

# *Temperature and frequency-dependent conductivity of polystyrene/polyaniline composite*

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**Abstract**— The electrical properties of polyaniline and polystyrene/polyaniline materials are investigated using the dielectric relaxation spectroscopy. The measurements showed that Polyaniline has a conductivity of  $10^{-5}$  S/cm, while polystyrene/polyaniline exhibits nearly  $10^{-6}$  S/cm. The observed increase in conductivity with temperature is a property of semiconductor but the decreasing conductivity above 293.5K could be due to the presence of absorbed water and its removal may have caused structural changes in the hygroscopic PANI polymer chains.

**Keywords**— Polyaniline, polystyrene, dielectric, conductivity, composites.

## I. INTRODUCTION

The discovery of conducting polymers has opened up a promising field in material science and engineering. Conducting polymers are used in advanced applications like gas sensors, plastic batteries, electrochromic displays, super capacitors, electronics, drug delivery, corrosion protection, nonlinear optics, gas separation membranes, humidity sensors and enzyme immobilization [1].

Among these polymers, conducting polyaniline (PANI) is one of the most promising materials because of its unique optoelectrical properties, low cost, its excellent environmental stability [2] it is easy to prepare and can protect various metallic materials such as stainless steel, iron, copper, zinc and aluminum against corrosion in saline and acid media [3].

PANI can be synthesized by chemical or electrochemical oxidation of aniline to obtain a powder or thin film on electrodes, respectively. Polyaniline in its base form

(emeraldine base, EB) is dark blue, insulating powder. Because of its basic character, it may react with organic acids forming conducting salts [4].

However, polyaniline has poor mechanical properties and poor solubility in common solvents due to the stiffness of backbone and H-bonding interactions between adjacent chains [5], therefore, several studies have focused on eliminating such problems by embedding polyaniline in various polymeric matrices (polyvinyl acetate, polymethyl methacrylate, sodium polystyrene sulfonate...etc) [6], among them, polystyrene has been used to improve the mechanical properties and the transparency of the composites [7]. It has some useful features, such as good thermal stability, a degradation temperature above 400°C, good chemical resistance, and significant mechanical toughness. [8]

The resulting polymer composite is used in many applications such as dielectric materials in photovoltaic systems [9], optoelectronic components [7], membranes for electro dialysis [10], and in the areas of electromagnetic interference (EMI) shielding and electrostatic dissipation (ESD) [11].

In this paper, we have synthesized and studied the electrical and properties of polystyrene/polyaniline composite by using broadband dielectric spectroscopy which is a customary tool for examining the electrical response of substances involving conductivity and dielectric polarization [12]. The main advantage of DRS compared to other spectroscopies is its wide range of frequencies which can be easily covered [13].

## II. EXPERIMENTAL PART

The core-shell particles containing 20 wt. % of polyaniline were obtained by in-situ polymerization of aniline ( $C_6H_5NH_2$ ) around particles of polystyrene (PS), using APS ( $(NH_4)_2S_2O_8$ ) as an oxidizer, and the oxalic acid ( $C_2H_2O_4$ ) as a dopant. After 24h of continuous mechanical stirring, the transformation of white powder to a dark green precipitate was observed. The polystyrene/polyaniline / (PS/PANI) was filtered and washed several times by distilled water, and the resulting powder dried for 24h at  $70^\circ C$ . The dielectric characterization in the low frequency range ( $10^{-1}$  - $10^6$  Hz) was monitored by a Novocontrol broad band dielectric spectrometer. The DC conductivity of the obtained powders was determined from the frequency independent part of the AC conductivity measurements.

## III. RESULTS AND DISCUSSION

### A. Electrical properties

Fig. 1 shows a comparison of the conductivity evolution versus frequency between PANI, PS/PANI and pure PS samples at room temperature. While the polystyrene alone exhibits an insulating behavior (frequency dependent conductivity), it is observed that AC conductivity remains constant up to  $10^6$  Hz for PANI and  $10^4$  for PS/PANI meaning that the conduction is well established. Indeed, the chosen concentration of PANI exceeds the known percolation threshold. The incorporation of 20 wt. % of polyaniline in a polystyrene matrix enhances its DC conductivity from  $10^{-15}$  S/Cm to  $10^{-6}$  S/Cm, close to the DC conductivity of pure PANI ( $10^{-5}$  S/Cm). At high frequencies, the AC conductivity increases slightly with increasing frequency.

Fig. 2 shows the electrical conductivity evolution of the PANI/PS composite pellet between  $-100$  and  $20^\circ C$  in the  $10^{-1}$  - $10^6$  Hz frequency range. One can observe that the conductivity increases with increasing temperature while it remains constant versus frequency up to a certain value where it starts increasing versus frequency. This value shifts toward higher frequencies with increasing temperature.

Due to its semiconducting nature, the total conductivity  $\sigma_T$  of the PS/PANI sample can be analyzed using the following expression:

$$\sigma_T = \sigma_{DC}(T) + \sigma(\omega) \quad (1)$$

The DC conductivity  $\sigma_{DC}$  of the PS/PANI composites is related to the drift of electric charge carriers via band conduction mechanism and its temperature dependence relationship can be defined by the Arrhenius law [14]:

$$\sigma_{DC} = \sigma_0 + \exp(-E_a/KT) \quad (2)$$

Where T is the absolute temperature in K,  $k_B$  is the Boltzmann constant,  $\sigma_0$  is the minimum electrical conductivity at 0 K and  $E_a$  is the activation energy (eV).

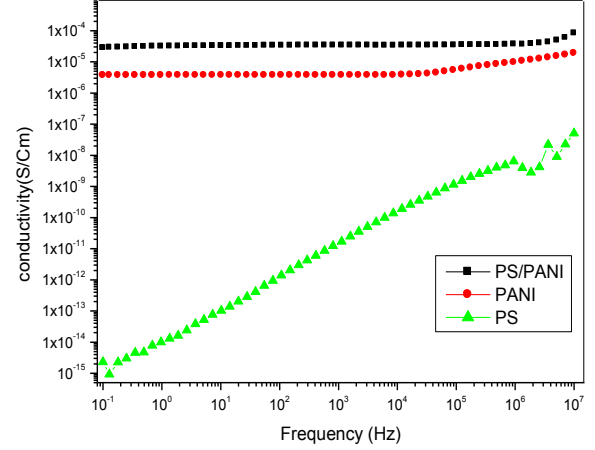


Fig. 1. Electrical conductivity plot versus frequency for PS/PANI, PANI and PS pellets at room temperature

The activation energy is the minimum energy required to overcome the potential barrier in polymeric systems. The value of the activation energy (0.14eV) is calculated from the slope of Fig.3.

This value is synonym of a hopping conduction mechanism [14].

The second term of equation (1),  $\sigma(\omega)$  depends on frequency which is considered to be a result of interface charge polarization (Maxwell-Wagner-Sillars effect) and intrinsic electric dipole polarization. This phenomenon appears in heterogeneous systems like metal-polymer composites due to the accumulation of mobile charges at the interfaces [8].

Fig. 4 shows the electrical conductivity of PS/PANI composite in the temperature range of 173.5-373.5 K at 10 kHz. It is noted that the conductivity of the composites increases slowly

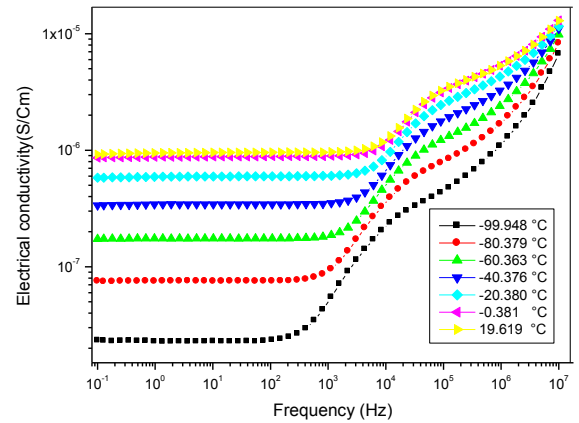


Fig. 2. Electrical conductivity plot versus frequency for PANI/PS pellet at different temperatures

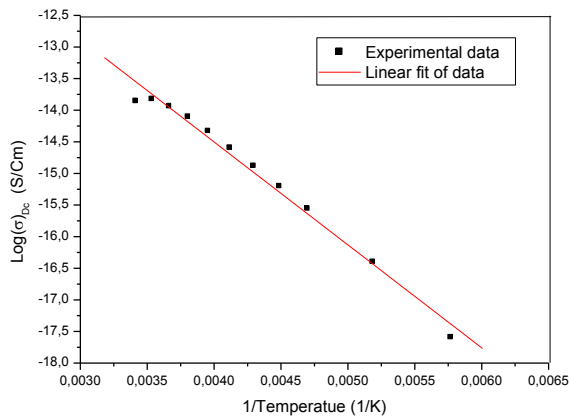


Fig. 3. Plot of  $\log(\sigma_{AC})$  versus  $1/T$  for PS/PANI pellet at 10 kHz.

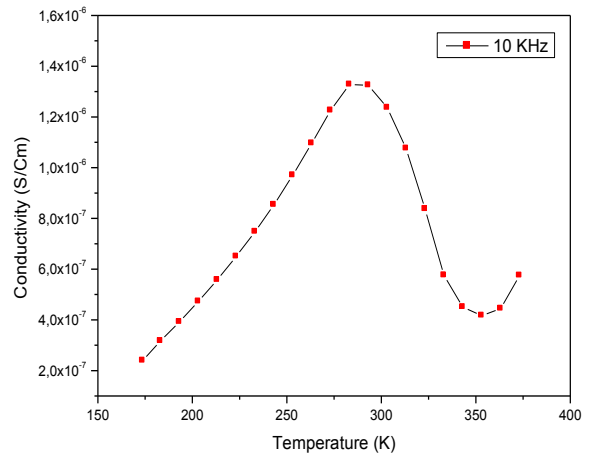


Fig. 4. Electrical conductivity plot at different temperatures for PANI/PS pellet at 10 kHz.

with the increase of temperature until a temperature around 293.5 K, after this point the conductivity decreases gradually. The increase in conductivity with temperature is a property of semiconductors. The decreasing conductivity above 293.5K could be due to the presence of absorbed water and its removal may have caused structural changes in the hygroscopic PANI polymer chains which revealed a small weight loss. The decreasing conductivity with increasing temperature is owing to chemical change, its degradation or evaporation of dopant. Furthermore, it has been reported that a dry sample has lower conductivity than a hydrated sample and loss of moisture results in a decrease of conductivity. [16],[17].

We did not see any change in the conductivity in any of our samples as the temperature went through the freezing point of water.

### CONCLUSION

In this study, conductive powders of PANI/PS are successfully synthesized by oxidative polymerization. The incorporation of the polyaniline in a polystyrene matrix over the percolation threshold (20 wt. %) enhance its DC conductivity from  $10^{-15}$  S/cm to  $10^{-6}$  S/Cm which is suitable for semiconductive applications were flexibility is also needed.

AC conductivity of PANI/PS showed a plateau in the low frequency region and dispersion at the high frequency. The dispersion of AC conductivity is explained on the basis of Maxwell-Wagner. The increase in ac conductivity was due to the creation of additional hopping sites in the polymeric composite.

The AC conductivity of the composites shows a dependence temperature at the range of 173.5-373.5K at 10 KHz. It is noted the AC conductivity has a Gaussian shape versus temperature centered around 293.5K.

### REFERENCES

- [1] G. Murtaza, and I. Ahmad, "Synthesis ,study of electrical, thermal behavior of polyaniline-polystyrene sulphonic acid composite," *Digest journal of nanomaterials and biostructures* **2016**, 11(4), 1261-1269.
- [2] K. Molapo, P. Ndangili, R. Ajayi, G. Mbambisa, S. Mailu, N. Njomo, M. Masikini, P. Baker, and E. Iwuoha, "Electronics of conjugated polymers (I): polyaniline," *International journal of electrochemical science*, pp. 11859 – 11875, 2012.
- [3] L. Gu1, X. Zhaol, X. Tong, J. Ma, B. Chen, S. Liu, H. Zhao, H. Yu1, and J. Chen," *Facile Preparation of Polyaniline Nanoparticles and Their Dispersion for Waterborne Anticorrosion Coatings,*" *International Journal of Electrochemical Science,*" pp. 1621 – 1631, 2016.
- [4] J.Haberko, A. Bernaski, J. Miskiewicz, W.Luzny, J. Raczowska, J.Rysz, and A.budkowsk, "The structure of thin films of polyaniline/polystyrene polymer blends studied by SIMS," *Fibres et Textiles in Eastern Europe*, vol. 13, No. 5(53), 2005.
- [5] H. Zeghioud, S. Lamouri, Z. Safidine, and M. Belbachir,"*Chemical synthesis and characterization of highly soluble conducting polyaniline in mixtures of common solvents,*" *Journal of Serbian Chemical Society*, 80 (7) 917–931 (2015) *JSCS*–4769
- [6] S. Zitouni, Z. Ghebache, and S. Lamouri, "Thermoelectrical characterization of new material based on pani/zeolite hy composites, used for the detection of carbon dioxide," *Polymer journal*, doi:10.1038/pj.2012.232, 1-9, 2013.
- [7] M. Zoeter, Y. Baalbaki, and C. Fakh, "Caractérisation des nanocouches de melanges de polystyrène et de

- polyaniline dopée en vue de leur utilisation dans l'affichage lumineux, " Journal of electron devices, 10-16, 2003.
- [8] N. Althani, M. Hassan, and J. Bhadra, "Polyaniline/polystyrene blends: in-depth analysis of the effect of sulfonic acid dopant concentration on AC conductivity using broadband dielectric spectroscopy," *International Journal of Polymer Science*, doi.org/10.1155/2018/1416531, 2018.
- [9] D. Mezdour, M. Tabellout, J. Bardeau, and S. Sahli, "Dielectric and electrical properties of PANI composite films," *IEEE Conference publications*, doi:10.1109/NAWDMPV.2014.6997612, pp. 1-4, 2014
- [10] F. Amado, E. Gondran, J. Ferreira, M. Rodrigues, and C. Ferreira, "Synthesis and characterisation of high impact polystyrene/polyaniline composite membranes for electro dialysis," *Journal of Membrane Science*, pp. 139-145, 2004.
- [11] P. Saini, and V. Choudhary, "Enhanced electromagnetic interference shielding effectiveness of polyaniline functionalized carbon nanotubes filled polystyrene composites," *Journal of Nanoparticle Research*, DOI: 10.1007/s11051-012-1415-2, January 2013.
- [12] G. Madhusudhana and J. Raj, "Characterization, AC Impedance Study and Dielectric Properties of Chemically Synthesised Poly Para-Toluidine," *Research Journal of Chemical Sciences*, Vol. 5(9), pp. 1-10, September 2015.
- [13] A. Kyritsis, P. Pissis, and J. Grammatikakis, "Dielectric Relaxation Spectroscopy in Poly(hydroxyethyl Acrylates)/Water Hydrogels," *Journal of Polymer Science: Part B: Polymer Physics*, Vol. 33, pp. 1737-1750, 1995.
- [14] K. Choi, E. Lee, J. Park, and K. Kim, "The chemical and physical properties of electrochemically prepared polyaniline perchlorate (PAP)," *Journal of applied polymer science*, doi.org/10.1002/app.1991.070420803.
- [15] S. Reda and S. Al-Ghannam "Synthesis and Electrical Properties of Polyaniline Composite with Silver Nanoparticles" *Advances in Materials Physics and Chemistry*, Vol. 2, No. 2, 2012, DOI:10.4236/ampc.2012.22013.
- [16] Y. Wankhede, S. Kondawar, S. Thakare, and P. More, "Synthesis and characterization of silver nanoparticles embedded in polyaniline nanocomposite," *Advanced material Letters*, DOI: 10.5185/amlett.2013.icnano.108
- [17] R. Ansarim, And B. Keivani, "Polyaniline Conducting Electroactive Polymers: Thermal and Environmental Stability Studies," *E-Journal of Chemistry*, Vol. 3, No.4, pp. 202-217, October 2006