The absorption bands resulting from the stretching vibrations of the -C=C- bonds related to the aromatic ring are found at 1598 and 1448 cm^{-1}, along with the bending vibration of the -N-H bonds at 1547 cm^{-1}. The peak corresponding to the stretching vibrations of the -S-H bond is detected in 2532 cm^{-1}. The peak observed at 1417 cm^{-1} is attributed to the -C-S- in the -S-CH2- group, while the absorption peak for the stretching vibrations of the -C-C- bond can be seen at 1218 cm^{-1}.

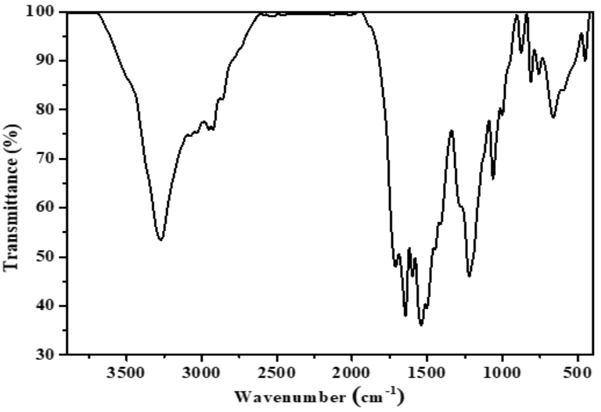


Fig. 1. The FTIR spectrum of PETDTC

According to the ^{1}HNMR spectrum in **Fig. 2.**, the peaks corresponding to the -S-H and -S-CH2- protons (f and e) appeared at 1.65 ppm, 2.89 ppm, and 2.96 ppm, respectively.

The peaks corresponding to the protons of the aromatic ring and the peak of the protons of the methyl group of the ring are visible at 7.26 ppm, 8.02 ppm, 6.91 ppm and 2.17 ppm, respectively. The proton of the amide group appears at 3.53 ppm. This spectrum was taken in CDCl3 solvent.

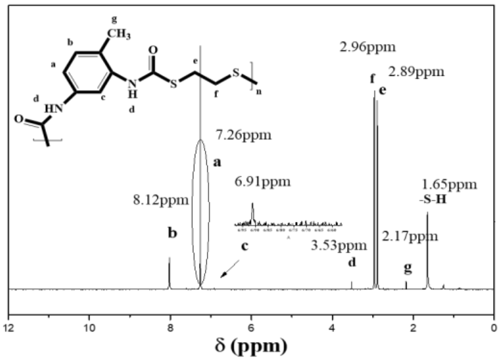


Fig. 2. 1H NMR spectrum of PETBTC polymer

The peaks corresponding to the protons of the aromatic ring and the peak of the protons of the methyl group of the ring are visible at 7.26 ppm, 8.02 ppm, 6.91 ppm and 2.17 ppm, respectively. The proton of the amide group appears at 3.53 ppm.

Fig. 3. illustrates the DSC analysis of PETDTC. The findings from this analysis are compiled in **Table 1**. The analysis was conducted at a scanning rate of 5 °C/min in a nitrogen environment.

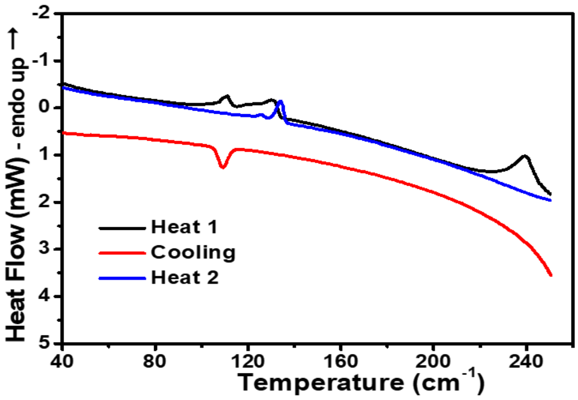


Fig. 3. DSC thermogram of PETDTC polymer

Table 1

Data extracted from DSC thermograms of PET DTC

T_m (°C)	Melting temperature	135
ΔH_m (J. g^{-1})	Enthalpy of melting	19.09
T_c (°C)	Crystallization temperature	100
ΔH_c (J. g^{-1})	Enthalpy of crystallization	-25.71
T_g (°C)	Glass transition temperature	120

According to the FE-SEM image (**Fig. 4**) at a scale of 1, 2 and 5 μm, the pristine PETDTC displays a nearly sheet-like configuration that is interconnected and shows a certain level of porosity.

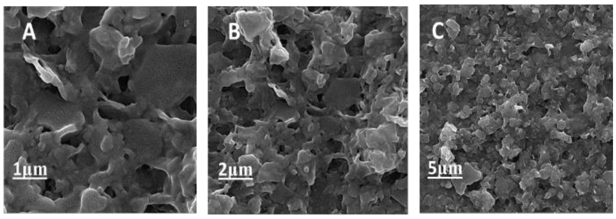
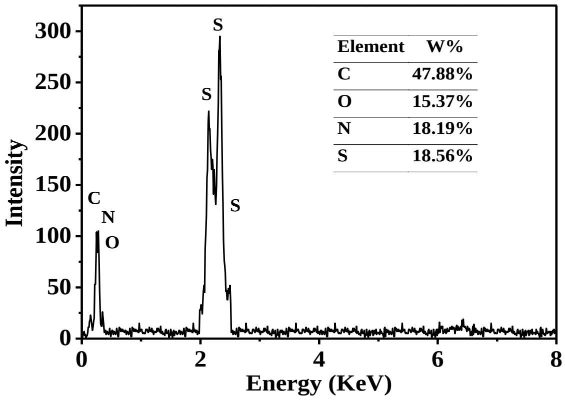


Fig. 4. FE-SEM image of PETDTC at the scale of 1, 2 and 5 μm.

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



Element	W%
C	47.88%
O	15.37%
N	18.19%
S	18.56%

Fig. 5. EDAX spectrum of PETDTC

Electrochemical measurements

To prepare the sample for studying the supercapacitive behavior, first pure polythiourethane is completely dispersed in DMF solvent. Then, 6µl were placed on a glassy carbon electrode with a surface area of 0.1256 cm^2 as the working electrode. After evaporation of the solvent, their electrochemical behavior was carried out by cyclic voltammetry, charge/discharge and electrochemical impedance spectroscopy techniques in 0.5 M aqueous sodium sulfate electrolyte in a three-electrode system with a calomel electrode as the reference electrode and a 2*1cm^2 platinum sheet electrode as the auxiliary electrode. In the next step, Polymer nanocomposite was prepared with multi-walled carbon nanotubes in a ratio of 1 to 0.5 and the addition of 3% nickel cobalt hexacyanoferrate Ni_2CoHCF synthesized [17] nanoparticles and electrochemical analyses were performed under the same conditions as before.

Fig. 6A-6B. shows the CV curve of pure PETDTC.The quasi-rectangular shape of the graph shows the non-Faradic behavior of the electrode. In the presence of Ni_2CoHCF nanoparticles (**Fig. 6B**), the shape of the graphs of these electrodes is outside the ideal rectangular shape, and the oxidation and reduction peaks that appear are related to the $Fe^{II/III}$ redox reaction, which appears at a potential of 400 mV. The change in the shape of the graphs from rectangular indicates the Faradaic behavior of the electrodes. The charge and discharge diagrams are shown in **Fig. 6C-6D.** The shape of the curve for the neat polymer **Fig. 6C** is a symmetrical triangle, indicating the reversibility of the charging and discharging process.

For the electrodes containing nanoparticles (**Fig. 6D**), the shape of the curves is non-linear and due to the Faradaic behavior of Ni_2CoHCF, the curves do not follow the ideal linearity. The synergistic effect and interaction between the constituent materials creates a proper connection between the electrolyte ions and the electrode, increasing the charge and discharge time of PETDTC/MWCNT+3%Ni_2CoHCF composite. Electrochemical impedance spectroscopy (EIS) has been used to further investigate the electrodes. A critical factor influencing the analysis of electrode behavior, which can be investigated using electrochemical impedance spectroscopy, is the charge transfer resistance (R_{ct}). The Nyquist plots of the electrodes are shown in **Fig. 7** .

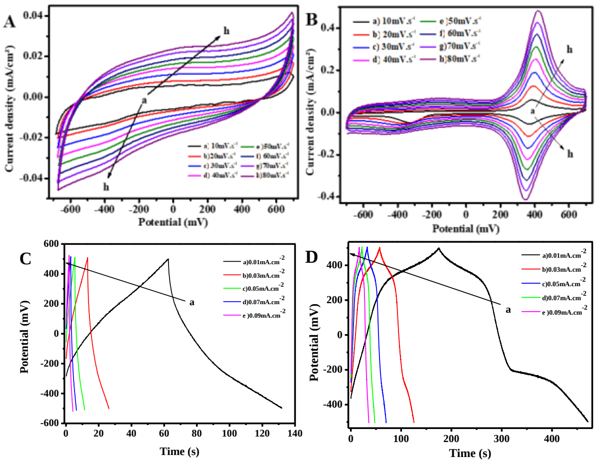


Fig. 6. CV curve of A) PETDTC B) PETDTC/MWCNT composite(1:0.5)+3% Ni_2CoHCF . Charge/discharge curve of C) PETDTC D) PETDTC/MWCNT composite(1:0.5)+3% Ni_2CoHCF .

The equivalent circuit in Figure where R1, CPE1, R2, and W1 are the solution resistance, the electric double layer constant phase element, the charge transfer resistance, and the Warburg element, respectively, aligns closely with the experimental data. In **Table 2** as the data show , the electrodes containing Ni_2CoHCF nanoparticles have much lower charge transfer resistance and the charge transfer resistance for these electrodes is also significantly lower than that of pure PETDTC. The low charge transfer and mass transfer resistance of these nanocomposites is due to the faradaic processes of the nanoparticles and the synergistic effect of the nanoparticles with MWCNT, which leads to increased ionic conductivity and CPE.

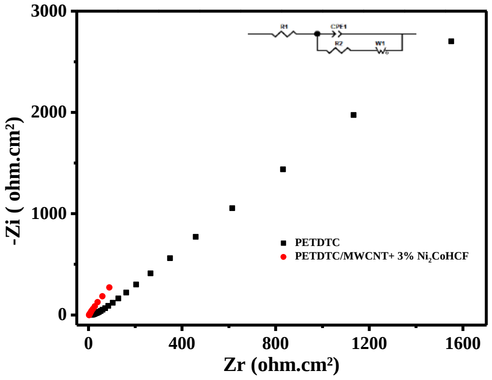


Fig. 7. Nyquist diagram of PETDTC and its composites as electrode material and equivalent circuit for fitting experimental impedance data of electrodes, Nyquist diagram of equivalent circuit for fitting experimental impedance data of various supercapacitor electrode made by various materials: ☐) PETDTC ○) PETDTC/MWCNT+3%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** **($\Omega s^{-0.5}$)**
PETDTC	13.92	0.0004117	0.57	16.15	1577
PETDTC/MWCNT + 3% Ni_2CoHCF	4.11	0.0002199	0.93	3.62	72.36

4- Conclusions

In this work, poly(ethylene 2,4-toluene dithiocarbamate) was synthesized. Polymer identification was investigated by FT-IR and ^{1}HNMR. Based on the DSC analysis of polymer melting points was 135 °C. Also, the morphology of the polymer showed a sheet-like structure. The quasi-rectangular shape of the CV diagram and the symmetrical triangular shape in the charge-discharge analysis show non-Fardaic behavior for this polymer as an electrode. The use of Ni_2CoHCF cubic nanoparticles to prepare nanocomposites has changed the behavior of supercapacitor to Faradaic, and the morphology of these nanoparticles has caused the rapid migration of ions and increased the ionic conductivity.

Acknowledgement

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