

This article was downloaded by: [Kocaeli Universitesi]

On: 25 August 2012, At: 02:56

Publisher: Taylor & Francis

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Macromolecular Science, Part B: Physics

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/lmsb20>

Synthesis, Characterization, and AC Conductivity of Polyaniline/Selenium Composites

Ersel Ozkazanc^a, Sibel Zor^b & Hatice Ozkazanc^b

^a Department of Physics, Kocaeli University, Kocaeli, Turkey

^b Department of Chemistry, Kocaeli University, Kocaeli, Turkey

Accepted author version posted online: 24 Feb 2012. Version of record first published: 22 Aug 2012

To cite this article: Ersel Ozkazanc, Sibel Zor & Hatice Ozkazanc (2012): Synthesis, Characterization, and AC Conductivity of Polyaniline/Selenium Composites, Journal of Macromolecular Science, Part B: Physics, 51:11, 2122-2132

To link to this article: <http://dx.doi.org/10.1080/00222348.2012.664451>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.tandfonline.com/page/terms-and-conditions>

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae, and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand, or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Synthesis, Characterization, and AC Conductivity of Polyaniline/Selenium Composites

ERSEL OZKAZANC,¹ SIBEL ZOR,²
AND HATICE OZKAZANC²

¹Department of Physics, Kocaeli University, Kocaeli, Turkey

²Department of Chemistry, Kocaeli University, Kocaeli, Turkey

This study reports structural and thermal properties and temperature-dependent alternating current (AC) conductivity of polyaniline/selenium (PANI/Se) composites in emeraldine salt form prepared by a chemical polymerization method. Fourier transform infrared spectroscopy showed that the doping process significantly affected the N-H bond in PANI chain. The free energy change, which was calculated from the Langmuir adsorption isotherm, showed that Se was electrostatically adsorbed on PANI molecules. From the scanning electron microscopy images it was determined that morphological changes caused by the doping process on PANI surface could affect conductivity. Thermal analysis, which was performed with differential scanning calorimetry, showed that the addition of Se increased the degradation temperature of PANI. Depending on the doping level, significant increase was observed in the AC conductivity of PANI, approximately 11, 13, and 17 times for 300, 350, and 400 K temperatures respectively.

Keywords AC conductivity, morphology, polyaniline, polymer composites, selenium

Introduction

Conducting polymers, having very wide application areas such as organic field effect transistors, electrochromic devices, sensors, light-emitting diodes, capacitors, organic solar cells, and anticorrosive materials, have become one of the interesting study areas in recent years.^[1–14] Within conducting polymers, polyaniline (PANI) has a particular importance due to its low cost, easy synthesis, high electrical conductivity, and excellent environmental stability. PANI can be found in four different forms (leuco-emeraldine base, pernigraniline base, emeraldine base, and emeraldine salt (ES)) depending on the pH of the aqueous solution (which contains an oxidizing agent and concentrated acid) and oxidation potential. Only the ES form is electrically conducting and can be synthesized electrochemically or chemically in an acidic medium by means of oxidants.^[1–12,14–21]

Received 12 October 2011; accepted 23 January 2012.

This study was supported by the Research Fund of the Kocaeli University (Project No. 2010/51). The authors would also like to thank Dr. Umit Ay and Prof (Dr.) Muzaffer Zeren for AAS and SEM measurements respectively. Last but not least, our thanks to Dr. Özcan Gündoğdu of Kocaeli University for his helpful comments and advice.

Address correspondence to Ersel Ozkazanc, Department of Physics, Kocaeli University, 41380 Kocaeli, Turkey. E-mail: erseloz@kocaeli.edu.tr

The need for renewable energy sources has directed researchers toward cheap and clean photovoltaic devices. In such studies, research on conducting polymers has exhibited an obvious increase due to their ease of production, cost advantages, particularly in production of photovoltaic devices when compared with inorganic materials. But, disadvantages, such as poor processability and stability, affect the physical properties and usefulness of the conducting polymers negatively. Being insoluble and not melting, they are hard to shape, thereby restricting their application areas. In order to decrease or avoid these disadvantages, particular attention has been focused on conducting polymer matrix composites. Various materials are doped into the polymer, interacting with polymer chains at molecular level, thereby improving their structural and physical properties. These composites are usually prepared by doping metal or metallic salts into the conducting polymers and their derivatives by different methods and under various conditions.^[5,7,9,12–15,17,22] The type of conducting polymer used, polymerization conditions, and physical/chemical properties of the doping material are very important in terms of the properties of the composite materials to be prepared.

In this study, we doped various mass fractions of selenium (Se) into the ES form of PANI, which was synthesized via a chemical oxidation method. While Se is commonly used in the production of circuit elements, such as photocells, current transformers, and diodes, studies involving doping Se into PANI and its derivatives are extremely limited.^[14,22] Unlike other studies, we measured with atomic absorption spectroscopy (AAS) the quantity of Se remaining in the filtrate after polymerization, and investigated in considerable detail the interaction mechanism between polymer and metal cations. The effect of the doping process on conductivity as a function of temperature and frequency was also investigated in addition to structural and thermal properties. Hence, it is suggested that the results obtained from this study may be interesting in terms of the above-mentioned applications.

We first describe the Fourier transform infrared (FT-IR) spectroscopy, scanning electron microscopy (SEM), and differential scanning calorimetry (DSC) results. We then report the quantity of Se that remained in the filtrate after chemical polymerization, determined by using AAS. Finally, the conductivity measurements carried out in the frequency range of 1 kHz to 1 MHz at different temperatures (300–400 K) are described.

Experimental

Materials

Aniline, ammonium peroxy disulphate ((NH₄)₂S₂O₈), and nitric acid (HNO₃) (65 wt%) were supplied by Merck (Germany). Metallic Se powder was supplied by BDH Chemicals Ltd. (England). These materials were used without undergoing any processing.

Synthesis of Polyaniline

Aniline, 5 mL, was added into 0.7 M 100-mL HNO₃ and stirred at a constant speed. (NH₄)₂S₂O₈, 10 g, in 20-mL distilled water was then added to the solution as oxidant and stirred at 5°C for 5 h. The precipitate obtained after the polymerization was filtered by using a coarse filter paper and washed three times with deionized water. The dark green colored PANI powder was obtained after drying at 60°C for 24 h.

Doping Process

Selenium, 0.2 g, was dissolved in 5-mL concentrated HNO₃ yielding a yellow solution. This mixture was added to 95-mL distilled water and stirred thoroughly. Aniline, 5 mL,

was added to the solution and the stirring was continued. Then 10-g $(\text{NH}_4)_2\text{S}_2\text{O}_8$ in 20-mL distilled water was added to the solution as an oxidant and stirred at 5°C for 5 h. After filtration, washing, and drying processes, as mentioned above, 0.2-g Se-doped PANI samples were obtained. The same procedure was repeated for 0.4, 0.6, 0.8, and 1 g Se yielding PANI/Se composites having different quantities of Se. Each of the composites was filtered individually and the filtrates obtained were topped up to a certain volume by using deionized water. Se concentrations in the filtrates were then determined from calibration curves obtained from predetermined standard concentrations of Se solutions via AAS.

Structural Characterization

Samples were characterized by FT-IR (Shimadzu FTIR 8201 spectrophotometer, Japan) between 4000 cm^{-1} and 400 cm^{-1} . Se quantities remaining in the filtrates after polymerization were determined by AAS (Perkin Elmer AA-Analyst 800, USA). Surface morphologies of the samples were examined by SEM-EDX (JEOL 50 A, Japan) micrographs taken at 15 kV. Thermal properties were determined by DSC (Perkin Elmer DSC 4000, USA) at a heating rate of $10^\circ\text{C}/\text{min}$ between 0°C and 400°C .

Alternating Current (AC) Conductivity Measurement

Pellets with 13-mm diameter were prepared for AC conductivity measurements by applying a pressure of 10 tons by using a hydraulic press. Each pellet weighed between approximately 0.1 g and 0.13 g, and their thickness varied between 0.8 mm and 0.9 mm. Both sides of the samples were coated with aluminum for electrodes by using a vacuum coating system (Univex 300, Germany). Conductivity measurements, carried out at 1 kHz–1 MHz frequency and in the temperature range of 300–400 K in a vacuum of 10^{-3} Torr, were performed by an LCR meter (Agilent 4284A, USA). The temperatures were controlled by using a temperature controller (Oxford-ITC 502, USA).

Results and Discussion

Polymerization of Aniline

After oxidation of aniline with $(\text{NH}_4)_2\text{S}_2\text{O}_8$ in diluted (0.7 M) aqueous HNO_3 solution, dark green-colored PANI powder was obtained (see Fig. 1). PANI synthesized by this method was in the electrically conductive ES form.

FT-IR Results for PANI and PANI/Se Composites

Characteristic absorption bands of undoped PANI were observed in all FT-IR spectra for all samples (see Fig. 2). These results observed for the undoped PANI are similar to the results reported in previous studies.^[3,5–7,9–12,15–19]

The peaks in the spectrum of the undoped PANI were observed at 3443 cm^{-1} (N-H stretching mode), 1558 cm^{-1} (C=C stretching of the quinoid ring), 1467 cm^{-1} (C=C stretching of the benzenoid ring), 1385 cm^{-1} (C-N stretching mode for quinoid units), 1294 cm^{-1} (C-N stretching mode), 1236 cm^{-1} (C-N stretching mode for quinoid units), 1096 cm^{-1} (C-H bending), and 791 cm^{-1} (C-H stretching).^[2,3,5–7,9–12,15–21] Absorption bands at 791, 1236, 1294, and 1558 cm^{-1} are characteristic peaks of the ES form of PANI.^[5,6,9,17]

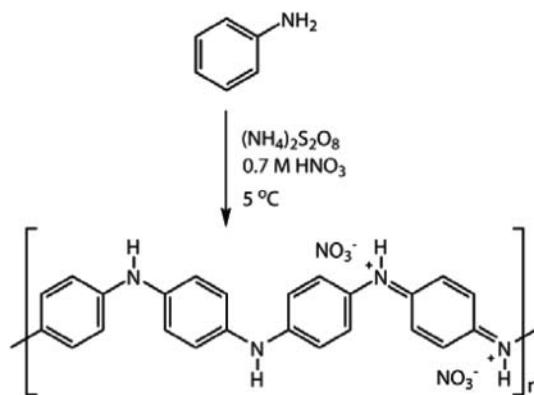


Figure 1. Chemical oxidative polymerization of undoped PANI.

The N-H stretching band observed, for 3443 cm^{-1} of undoped PANI, gradually decreases with Se doping, which might be due to interaction between metal cations and nitrogen atoms in the polymer chain. The peak observed at around 3100 cm^{-1} is thought to be due to O-H bands, which may have been the result of variations in the humidity of samples during pellet preparation and measurement.

AAS Characterization of Composites

Basic information on the interaction between polymer molecules and metal cations can be provided by adsorption isotherms. The simplest, the Langmuir isotherm, is based on the assumption that all adsorption sites are equivalent. The Langmuir isotherm can be expressed

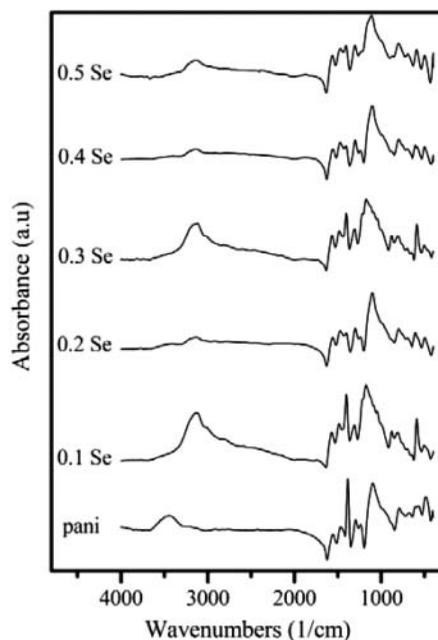


Figure 2. FT-IR absorbance spectra of PANI and its composites.

as

$$\frac{C}{\theta} = \frac{1}{K_{\text{ads}}} + C, \quad (1)$$

where C is the concentration of metal cations (mol/dm^3), K_{ads} (M^{-1}) is the adsorption equilibrium constant, and θ is the fraction of Se absorbed as determined by Eq. (2),^[5]

$$\theta = \frac{C_0 - C}{C_0}, \quad (2)$$

where C_0 (mol/dm^3) is the initial concentration of Se in the polymerization process and C (mol/dm^3) is the concentration of Se in the filtrate after polymerization. The equilibrium constant of the adsorption process was determined from the slope of the isotherm curve (see Fig. 3) and is related to the free energy change of adsorption (ΔG_{ads}^0) by Eq. (3),

$$K_{\text{ads}} = \frac{1}{55.5} \exp\left(-\frac{\Delta G_{\text{ads}}^0}{RT}\right), \quad (3)$$

where R is the universal gas constant, T is the thermodynamic temperature, and the constant value of 55.5 is the concentration of water in the solution (mol/dm^3).

When the obtained K_{ads} was placed in Eq. (3), the adsorption-free energy change, ΔG_{ads}^0 , was calculated as -26.03 kJ/mol. The adsorption type is generally regarded as physisorption if ΔG_{ads}^0 is between -20 kJ/mol and 0 kJ/mol. When the value of ΔG_{ads}^0 is between -80 kJ/mol and -400 kJ/mol, the adsorption would be considered as chemisorptions. Our value showed that the metal cations were adsorbed physically on the polymer

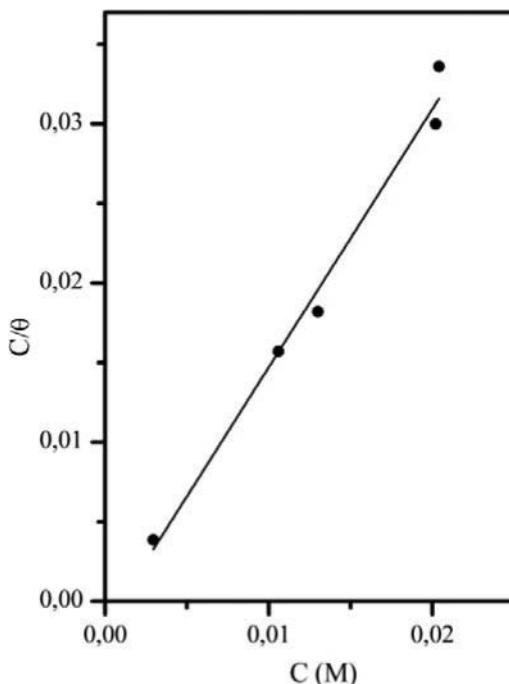


Figure 3. Langmuir's adsorption plot of C/θ versus C .

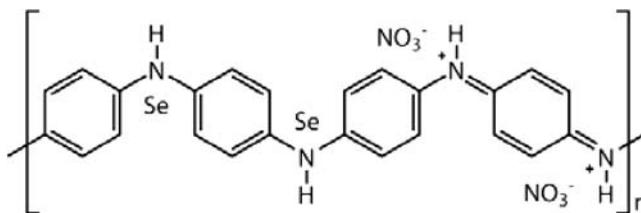


Figure 4. Possible PANI–Se interaction.

molecules by electrostatic interactions.^[5] N–H units without adsorbed Se were neutralized with nitrate ions. This interaction mechanism is given in Fig. 4.

SEM Measurements of PANI and PANI/Se Composites

Figure 5 shows scanning electron micrographs of PANI and some of its composites.

In the micrographs of pure PANI, spaces between the particles are very clear (see Fig. 5a). In samples doped with Se, these spaces disappear and a secondary phase consisting of small spherical particles occurs in relatively brighter contrast on the surface (see Figs. 5b and c). The bonding between the PANI particles was relatively stronger in the doped samples compared with undoped PANI as it affects the motion of the charge carriers. Accordingly, it may be expected that the doping process positively affects the electrical conductivity of PANI.

DSC Analysis

In the DSC thermograms of undoped PANI, two endothermic and one exothermic peaks were observed (see Fig. 6a). While these endothermic peaks were also observed in all the composites, the exothermic peak was not seen in any of the composites.

The endothermic peaks around 100°C for PANI and its composites could not be clearly observed in the second heating (see Fig. 6b). This is attributed to loss of moisture in the material in this temperature region. A similar situation has also been observed in other studies.^[2,4,6,12,17,21]

The exothermic peak observed for undoped PANI at about 200°C has been generally attributed to cold crystallization (T_{cc}) or a crosslinking reaction of the polymer.^[20] This peak was not observed in the composites, which can be due to restriction in the mobility of polymer chain by Se doping, and also because Se on the chains prevent packing in a lattice for a random copolymer.

The second endothermic peak observed for undoped PANI, at about 260°C, is related with the degradation process due to strongly bonded water and/or organic molecules coming from the solvent being removed from the structure of the polymer.^[4,6,12,17,20,21] It is considered that the shift to higher temperatures observed in this peak (see Table 1) by doping may be related with the secondary phase observed in SEM micrographs. This phase, which is thought to have developed during metal doping, may have caused small increase in the crystallinity of undoped PANI, which itself is a semicrystalline conducting polymer. It is therefore possible to say that Se increases the degradation temperature (T_d) of PANI. However, there is an oscillation of around 15°C in the degradation temperature of doped samples (also evident in Table 1), which might be due to remaining water and/or solvent molecules possibly having differing quantities for each sample. Possible morphological changes (such as changes in the degree of crystallinity and interactions at a molecular level) in the structure of PANI as a result of doping process could be another factor.

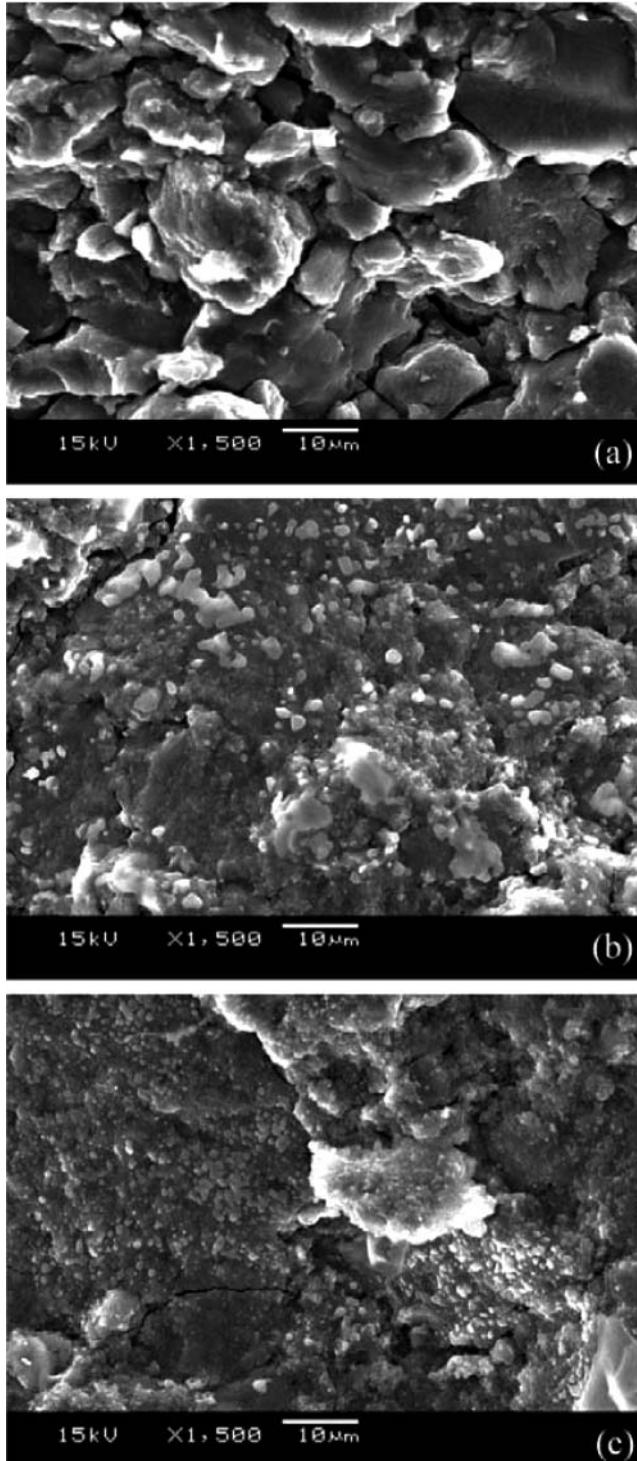


Figure 5. SEM micrographs of (a) undoped PANI, (b) PANI/0.3 Se, and (c) PANI/0.5 Se.

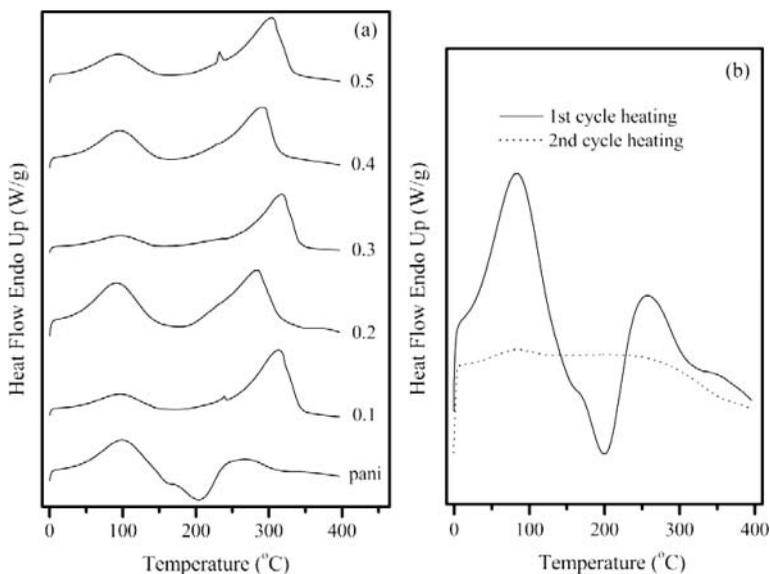


Figure 6. (a) DSC curves of PANI and its composites, (b) double cycle heating of undoped PANI.

AC Conductivity

The real (ϵ') and imaginary (ϵ'') parts of complex dielectric constant ($\epsilon^* = \epsilon' - i\epsilon''$) and the dielectric loss factor ($\tan \delta$) can be calculated from the equations below:

$$\epsilon' = C_p d / \epsilon_0 A, \quad (4)$$

$$\tan \delta = \epsilon'' / \epsilon', \quad (5)$$

where C_p is the capacitance of the sample, A is the electrode area, d is the sample thickness, and ϵ_0 is the vacuum permittivity (8.85×10^{-14} F/cm). The AC conductivity (σ_{AC}) was calculated using

$$\sigma_{AC} = 2\pi f \epsilon_0 \epsilon' \tan \delta, \quad (6)$$

where f is the frequency of the applied AC field (in Hz).^[5,8] From the measured C_p and $\tan \delta$, the AC conductivity of the samples was calculated.

Table 1
 T_d values of PANI and its composites

Sample	T_d (°C)
Undoped PANI	262.52
PANI/0.1 g Se	310.18
PANI/0.2 g Se	283.95
PANI/0.3 g Se	315.62
PANI/0.4 g Se	291.31
PANI/0.5 g Se	303.14

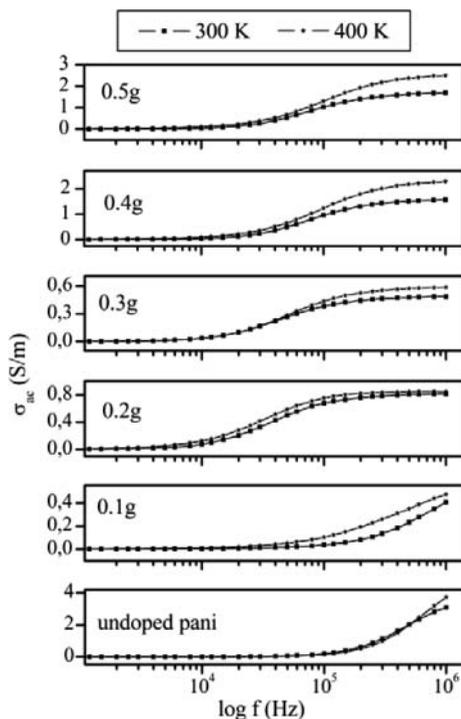


Figure 7. Frequency dependence of AC conductivity for PANI and its composites at two different temperatures.

The conductivity in the conducting polymers is generally due to the motion of delocalized electrons through conjugated systems and a hopping process of electrons between the nearest neighbor redox sites on the polymer chain. Figure 7 shows the dependence of the conductivity of PANI and its composites on the frequency for two temperatures.

Different trends in the conductivity dependence of both PANI and its composites can be seen clearly. While there was no change in the conductivity of undoped PANI up to 10^5 Hz, a rapid increase was observed after this frequency. This behavior is interpreted in terms of the hopping conductivity of electrons increasing at relatively high frequencies. Similar behavior also exists for composites. However, the increase seen in the conductivities of the composites above a certain frequency became slower. This behavior, which became clear at and above the 0.2-g doping level, can be due to the morphological structure of composites. As can be seen from SEM micrographs, adding Se resulted in partly filling the spaces in the polyaniline matrix, and the bonding between the particles was improved. This can result in the occurrence of conductive paths with different lengths. In this case, both motion of the charge carriers through the conjugated system and their hopping between localized sites can be affected by the frequency and doping level positively. There was also an increase in the conductivity at high temperatures for PANI and its composites. The increase that takes place in the polymer-free volume at higher temperatures facilitates easy movement of charge carriers under external field.

The effect of the doping process on the conductivity of PANI at 300 and 400 K and 10 KHz and 1 MHz is shown in Fig. 8.

The most systematic increase was obtained for 10-kHz frequency. When 0.5-g Se was doped, the conductivity of PANI increased linearly by about 11, 13, and 17 times for 300,

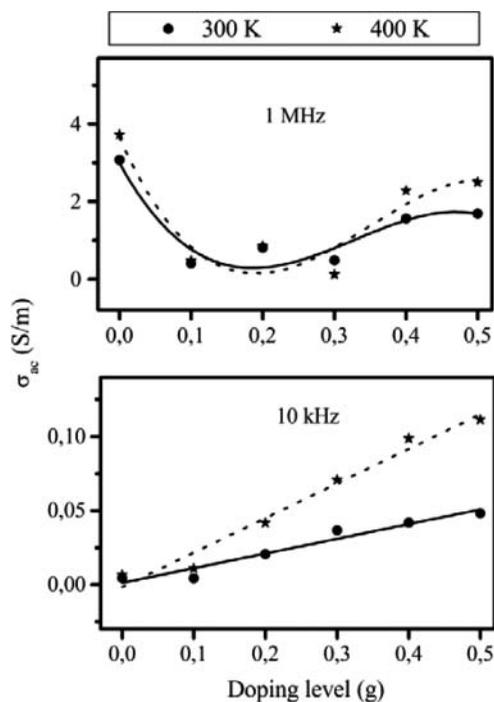


Figure 8. Variation of AC conductivity versus doping level for (a) 10 kHz, and (b) 1 MHz at two different temperatures.

350 and 400 K temperatures respectively. Although the conductivity values of PANI and its composites at 1 MHz were higher than at 10 kHz, there was no observation for a systematic variation with doping. The conductivity of PANI decreased up to approximately 0.3-g doping level, and then showed a tendency to increase afterwards. This might be related to different morphological structures of PANI and its composites.

Conclusions

The structural and thermal properties of PANI and its composites synthesized via a chemical polymerization method were investigated by FT-IR, AAS, SEM, and DSC measurements. The effect of the doping process on the AC conductivity was studied as a function of temperature.

FT-IR spectroscopy showed that PANI and its composites were in the electrically conducting ES form. Significant shifts of the absorption peak of the N-H bond in the spectra showed that Se mostly interacted with nitrogen atoms. A weak electrostatic interaction between PANI and metal cations was determined by the free energy change calculated from the Langmuir adsorption isotherm curve. It was observed in SEM micrographs that the surface morphologies of doped samples were more homogeneous, and the bonding between the particles was stronger. A secondary phase was also developed as a result of the doping process. DSC analyses showed that the doping process increased the degradation temperature of PANI. An increase between 11 and 17 times was observed in its conductivity for the highest doping level, depending on temperature and frequency. Thus, we conclude that the electrical conducting behaviors of PANI/Se composites, depending on frequency

and temperature, could contribute to the production process of many electronic circuit elements such as transistors and diodes.

References

1. Freund, M.S.; Deore, B. *Self-Doped Conducting Polymers*. John Wiley & Sons Ltd.: Chichester, UK, **2007**, p. 1.
2. Zengin, H.; Kalaycı, G. Synthesis and characterization of polyaniline/activated carbon composites and preparation of conductive films. *Mater. Chem. Phys.* **2010**, *120*, 46.
3. Tang, Q.; Wu, J.; Sun, X.; Li, Q.; Lin, J. Shape and size control of oriented polyaniline microstructure by a self-assembly method. *Langmuir* **2009**, *25*, 5253.
4. Sinha, S.; Bhadra, S.; Khashtgir, D. Effect of dopant type on the properties of polyaniline. *J. Appl. Polym. Sci.* **2009**, *112*, 3135.
5. Ozkazanc, E.; Zor, S.; Ozkazanc, H. Structural and dielectric properties of CuCl_2 and ZnCl_2 doped polyaniline. *Polym. Composite* **2010**, *31*, 1862.
6. Izumi, C.M.S.; Constantino, V.R.L.; Temperini, M.L.A. Spectroscopic characterization of polyaniline formed by using copper(II) in homogeneous and MCM-41 molecular sieve media. *J. Phys. Chem. B.* **2005**, *109*, 22131.
7. Guo, Y.; Zheng, M.; Chen, J. Chemical synthesis, characterization and thermal analysis of polyaniline/copper composite powder. *J. Compos. Mater.* **2008**, *42*, 1431.
8. Ho, C.H.; Liu, C.D.; Hsieh, C.H.; Hsieh, K.H.; Lee, S.N. High dielectric constant polyaniline/poly(acrylic acid) composites prepared by in situ polymerization. *Synth. Met.* **2008**, *158*, 630.
9. Kazim, S.; Ali, V.; Zulfeqar, M.; Haq, M. M.; Husain, M. Electrical, thermal and spectroscopic studies of Te doped polyaniline. *Curr. Appl. Phys.* **2007**, *7*, 68.
10. Shen, W.; Shi, M.; Wang, M.; Chen, H. A simple synthesis of Fe_3O_4 nanoclusters and their electromagnetic nanocomposites with polyaniline. *Mater. Chem. Phys.* **2010**, *122*, 588.
11. Tiwari, A.; Singh, V. Synthesis and characterization of electrical conducting chitosan-graft-polyaniline. *Express Polym. Lett.* **2007**, *1*, 308.
12. Zhou, Su.; Wu, T.; Kan, J. Effect of Co^{2+} , Ni^{2+} , Cu^{2+} , or Zn^{2+} on properties of polyaniline nanoparticles. *J. Appl. Polym. Sci.* **2007**, *106*, 652.
13. De, S.; Dey, A.; De, S.K. Charge transport mechanism of vanadium pentoxide xerogel-polyaniline nanocomposite. *Eur. Phys. J. B.* **2005**, *46*, 355.
14. Zhang, L.; Li, Y.; Shen, Y.; Xie, A. One-step synthesis of poly(2-hexadecyloxyaniline)/selenium nanocomposite Langmuir-Blgett film by in situ redox reaction. *Mater. Chem. Phys.* **2011**, *125*, 522.
15. Li, X.; Gao, Y.; Zhang, X.; Gong, J.; Sun, Y.; Zheng, X.; Qu, L. Polyaniline/ CuCl nanocomposites prepared by UV rays irradiation. *Mater. Lett.* **2008**, *62*, 2237.
16. Li, X.; Li, X. Oxidative polymerization of aniline using NaClO_2 as an oxidant. *Mater. Lett.* **2007**, *61*, 2011.
17. Qi, Y.N.; Xu, F.; Ma, H.J.; Sun, L.X.; Zhang, J.; Jiang, T. Thermal stability and glass transition behavior of PANI/ γ - Al_2O_3 composites. *J. Therm. Anal.* **2008**, *91*, 219.
18. Yang, Q.; Wei, S.; Cheng, G. Preparation of conductive polyaniline/epoxy composite. *Polym. Compos.* **2006**, *27*, 201.
19. Arsalani, N.; Hayatigar, M. Preparation and characterization of novel conducting polyaniline-perlite composites. *Polym. Int.* **2005**, *54*, 933.
20. Luo, K.; Shi, N.; Sun, C. Thermal transition of electrochemically synthesized polyaniline. *Polym. Degrad. Stabil.* **2006**, *91*, 2660.
21. Qi, Y.N.; Xu, F.; Sun, L.X. Thermal stability and glass transition behavior of PANI/MWNT composites. *J. Therm. Anal.* **2008**, *94*, 137.
22. Bormashenko, E.; Pogreb, R.; Sutovski, S.; Shulzinger, A.; Sheshnev, A.; Gladkikh, A. Preparation of Se-doped polyaniline emeraldine base films. *Synth. Met.* **2003**, *139*, 321.