The Nucleus **48**, No. 1 (2011) 17-21

The Nucleus
A Quarterly Scientific Journal of Pakistan Atomic Energy Commission
NCLEAM, ISSN 0029-5698

INVESTIGATION OF AGEING EFFECTS ON THE ELECTRICAL PROPERTIES OF POLYANILINE / GOLD NANOCOMPOSITES

*ASMA B. AFZAL and M.J. AKHTAR[1]

Department of Chemical and Materials Engineering, PIEAS, P.O. Nilore, Islamabad, Pakistan

[1]Physics Division, Directorate of Science, PINSTECH, P.O. Nilore, Islamabad, Pakistan

(Received October 20, 2010 and accepted in revised form January 17, 2011)

PANI/Au nanocomposites, synthesized by incorporation of separately prepared gold nanoparticles in NMP solution of PANI have been aged at accelerated temperature of 120 °C to simulate a storage period of 2 years at 25 °C. The impedance spectroscopic studies of NMP plasticized aged nanocomposite films suggest microphase separation into reduced and oxidized repeat units. There is crosslinking of the PANI films during ageing thereby hindering the charge transfer between PANI chains and gold nanoparticles, as a result, resistivity is increased.

Keywords*: Gold nanoparticles, Polyaniline, Impedance, Ageing*

1. Introduction

Conducting polymers are interesting materials in modern technology because of their potential applications such as electromagnetic radiation shielding, antistatic coatings and sensors [1, 2]. The incorporation of nano-sized metallic particles has created considerable interest in these materials due to their unique properties [3, 4]. The nanocomposites containing organic polymers and inorganic particles in nanoscale regime provide a completely new class of materials with novel properties [5-7]. Polyaniline (PANI) is unique among the family of conjugated polymers due to its good environmental stability, ease of preparation, inexpensiveness and reversible control of conductivity both by charge-transfer doping and protonation.

The polyaniline emeraldine base (PANIEB) consists of equal number of reduced [–(C_6H_4) NH(C_6H_4)NH–] and oxidized [–(C_6H_4)N=(C_6H_4)=N–] repeat units. It is the most stable form of PANI and its conductivity can be enhanced by incorporation of metal nanoparticles. A number of studies have shown that the incorporation of metal nanoparticles can improve the electrical properties of the conducting polymers. Wang et al. [8] synthesized nanosized metallic particles via reduction of the metal salts by PANIEB in both NMP and aqueous media; as a result of these reactions, the polyaniline is converted to a higher oxidation state. Sarma et al. [9] have prepared PANI-gold nanocomposites by first reducing gold salt solution and then polymerizing aniline in the same medium. Ma et al. [7] employed one-step synthesis of water-soluble gold nanoparticles/PANI composite for glucose sensing applications. Breimer et al. [10] observed that the electrical conductivity of polypyrrole has been enhanced by incorporating gold nanoparticles into photosynthesized polypyrrole films. Previously we have prepared PANI/gold nanocomposites by incorporation of separately synthesized gold nanoparticles in NMP solution of PANI [11]. We have performed heatflow calorimetry (HFC) studies to calculate activation energy of the synthesized materials [12].

Activation energy can be calculated by using Arrhenius relationship:

$$k = A \cdot \exp\left(-\frac{E_a}{RT}\right) \tag{1}$$

where A is the pre-exponential factor, E_a the activation energy, R the gas constant (8.314 J $mol^{-1}K^{-1}$) and T the absolute temperature (K). Details of accelerated ageing have been mentioned previously [12]. This information has been used to age these materials at elevated temperature of 120 °C to simulate a period of 2 years storage at 25 °C. Impedance measurements

* Corresponding author: asma_binat@yahoo.com

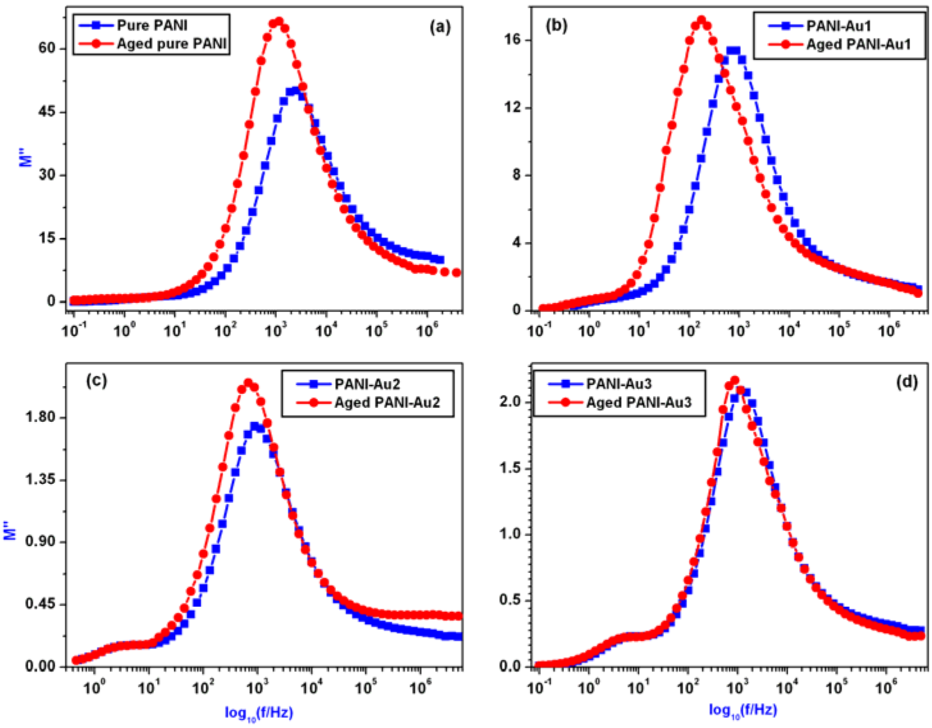

Figure 1. Comparison of M'' vs. $\log_{10}f$ of unaged and aged samples.

of aged PANI/ gold nanocomposites have been carried out for the determination of the electrical properties and compared with unaged ones.

2. Experimental

PANIEB was prepared by oxidative polymerization of aniline using APS as an oxidant [11]. The gold nanoparticles synthesized by NMP extract of black tea leaves were added in the NMP solution of PANIEB in different concentration (0.24 wt. % (PANI-Au1), 0.48 wt. % (PANI-Au2) and 0.72 wt. % (PANI-Au3)) to cast PANI gold nanocomposite films; details have been described elsewhere [11]. These films were aged at elevated temperature of 120 °C to simulate a storage period of 2 years at 25 °C.

Impedance measurements of all aged PANI samples were performed using an Alpha-N Analyzer, Novocontrol (Germany) in the frequency range $0.1 \leq f \leq 10^7$ Hz at 0.5 V at room temperature. WINDETA software has been used for data acquisition. The ac resistivity measurements were performed on films having a diameter of 13 mm and a thickness of ~2 μm. In this study we present the results of the complex impedance as $Z = Z' + jZ''$ and modulus as $M = M' + jM''$, where Z', M' and Z'', M'' are the real and imaginary parts of impedance and modulus, respectively. The relationship between M and Z is given by $M = j\omega C_c Z$; where $\omega = 2\pi f$ and C_c is the capacitance of the measuring cell [13].

3. Results and Discussion

Ageing has a strong influence on the electrical properties of PANI/Au nanocomposites which can be explored by employing impedance spectroscopy. The plots of imaginary part of modulus versus frequency for all aged and unaged samples are compared in Figure 1. A single strong relaxation peak in all samples has been observed. This peak is enlarged and shifted towards lower frequencies by ageing PANI samples for a period of 2 years at 25 °C signifying that aged samples are less conducting [14]. An additional small peak emerges at low frequency (below 5 Hz) in Figure 1. It is important to note that in all aged samples, the characteristic relaxation frequencies of oxidized and reduced phases were not resolved well in modulus plots although they are clearly resolved in impedance plots as discussed below. This behavior is similar to unaged PANI/Au nanocomposite samples [11].

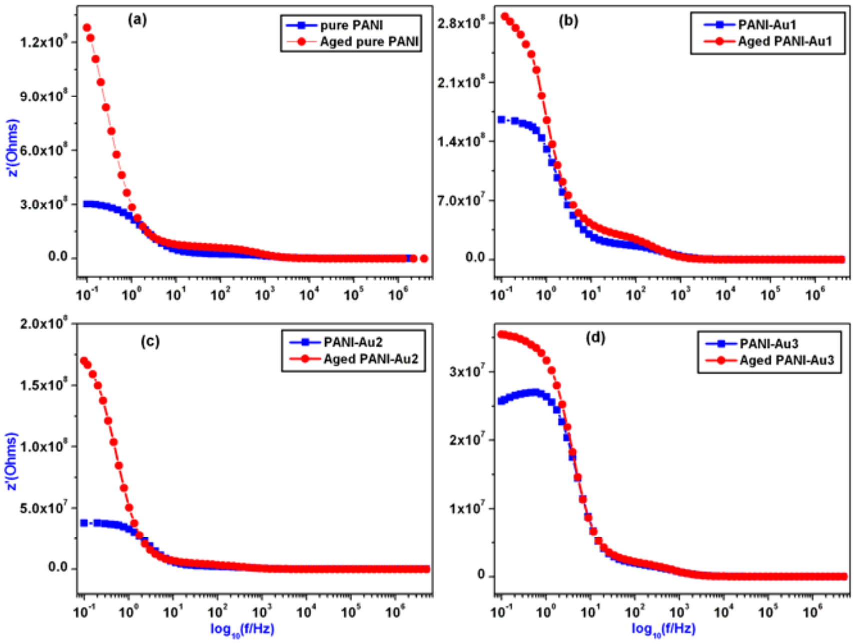

Figure 2. Real part (Z') vs. $\log_{10}f$ of unaged and aged samples.

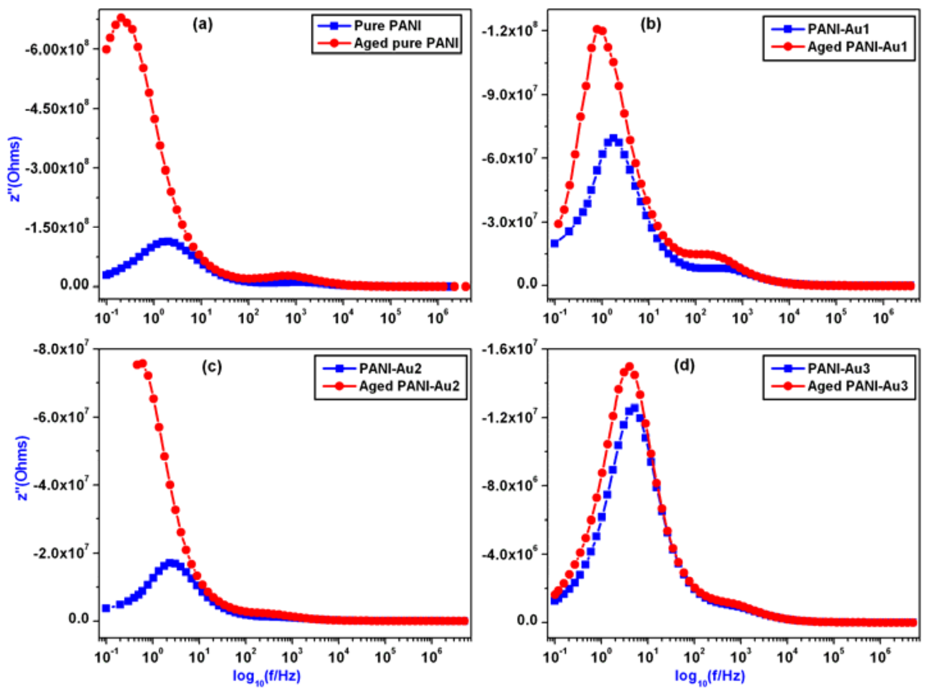

Figure 3. Imaginary part (Z'') vs. $\log_{10}f$ of unaged and aged samples.

Figures 2 and 3 illustrate Z' and Z'' plotted as a function of frequency for unaged and aged samples. Both spectra show a strong peak in the low frequency region and a weak peak in the high frequency region related to the phase of the reduced repeat units and the phase of the oxidized repeat units respectively [11]. It can be examined form Z'' plots that ageing causes an increase in size of the relaxation peaks of both phases with shift in peak positions to lower frequencies. These outcomes reveal that conductivity of samples is reduced with time [14].

From Figure 4, it has been observed that the impedance plane plots of aged pure PANI and PANI/Au nanocomposites show the presence of two arcs. Comparison of impedance plane plots of unaged [11] and aged samples (Figure 4) reveals that ageing causes an increase in size of the arcs representing both phases due to occurrence of crosslinking which occurs preferentially at the quinoid moieties thus obstructing the conduction mechanism between gold nanoparticles and PANI chains. Consequently charge transfer between PANI and gold nanoparticles is hindered thereby increasing the resistivity of aged samples.

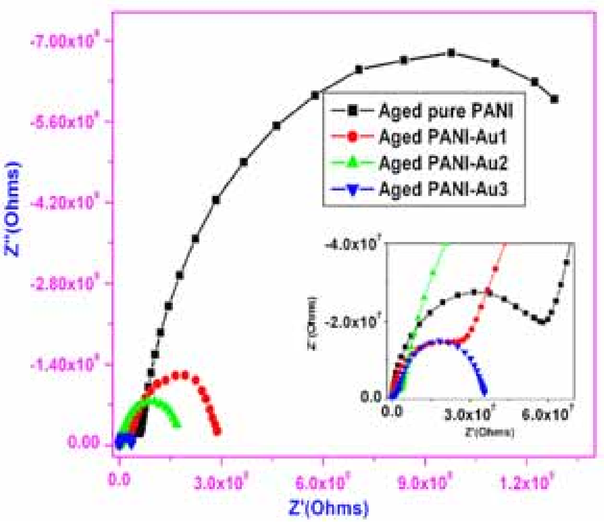

Figure 4. Impedance plane plots of aged pure PANI and aged nanocomposite films. Inset is enlarged portion of 1st small arc of the impedance plane plots.

The equivalent circuit model employed for fitting of impedance data of aged sample is shown in Figure 5. The equivalent circuit configuration of this model is (R_r, CPE_r) and (R_o, CPE_o) for reduced phase and oxidized phase respectively. Table 1 shows the fitting parameters of equivalent circuit model for unaged and aged PANI-Au3 samples. Comparison of these values with unaged samples reveals that resistance of both phases increases with ageing. Thus an increase in R_r (resistance of the phase of reduced repeat units) from 1.52×10^6 Ω and 1.70×10^6 Ω and R_o (resistance of the phase of oxidized repeat units) from 2.75×10^7 Ω to 3.39×10^7 Ω in PANI-Au3 has been observed after 2 years of ageing at room temperature. It is significant to mention that *CPE* parameter and value of n_r and n_o of both phases decrease with time; however, aged samples show more heterogeneity than unaged samples.

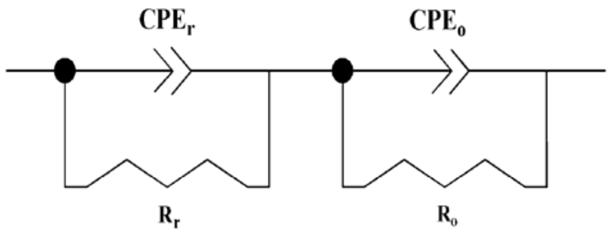

Figure 5. Equivalent circuit model used for fitting of unaged and aged pure PANI and PANI/Au nanocomposite films.

Table 1. Fitting parameters calculated from equivalent circuit model.

Parameters	PANI-Au3	Aged PANI-Au3
CPE_r (F)	1.60×10^{-10}	1.58×10^{-10}
n_r	0.96	0.95
R_r (Ω)	1.52×10^6	1.70×10^6
CPE_o (F)	1.60×10^{-9}	1.58×10^{-9}
n_o	0.91	0.90
R_o (Ω)	2.75×10^7	3.39×10^7

When PANI films are aged at elevated temperature of 120 °C to simulate a storage period of 2 years at 25 °C, two main processes occurs first is the loss of some NMP and second is the occurrence of crosslinking at the quinoid moieties. In PANI/Au nanocomposites crosslinking impede the conduction of electrons between PANI backbone and gold nanoparticles thus decreasing the number of charge carriers contributing to the relaxation process. As a result, conjugation is decreased and barrier height required for transport of charges is increased resulting in the enhancement of resistivity.

4. Conclusions

Gold nanoparticles, prepared by using NMP extract of black tea leaves were incorporated in PANI solution to cast PANI/Au nanocomposite films. Accelerated ageing of these samples was carried out at elevated temperature of 120 °C to simulate a storage period of 2 years at 25 °C. Aged nanocomposites show microphase separation into reduced and oxidized repeat units. Resistivity of aged nanocomposites is more than unaged ones; reason can be attributed to the crosslinking of the PANI films during ageing which obstruct the charge transfer between PANI chains and gold nanoparticles.

Acknowledgement

We gratefully acknowledge the financial support of the Higher Education Commission of Pakistan through the Indigenous Scholarship Scheme for Ph. D. studies of Asma Binat Afzal in Science and Technology (Batch II).

References

[1] V.E. Gul, Structure and properties of conducting polymer composites; VSP: Utrecht, The Netherlands (1996).

[2] A.N. Shipway and I. Willner, Chem. Commun. (2001) 2035.

[3] A.P. Alivisatos, Science **271** (1996) 933.

[4] J.W.G. Wildoer, L.C. Venema, A.G. Rinzler, R.E. Smalley and C. Dekker, Nature **391** (1998) 59.

[5] H.S. Nalwa and R. Gangopadhyay, Conducting Polymer Nanocomposites: Handbook of Organic-Inorganic Hybrid Materials and Nanocomposites, (Ed.) A. De; American Scientific Press Syracuse: New York (2003).

[6] R. Gangopadhyay and A. De, Chem. Mater. **12** (2000) 608.

[7] Y. Ma, N. Li, C. Yang and X. Yang, Physicochem. Eng. Aspects **269** (2005) 1.

[8] J. Wang, K.G. Neoh and E.T. Kang, J. Colloid and Interface Sci. **239** (2001) 78.

[9] T.K. Sarma, D. Chowdhury, A. Paul and A. Chattopadhyay, Chem. Commun. (2002) 1048.

[10] M.A. Breimer, G. Yevgeny, S. Sy and O.A. Sadik, Nano Lett. **1** (2001) 305.

[11] A. B. Afzal, M.J. Akhtar, M. Nadeem and M.M. Hassan, J. Phys. Chem. C **113** (2009) 17560.

[12] A.B. Afzal, M.J. Akhtar and L.G. Svensson, J. Therm. Anal. Calor. **100** (2010) 1017.

[13] J.R. Macdonald (Ed.) Impedance Spectroscopy, John Wiley & Sons, New York (1987).

[14] B.E. Mellander, I. Albinsson, BVR Chowdari, MAKL. Dissayanke and MA. Careem (Eds.) Solid State Ionics: New Developments, World Scientific, Singapore (1996) 83.