

# Modified Solution Technique for Preparing Poly(3,4-ethylenedioxythiophene) and a Poly(3,4-ethylenedioxythiophene)/Silver Nanocomposite: Optical and Thermal Behavior

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**ABSTRACT:** In this study, we prepared poly(3,4-ethylenedioxythiophene) (PEDOT) via the chemical oxidation of the 3,4-ethylenedioxythiophene monomer in a system consisting of miscible binary organic solvents, that is, acetonitrile ( $\text{CH}_3\text{CN}$ ) and chloroform ( $\text{CHCl}_3$ ). This successful technique was then used to synthesize a poly(3,4-ethylenedioxythiophene) (PEDOT)/silver (Ag) nanocomposite as well. In this facile and efficient technique, a higher solubility of the oxidizing reagent, which originated from a relative enhancement in the polarity of the reaction medium, led to significant changes in the optical and thermal behaviors of the resulting products. To investigate the degree of validity of the technique applied, a pure sample of PEDOT (PEDOT I) was also synthesized with  $\text{CHCl}_3$  alone, and this was then compared with a sample prepared in  $\text{CH}_3\text{CN}/\text{CHCl}_3$  binary solvents (PEDOT II). To prepare the PEDOT/Ag nanocomposite, first the PEDOT synthesized in binary solvents was thoroughly dissolved in a dimethyl sulfoxide solvent. Next, Ag nanopowder was uniformly dispersed in the previous solution of PEDOT with sonication. The PEDOT/Ag nanocomposite was then precipitated through the addition of a methanol nonsolvent. The approximate size of nano-Ag within the polymer matrix was found to be about 40 nm. Scanning electron microscopy images of the pure PEDOT II and PEDOT/Ag nanocomposite exhibited an agglomerated sponge and nanospherical homogeneity, respectively. In comparison with PEDOT I, considerable redshifts in the ultraviolet–visible absorption spectra of the pure PEDOT II and PEDOT/Ag nanocomposite were observed. In addition, the thermostability order was found to be PEDOT/Ag > PEDOT II > PEDOT I at all temperatures above 300°C. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2013

**KEYWORDS:** conducting polymers; optical properties; thermogravimetric analysis (TGA)

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## INTRODUCTION

Recently, considerable attention has been devoted to the preparation of polymer-based nanocomposites because of their potential applications in electrocatalysis, chemical sensors, electrochemical capacitors, and protective coatings against corrosion.<sup>1–3</sup> Nanocomposites of inherently conducting polymers (ICPs) and metal nanoparticles are one of the most important classes of these advanced materials.<sup>4,5</sup> Various methods for the preparation of these composites have been described, including the electrochemical deposition of nanoparticles onto electrodes previously coated with an ICP, photochemical preparation, the reduction of metal salts dissolved in a polymer matrix, the polymerization of the ICP around nanoparticles, and the mixing of nanoparticles into a polymer matrix.<sup>6</sup>

It is well known that silver ions and silver-based compounds are highly toxic to microorganisms and show strong biocidal effects on as many as 16 species of bacteria, including *Escherichia*

*coli*.<sup>7–9</sup> Moreover, because metallic silver exhibits the highest electrical and thermal conductivities among all of the metals, the combination of a conducting polymer with silver seems to be the best switch for preparing an important electroactive and thermostable composite.<sup>10–14</sup> On the other hand, PEDOT is one of the most successful conducting polymers because of its excellent environmental stability, high conductivity, and transparency in thin oxidized films.<sup>15–19</sup> Since PEDOT was first synthesized in the early 1990s by Heywnag and Jonas,<sup>20</sup> many studies on PEDOT have been done to modify its optical, thermal, and morphological properties and to extend its application fields.<sup>21</sup> This polymer can be prepared by either electrochemical or chemical methods. The chemical oxidative method is generally tunable and can lead to a more processable product compared with the electrochemical method. Among the many chemical methods available, oxidative polymerization with iron(III) chloride ( $\text{FeCl}_3$ ) as an oxidant is a simple and convenient route.<sup>22</sup> Among all of the conventional polymerization techniques, the

solution technique provides a facile route for attaining a polymeric material on a laboratory scale.<sup>23</sup> In the field of chemical oxidative polymerization in some cases, however, this technique is discomfited by the inadequate solubility of the oxidant in the reaction organic solvent. Herein, we focus on the application of this technique in the preparation of an ICP. Our solvents, which can be generally used to prepare polythiophene and its derivatives, are chloroform ( $\text{CHCl}_3$ ) and dichloromethane ( $\text{CH}_2\text{Cl}_2$ ). None of these solvents can dissolve the inorganic salt  $\text{FeCl}_3$  adequately. To overcome this problem, the idea of using binary miscible solvents might be efficient. In 2010, this idea was applied by Jeon et al.<sup>24</sup> for the first time to synthesize polythiophene itself. The product they prepared showed some better characteristics relative to that prepared conventionally. It seems that the idea of binary miscible solvents can be generalized to other cases, such as those in the field of nanocomposites. In this case, a more polar solvent than  $\text{CHCl}_3$  or  $\text{CH}_2\text{Cl}_2$  needs to be used because it must dissolve the reaction oxidant further. To attain this, acetonitrile ( $\text{CH}_3\text{CN}$ ) might be a good choice because of its miscibility with both  $\text{CHCl}_3$  and  $\text{CH}_2\text{Cl}_2$ .

This article deals with the preparation of a PEDOT/Ag nanocomposite by the trapping of nanosized silver particles from their presupplied dimethyl sulfoxide (DMSO)-based nanofluid into coiling PEDOT macromolecules during precipitation from the DMSO solution. The PEDOT polymer used to prepare the final nanocomposite (PEDOT II) was synthesized by a chemical oxidative method through a facile modified solution technique, that is, with binary miscible solvents. To compare the results, a reference sample of PEDOT (PEDOT I) was also prepared similarly by a conventional procedure. Both the pure PEDOT samples and the PEDOT/Ag nanocomposite were fully characterized with Fourier transform infrared (FTIR) spectroscopy, ultraviolet–visible (UV–vis) spectroscopy, X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and thermogravimetric analysis (TGA).

## EXPERIMENTAL

### Materials

3,4-Ethylenedioxythiophene (EDOT) monomer ( $\geq 98\%$ ) was purchased from Aldrich and was used without further purification. All other materials, including reagents and solvents, were purchased from Merck Chemical Co. Sodium borohydride ( $\text{NaBH}_4$ ), DMSO, and silver nitrate ( $\text{AgNO}_3$ ) were used without further purification. Silver nanopowder, with a mean size of less than 20 nm, was prepared according to a procedure from the literature.<sup>25</sup> Acetonitrile was dried by distillation in the presence of calcium hydride ( $\text{CaH}_2$ ) under reduced pressure. Chloroform was distilled after it was dried by calcium chloride ( $\text{CaCl}_2$ ) and was then stored in dark before use. Anhydrous iron(III) chloride (97%) was used as received. All of the aqueous solutions were prepared with distilled, deionized water.

### Measurements

The FTIR spectra of the samples were recorded on a PerkinElmer RX I FTIR spectrometer. The spectra of the solids were obtained with KBr pellets. UV–vis spectra were taken with a PerkinElmer PTP-1 Peltier System Lambda 25 UV–vis spectrometer. Wide-angle XRD patterns were performed at room

temperature with film specimens on a Bruker Advance D5 X-ray diffractometer with Ni-filtered  $\text{Cu/K}\alpha$  radiation (30 kV and 25 mA). The morphologies of the samples were determined with a Zeiss DSM 960A scanning electron microscope and a Philips CM10-HT 100 kV transmission electron microscope. TGA was performed on a Mettler TA 5000 system under  $\text{N}_2$  at a heating rate of  $15^\circ\text{C}/\text{min}$ .

### Synthesis of PEDOT I and PEDOT II

To synthesize PEDOT I, a 250-mL, round-bottom flask equipped with magnetic bar was charged with  $\text{CHCl}_3$  solvent (70 mL) and EDOT monomer (1 mL, 10 mmol). A solution of  $\text{FeCl}_3$  oxidant (3.244 g, 20 mmol) in the same solvent (40 mL) was slowly added to the reaction flask for 20 min with stirring. The mixture was stirred for another 24 h at  $0^\circ\text{C}$ . The dark green precipitate was filtered at reduced pressure and washed several times with chloroform, deionized water, and acetone, and it was finally dried at  $60^\circ\text{C}$  in a vacuum oven for 24 h. To prepare PEDOT II, a modified solution technique similar to the aforementioned procedure was used, except herein, the  $\text{FeCl}_3$  oxidant (12.165 g, 75 mmol) was dissolved in  $\text{CH}_3\text{CN}$  (40 mL) as the second solvent, which was fully miscible with  $\text{CHCl}_3$ .

### Synthesis of the PEDOT/Ag Nanocomposite

First, PEDOT II (0.300 g) was completely dissolved in DMSO solvent by magnetic stirring (120 mL) at  $25^\circ\text{C}$ . The presynthesized silver nanopowder, with a mean size of below 20 nm (0.300 g), was then added to the solution, and we tried to homogenize it well by sonication in an ultrasonic bath for 1 h ( $3 \times 20$  min). This resulted in a stabilized and homogeneous DMSO-based nanofluid of Ag containing the PEDOT polymer. No precipitate appeared after 5 h when the nanofluid was in a static state. Next, the nonsolvent methanol (200 mL) was added in one portion to the stirring nanofluid to precipitate the PEDOT/Ag nanocomposite. The obtained product was then filtered, washed with methanol and acetone, and dried at  $60^\circ\text{C}$  in a vacuum oven for 24 h.

## RESULTS AND DISCUSSION

### Characteristics of the Resulting Polymers

It has been demonstrated that some variable parameters, such as the reaction temperature, type of the solvent used, and molar ratio of the oxidant to the monomer, highly affect the characteristics of the obtained polymer, particularly its morphology and conductivity.<sup>24</sup> Herein, PEDOT I was synthesized conventionally by a solution technique with  $\text{FeCl}_3$  as the reaction oxidant and  $\text{CHCl}_3$  as the solvent. Once the drops of the oxidant solution were poured into the reaction vessel, a deep green color appeared. In this unmodified solution technique, because of the low solubility of the oxidant used in  $\text{CHCl}_3$ , we reached a molar ratio of only 2 of the oxidant to the monomer. To synthesize PEDOT II, however, we tried to modify this drawback by using a second solvent with more polarity relative to  $\text{CHCl}_3$  so that it could dissolve the  $\text{FeCl}_3$  oxidant further. To attain this goal,  $\text{CH}_3\text{CN}$  solvent seemed to be a good choice; it could dissolve the  $\text{FeCl}_3$  oxidant up to a fivefold molar ratio compared with the EDOT monomer. PEDOT II prepared by this binary system as a modified solution technique was then used for the preparation of the PEDOT/Ag nanocomposite. It should be noted that

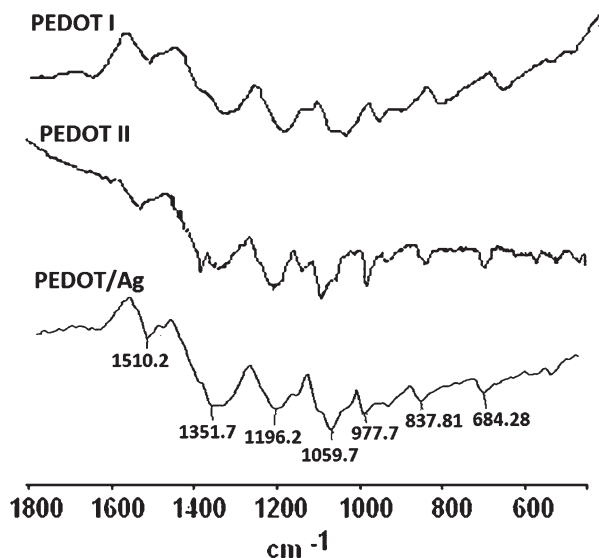


Figure 1. FTIR spectra of PEDOT I, PEDOT II, and PEDOT/Ag.

an *in situ* preparation of this nanocomposite by an on-site oxidative polymerization in a medium consisting presynthesized Ag nanopowder was not possible because of the oxidation of Ag to AgCl by the FeCl<sub>3</sub> oxidant present in the medium. In this case, however, homogeneously dispersed nano-Ag in a solution of previously prepared PEDOT in DMSO solvent could be trapped within the macromolecules once they coiled during precipitation process; this occurred by the addition of the CH<sub>3</sub>OH nonsolvent to the mixture. Eventually, PEDOT I, PEDOT II, and PEDOT/Ag were fully characterized by FTIR spectroscopy and XRD analyses.

Figure 1 shows the FTIR spectra of PEDOT I (top), PEDOT II (middle), and PEDOT/Ag (bottom). As shown, no significant difference was observed in the spectra of the pure PEDOT samples and Ag-incorporated nanocomposite; this indicated that the polymer-embedded Ag nanoparticles did not create remarkable changes in the bond vibrations. A strong band related to the C–H bending mode, which always appeared at about 890 cm<sup>-1</sup> in the monomer IR spectrum,<sup>6</sup> disappeared here in all of the spectra; this demonstrated the formation of PEDOT chains with  $\alpha,\alpha'$ -coupling. Vibrations at 1352 and 1510 cm<sup>-1</sup> were attributed to the stretching modes of C–C and C=C in the thiophene ring. The vibration modes of the C–S bond in the thiophene ring were observed at 684, 838, and 978 cm<sup>-1</sup>. The bands at about 1120 and 1200 and cm<sup>-1</sup> were assigned to the stretching modes of the ethylenedioxy group, and the band around 920 cm<sup>-1</sup> was due to the ethylenedioxy ring deformation mode.

Figure 2 displays the XRD pattern of the pure PEDOT I and PEDOT II samples along with that of the Ag-incorporated PEDOT nanocomposite. In addition, to compare the results, the diffraction pattern of the nano-Ag itself is also depicted. As expected for a pure sample of PEDOT, the pattern did not yield any characteristic peaks, except that which appeared at  $2\theta \approx 25^\circ$ , which indicated the amorphous nature of PEDOT.<sup>26</sup> As the

diffraction patterns were the same for both pure samples. The PEDOT/Ag nanocomposite, however, showed diffraction features appearing at  $2\theta$  values of 38.1, 44.4, 64.5, 77.5, and 81.6°; these corresponded to the (111), (200), (220), (311), and (222) planes, respectively, of the standard cubic phase of silver.<sup>27</sup> It has been demonstrated that when silver ions play the role of the polymerization oxidant, the amount of the nano-Ag deposited into the polymer matrix should be generally high.<sup>28</sup> In our study, however, silver ions were not the polymerization oxidant; consequently, the amount of deposition was not so high, and this was confirmed by TEM analysis, as discussed in the following section. This low incorporation could result in a significant similarity between the diffraction features of the PEDOT/Ag nanocomposite and that of the Ag nanopowder. Nevertheless, unlike in the diffractogram of the Ag nanopowder, the characteristic wide peak of PEDOT appearing at about 27° was clearly detectable. Moreover, for the PEDOT/Ag nanocomposite, the approximate mean size of Ag nanoparticles estimated by the Scherrer equation was found to be about 40 nm. Therefore, the mean size of Ag nanoparticles after their incorporation into the PEDOT matrix grew up to 40 nm compared with the initial mean size. This size growth arose from the particle aggregation phenomenon occurring during the polymerization reaction.

Because the morphologies of a polymeric sample are generally dependent on the synthesis technique and sample composition, we thought that the samples should also be characterized by their SEM and TEM analyses. Although no obvious difference was seen between the micrographs of PEDOT I and PEDOT II, the images of the pure PEDOT II and PEDOT/Ag nanocomposite were clearly different from each other. Figure 3 (left and middle) shows the scanning electron micrographs of these samples. The micrograph of pure PEDOT II exhibited an agglomerated sponge, and here, a rough morphology could be observed. For the PEDOT/Ag nanocomposite, however, the micrograph showed a clearly nanospherical homogeneity. The SEM results

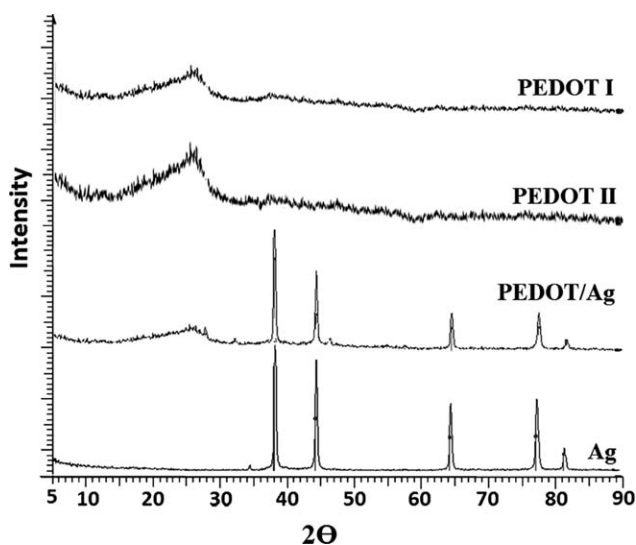
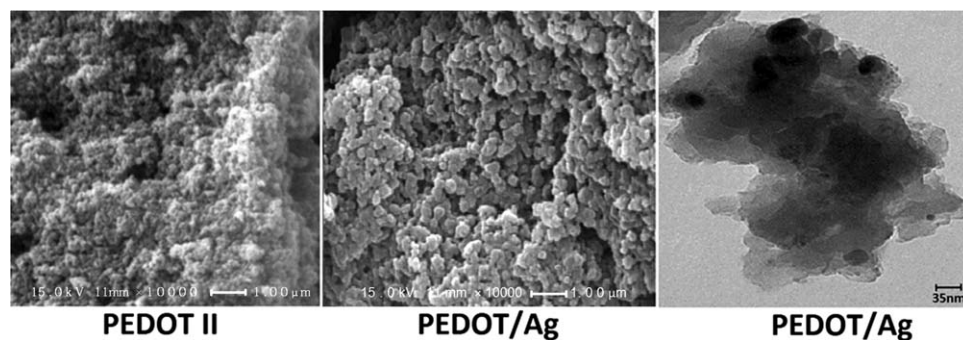


Figure 2. XRD patterns of PEDOT I, PEDOT II, PEDOT/Ag, and the used nano-Ag.



**Figure 3.** SEM micrographs of PEDOT II (left) and PEDOT/Ag (middle) along with a TEM image of PEDOT/Ag (right).

show the presence of agglomerated nanospheres with an average diameter of about 200 nm. Nevertheless, the accurate sizes and morphology of the nanoparticles could be estimated from the TEM analysis. Although the SEM images provided the surface morphology, the TEM images revealed the internal structure and a more accurate measurement of the particle size and morphology. Figure 3 (right) clearly shows that the silver nanosized particles (displayed as dark spheres) were successfully embedded into the polymeric matrix. Meanwhile, we concluded that approximate size of the nanospheres appearing in the TEM micrograph was in agreement with that found from the XRD measurements.

#### Optical Behavior

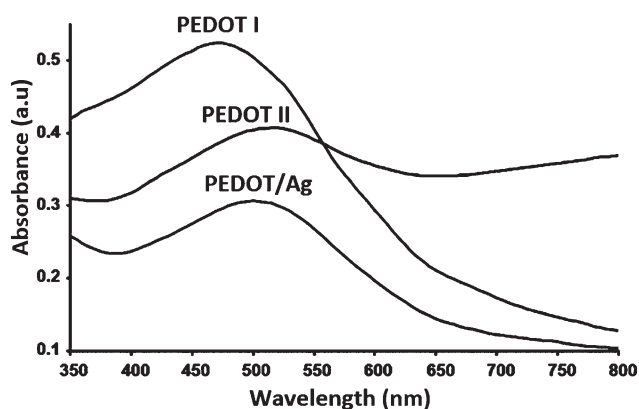
The near UV–vis absorption spectra of the resulting samples are presented in Figure 4. In all of the spectra, the absorption maximum located at about 500 nm was characteristic of PEDOT and was associated with the  $\pi \rightarrow \pi^*$  transition.<sup>29–31</sup> For the pure PEDOT prepared through a conventional solution technique (PEDOT I), this broad band was centered around 470 nm. However, it was redshifted somewhat for the other two samples involving the pure PEDOT II and PEDOT/Ag nanocomposite and appeared at about 520 and 500 nm, respectively. These significant redshifts observed in the absorption spectra of PEDOT II and PEDOT/Ag should have been related to the change in the technique used and the presence of nano-Ag particles within the polymer matrix; among these two influencing factors, the former was efficient for PEDOT II, and both of them were efficient for the PEDOT/Ag nanocomposite. In addition to the previous peak, a weaker and wider band beyond 700 nm was also evident in the absorption spectrum of PEDOT II. As stated elsewhere, this band usually appears because of the bipolaron sub-gap transition in expanded coil conjugated macromolecules.<sup>30</sup> For PEDOT II, which was technically prepared in a medium possessing an excess amount of  $\text{Cl}^-$ , this band could have originated from the polarons and bipolarons because of the partial doping of PEDOT by  $\text{Cl}^-$  during the polymerization process. However, for pure PEDOT I, prepared in  $\text{CHCl}_3$  alone, and for the PEDOT/Ag nanocomposite, no peak appeared in the region of 700–800 nm.

Although like PEDOT II, the PEDOT/Ag nanocomposite was also prepared with  $\text{CHCl}_3/\text{CH}_3\text{CN}$  binary solvents, the effect of the excess chloride ions was compensated for by the interaction

of polymer-embedded  $\text{Ag}_{\text{nano}}$  grains with the macromolecular chains. This interaction prevented the chains from becoming more positively charged bipolaron units. Accordingly, in the absorption spectra of both the pure PEDOT I and PEDOT/Ag nanocomposite, no peak related to polaron-to-bipolaron transition was observed. Furthermore, the absorption peak appearing below 400 nm in the spectrum of the PEDOT/Ag nanocomposite was attributed to the surface plasmon band of silver nanoparticles.

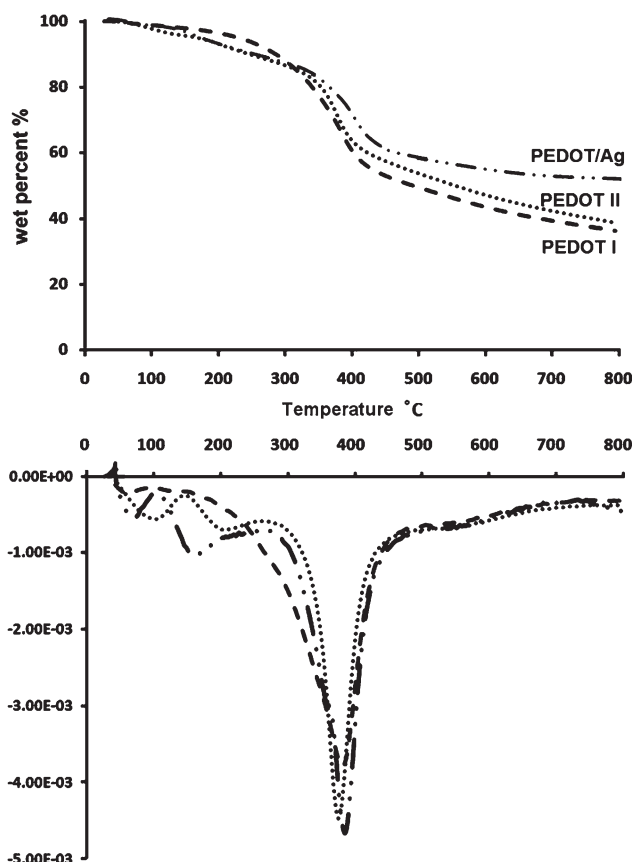
#### Thermostability

As an important dynamic method to detect the degradation behavior of the synthesized samples, TGA was carried out under a nitrogen atmosphere. The TGA/differential thermogravimetry (DTG) thermograms of the conventionally prepared pure PEDOT (PEDOT I), pure PEDOT prepared in binary organic solvents (PEDOT II), and Ag-incorporated PEDOT nanocomposite (PEDOT/Ag) are presented in Figure 5. A distinct three-step thermal decomposition was observed for both pure samples and the PEDOT/Ag nanocomposite, in which the main decomposition for these samples prepared in binary miscible solvents appeared in the thermal range of 300–425. It was obvious that the PEDOT/Ag nanocomposite had a better thermostability behavior relative to the pure samples PEDOT I and PEDOT II at all temperatures greater than 320°C. The char yield of the PEDOT/Ag nanocomposite at 800°C was found to be greater than those of the other two samples at up to 20%. This should



**Figure 4.** Near UV–vis absorption spectra of PEDOT I, PEDOT II, and PEDOT/Ag.





**Figure 5.** TGA/DTG thermograms of PEDOT I, PEDOT II, and PEDOT/Ag.

chiefly have been related to the Ag<sub>nano</sub> powder embedded in the polymer matrix. Furthermore, when the curves of the pure samples PEDOT I and PEDOT II were compared with each other, we deduced that the choice of binary solvents instead of a single solvent showed a significant preference from the thermostability point of view. This might have been due to the difference in macromolecular form and size caused by the amount of the chloride ions present in the polymerization medium.

## CONCLUSIONS

A modified solution technique was successfully used with binary miscible solvents to synthesize PEDOT. Three steps were consecutively accomplished to prepare an Ag<sub>nano</sub>-incorporated PEDOT nanocomposite.

1. Pure PEDOT was completely dissolved in DMSO solvent.
2. The preprepared Ag nanopowder was homogeneously dispersed in the previously prepared PEDOT solution with sonication.
3. The PEDOT/Ag nanocomposite was eventually precipitated from the DMSO-based nanofluid.

The approximate mean size of the Ag nanoparticles was found to be about 40 nm. The SEM micrograph of the pure PEDOT II and PEDOT/Ag nanocomposite exhibited an agglomerated sponge and nanospherical homogeneity, respectively. The effects of the technique used and the presence of Ag<sub>nano</sub> on the optical

behaviors were fully investigated by near UV–vis spectroscopy. Furthermore, the thermostability of the resulting samples was studied by TGA/DTG, and from this viewpoint, we concluded that at all temperatures above 320°C, the samples prepared with binary solvents had more resistance toward heat relative to those prepared conventionally with a single solvent.

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