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Synthesis and electrical, thermal and structural characterization of polyaniline doped with Ho_2S_3-In_2S_3

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Recently, interest in inorganic-organic composites has increased rapidly due to the wide potential use in devices. We have investigated the thermal and electrical properties of polyaniline (PANI) doped with Ho_2S_3-In_2S_3. In order to synthesize Ho2S3 and In2S3, we used elemental holmium, indium and sulphur. Polyaniline/Ho_2S_3-In_2S_3 (1:1) composites have been synthesized employing in-situ oxidative polymerization procedure with aniline monomer at different rates by weight (%1, %3, %5). Several steps of thermal and electrical characterization measurements were carried on Polyaniline/Ho_2S_3-In_2S_3 (1:1) composites. The resulting composites were also characterized by thermogravimetric analysis (TGA).

Keywords: Polyaniline (PANI), Thermoelectric, Ho_2S_3-In_2S_3 chalcogenide, Oxidative polymerization, TG, DTA, I-V

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1. Introduction

Recently, conductive polymer-chalcogenide composites have been preferred as propitious contenders for thermoelectric applications due to their light-weight, cost-saving, and non-hazardous properties. Researchers have interested in conductive polymers considerably since these polymers have a technological importance. Polypyrrole and polyaniline (PANI), among the conductive polymers, are the most promising materials because they are easy to prepare, have low cost and high conductivity, and they are relatively stable in terms of environment. In order to enhance magnetic, electrical, and optical properties; researchers commonly employ conductive polymers, especially polypyrrole and polyaniline, which serve as host matrix for inorganic nanoparticles [1-3]. Inorganic compounds of tellurides, sulphides and selenides are chalcogenides. Unique physico-chemical properties are found in rare-earth chalcogenides and these chalcogenides are employed in various advanced technological applications [4, 5]. The data regarding the phase equilibria between rare-earth and (X=Ga, In, TI) chalcogenides were previously studied [6-15]. The optical property of chalcogenides is significantly improved to a large extent when combined with PANI. In energy devices and sensors, nanocomposites of PANI and chalcogenides (such as CdS, ZnS and CdSe) can be potentially applied. Inorganic nanoparticles enable deposition of nanoparticles to be stable when combined with polymeric matrices so that the films do not consist agglomeration. The studies of conductive polymers which contain chalcogenides have attracted a great deal of interest recently (CdS, CdSe, PbS, CdTe) [16].

2. Experimental details

2.1. Materials

Materials such as aniline ($C_6H_5NH_2$, 99%), ammonium persulphate (APS) and hydrochloric acid (HCl %37) were purchased from Sigma-Aldrich. All aqueous solutions were prepared with ultra pure water. Elemental holmium, indium and sulfur were used as received.

2.2. Preparation of PANI/Ho_2S_3-In_2S_3 (1:1) Composite

PANI/ Ho_2S_3-In_2S_3 (1:1) composites were prepared using conventional template-based in situ oxidative chemical polymerization of aniline with Ho_2S_3-In_2S_3 (1:1). In the beginning, Ho_2S_3-In_2S_3 systems were prepared using holmium and indium sesquisulfides as starting reagents. To do this, appropriate sulfide mixtures were reacted by melting at temperatures from 1270 to 1370 K in evacuated silica ampules. The resultant alloys were equilibrated (as verified by X-ray diffraction) by annealing at 1000–1100 K for 400–500 h [17]. In second step, Polyaniline / Ho_2S_3-In_2S_3 (1:1) composites were prepared in-situ at different rates by weight (%1, %3, %5) [5]. For the preparation of the composites, total volume of 1 mL aniline with 2.70 g ammonium persulfate (APS as oxidant) was oxidized in an acidic aqueous medium. Aniline and ammonium persulfate (APS) were dissolved, separately, in 50 mL solution of 1 M HCl in deionized water. Ho_2S_3-In_2S_3 (1:1) system was dispersed in 5 mL solution of 1 M HCl for 10 h using an ultrasonic bath. APS and this mixture were added to the aniline solution. The solution was carefully stirred and left for polymerization about 5 h in an ice–bath (0–5 °C) condition. The final dark-green precipitate was filtrate and washed 20 mL of 1 M HCl, thoroughly with distilled water and absolute acetone repeatedly. Finally, powder was dried in a vacuum oven at 60 °C for 12 h.

2.3. Characterizations

The electrical dc current-voltage (I-V) measurements of the pure polyaniline and doped polyaniline samples in pellet forms were carried out by two point probe method at between 0-4 Volt by taking steps of 0.1 Volt under dark and room temperature conditions via using a Fytronix FY 7000 Solar Simulator model I-V test instrument. For this purpose, to prepare the pellets as each to have 1 cm^2 area and 1 mm thickness, the samples as being mixture of varied minuscule and powder forms were pelletized under pressure in a pressing tool. Differential thermal analysis with thermogravimetric analysis (DTA-TG) measurements for each sample were singly taken by using a Shimadzu DTG 60AH equipment under a non-stop inert argon gas flow from room temperature to 300 °C and at a heating rate of 20 °C/min. At room temperature, a Zeiss Evo MA-10 model scanning electron microscopy (SEM) equipment was used at 500X magnification to shot the surface images of the polyaniline samples in detail.

3. Results and discussion:

The I-V results of the samples as multiplots can be seen all together in Fig.1-a. According to these plots, the electrical current increased with increasing doping ratio of metallic Ho_2S_3-In_2S_3 compound content, but the largest current flowed through the pure polyaniline sample.This is an interesting result, so that it can be deduced that the least % 1 percent of Ho_2S_3-In_2S_3 doping caused a chemical and conductivity distortion in the host matrix of polyaniline material at first i.e. the minor amount of metallic compound reduced the conductivity of this % 1 doped polyaniline sample, but then, as to % 3 and % 5 percent Ho_2S_3-In_2S_3 doped polyaniline samples, the conductivity increased with increasing doping ratio and approached that of pure polyaniline sample (meanwhile, here the obtained dc electrical conductivity value of pure polyaniline pellet sample written in Table-1was found well compatible within range of the values found in the literature [18-22]). These changes can be better seen between the calculated electrical resistance (*R*), resistivity (ρ), conductivity (σ) and conductance (*G*) values of the samples listed in Table-1. Also, even to discern more obviously, the resistivity and conductivity changes between the samples were drawn as linear and columnargraphics and displayed in Fig.1-b, -c, -d and -e. Since it is known that polyaniline is a conducting polymere of the semi-flexible rod polymer family, the minor addition of dopant material (Ho_2S_3-In_2S_3) having ionic bonds and polymorhph structure at room temperature broke or changed some of covalent bonds and rods of conjugated polyaniline molecules by some new types of bindings (most likely occured between sulphur and hydrogen atoms which have high electronegativity and electropositivity values, respectively) and this reduced the original conductivity of polyaniline, but then by increment of doping ratio the conductivity increased again due to the increment of electron concentration by freed rare earth metal elements of holmium and indium contents in % 3 and % 5 doped samples which released or disentangled after their sulphur partners broke them off and left them alone, i.e. increased the number and mobility of charge carriers that correlated with the chemical composition [21]. Here, to determine the values of all these electrical parameters listed in Table-1 the linear fitting slopes of the I-V plots (in Fig.1-a) which are directly equal to the conductance (*G*) values were found and then the resistance, resistivity and conductivity values of the sampleswere calculated by using these fundemental formulas as following;

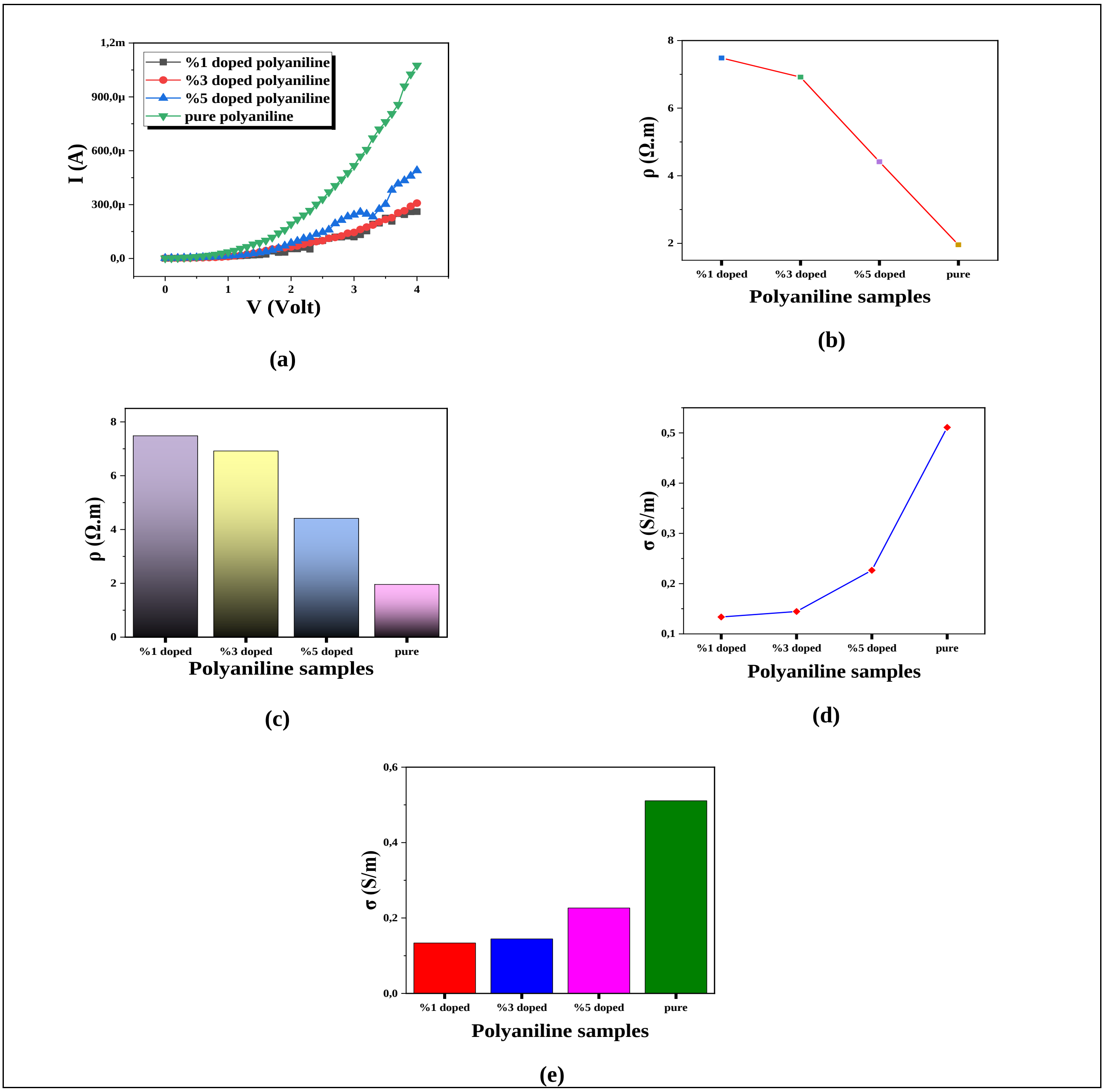
$$R = \frac{1}{G} = \frac{1}{slope} \qquad (1)$$

$$\rho = \frac{1}{\sigma} = \frac{R.A}{t} \qquad (2)$$

here, *slope* is the slope value obtained from linear fitting of an I-V plot, *A* is contact area (=0.5 mm2) of point of probing needle and *t* is the thickness of sample (=1 mm). In Table-1, standart error values for each slope value were also written.

Table-1. The electrical parameters of the pure and doped polyaniline samples.

Sample ID	**Resistance** ***R*** (kΩ)	**Resistivity** ***ρ*** (Ω.m)	**Conductivity** ***σ*** (S/m) (or S/cm x10^{-2})	**Conductance** ***G*** (S)x10^{-5}	**Standart error (%)**
%1 doped polyaniline	14.965	7.482	0.134	6.682	±4.07
%3 doped polyaniline	13.839	6.919	0.145	7.226	±3.82
%5 doped polyaniline	8.827	4.414	0.227	11.328	±7.19
Pure polyaniline	3.915	1.957	0.511	25.546	±1.50



(a)

(b)

(c)

(d)

(e)

Figure-1. a) *Multiplotted I-V results of the samples all together,* ***b)*** *plot of electrical resistivity change between samples,* ***c)*** *column chart of electrical resistivity change between samples,* ***d)*** *plot of electrical conductivity change between samples and* ***e)*** *column chart of electrical conductivity change between samples.*

According to the original DTA-TGA results given in Fig.2, around 25% of weight losses were observed in each sample from analyses of their mass change curves (the blue curves). The least mass loss occured in pure polyaniline sample (23.47 %) due to its chemical stability. These mass decrements were matched with the endothermic downfalls of the DTA curves mainly at around 100 °C and 250 °C. Here, apparently the water content and some volatile matter went away from the samples by heating effect after 100 °C seen in the first endothermic wide peaks and doping caused a retardation of the complete evaporation of the water content and this can be understood by expansion of these peaks towards above 100 °C because doping increased the boiling point of water, like the salt addition does. By the second but wider peaks the samples underwent degradations, at where the main parts of the mass losses occured. The glass transition temperature (T_g) values for the samples were also tried to be determine by T_g analyses and they are thought as in the analysed original data boxes placed in each DTA-TG graphic in Fig-2.

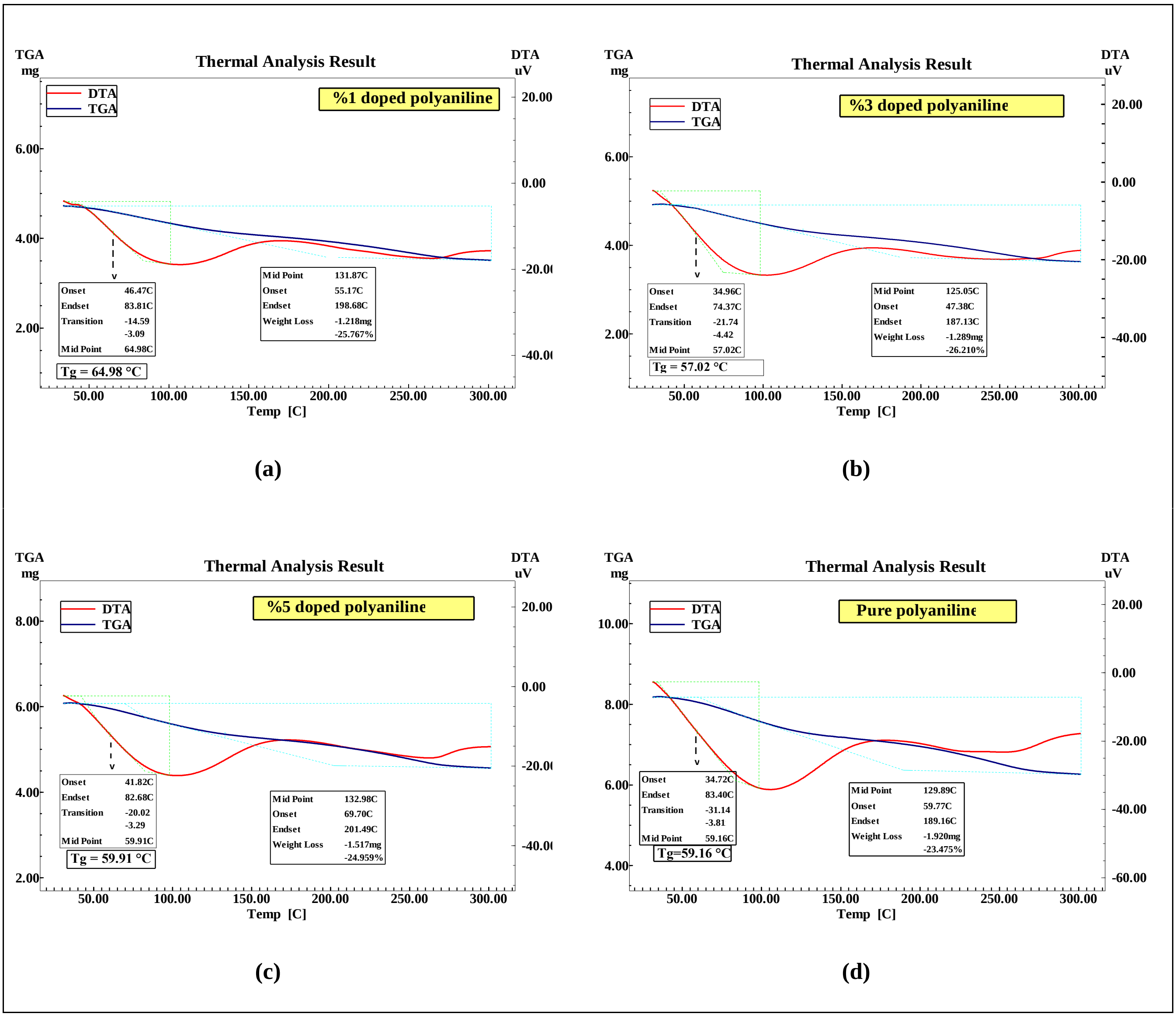
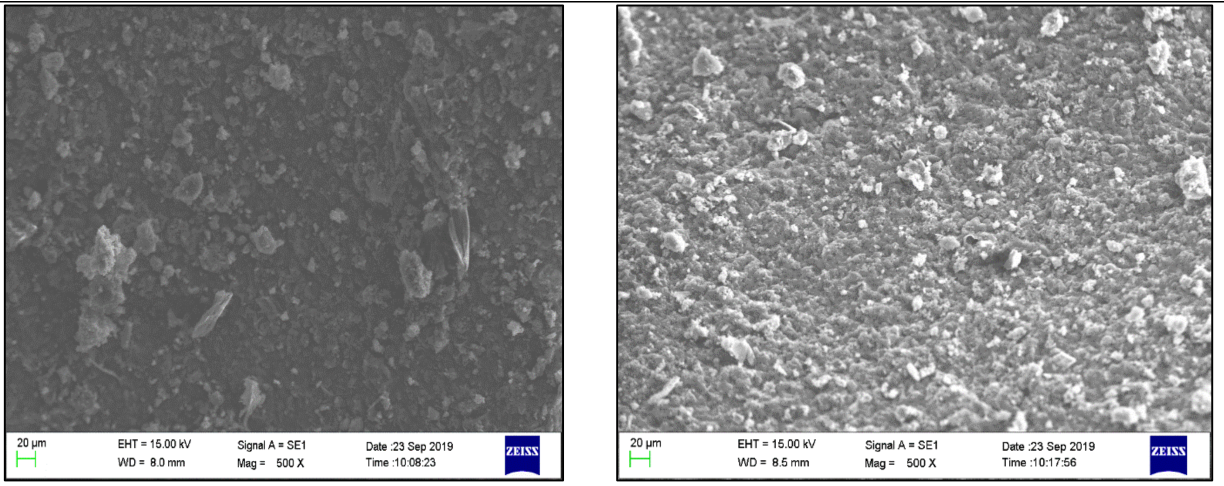


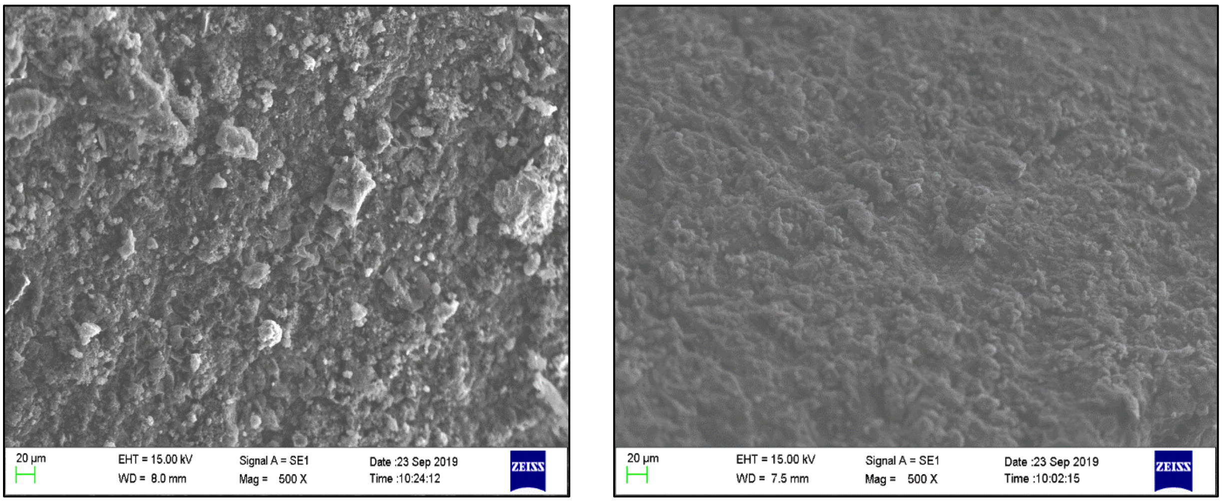
Figure-2. *DTA and TGA curves for;**a)**%1, **b)** %3, **c)** %5 doped polyaniline and **d)** pure polyaniline samples.*

SEM imaging results of the samples can be seen in Fig.-3-a, b, c and d. As seen in these figures, the nearly uniform and equal shaped corpuscles of the pure polyaniline sample on Fig.3-d image were changed into a more irregular and arbitrary shaped and sized particle objects having stone-like complex geometries by doping pure polyaniline with Ho_2S_3-In_2S_3 content seen on the images in Fig-3-a, b and c. The largest stone-like objects were observed by the highest doping ratio of %5 seen in Fig.-3-c. These morphological changes in polyaniline surface by doping supported the electrical results mentioned above.



a) *SEM image of %1 doped polyaniline sample.*

b) *SEM image of %3 doped polyaniline sample.*



c) *SEM image of %5 doped polyaniline sample.*

d) *SEM image of pure polyaniline sample.*

Fig.-3: *SEM images of a) %1, b) %3, c) %5 doped and d)pure polyaniline samples.*

Conclusions

In this work, the pure polyaniline (PANI) polymer as a conductive thermoelectric material was produced by conventional template-based in situ oxidative chemical polymerization of aniline and doped with different percentages of inorganic Ho_2S_3-In_2S_3 chalcogenide. The values of electrical conductivity parameters of pure and doped PANI samples were determined by two point probing methot. The value of dc conductivity of pure PANI was found in the value range present in the literature. By doping %1 of chalcogenide the conductivity was decreased at first due to the disrupting effect of Ho_2S_3-In_2S_3 chalcogenide on the structure of pure PANI. But then it was seen that with higher percentages of doping content the conductivity raised again and approached the that of pure sample. These structural changes caused by doping were also seen on the surface morphology SEM images of the samples. Furthermore, doping caused increments in the weight losses and in the temperatures of differentiated peaks on the TG-DTA curves of the samples, too. In conclusion, doping PANI with chalcogenide made significant changes in its electrical, structural and thermogravimetric features.

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