# Investigation of ageing effects on the electrical properties of polyaniline/silver nanocomposites

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Polyaniline(PANI)/Ag nanocomposites, synthesized by incorporation of separately prepared silver nanoparticles in 1-methyl-2-pyrrolidinone(NMP) solution of PANI, have been aged at the accelerated temperature of 120 °C to simulate a storage period of 2 years at 25 °C. The accelerated ageing of these materials is done by using the activation energy calculated from data collected using heat flow calorimetry (HFC). The impedance spectroscopic studies of NMP plasticized aged nanocomposite films suggest a microphase separation into reduced and oxidized repeat units. There is crosslinking of the PANI films during ageing thereby obstructing the charge transfer between PANI chains and silver nanoparticles. As a result, the resistivity is increased.

**Keywords:** polyaniline, Ag nanoparticles, impedance spectroscopy, ageing

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## 1. Introduction

The polyaniline (PANI) is known as one of the most important conducting polymers having potentials for multitude applications, especially in electronic devices, chemical sensors and antistatic coatings.[1−3] Metal nanoparticles, particularly copper, silver and gold have been the focus of great interest because of their unique properties.[4−6] Polyaniline–metal nanoparticle composites are reported to show enhanced sensing, electrical and catalytic capabilities, as compared with those of pure PANI.[7,8]

Depending on the oxidation state, PANI exists in various forms, including fully reduced leucoemeraldine base (LEB), fully oxidized pernigraniline base (PNB) and half oxidized/half reduced emeraldine base (PANIEB). Among these, the PANIEB is most stable and can be made conducting by doping with acids or inorganic nanoparticles. It is insoluble in common organic solvents (such as chloroform, xylene and THF) and mostly soluble in 1-methyl-2-pyrrolidinone (NMP).

PANI/Ag nanocomposites can be synthesized by various methods. Khanna *et al.*[9] prepared Ag/PANI nanocomposites via in situ photo-redox mechanism employing UV radiations to reduce silver salt to nanoparticles, which in turn catalyze the oxidation of aniline to PANI. Kang *et al.*[10] synthesized nanocomposites by oxidative polymerization of aniline-stabilized Ag colloids with the $\gamma$-irradiation. Karim *et al.*[11] used in situ gamma radiation induced chemical polymerization method to synthesize the core-shell silver nanocomposites. Previously, we had dispersed Ag nanoparticles in NMP solution of PANIEB by sonification after separate syntheses and then cast into films.[12] The impedance spectroscopy was employed to investigate the effects of Ag nanoparticles on the electrical properties of PANI.

In polymeric materials, the properties change with time and this process is termed as 'ageing'. The ageing is generally categorized by three primary mechanisms: chemical, physical and mechanical.[13] Physical and chemical ageing are intrinsically time-dependent processes; ageing studies are concerned amid understanding how materials and their properties change with time. Knowing how a material degrades means that lifetimes of components can be predicted and with this knowledge the shelf life of materials can be improved. With novel materials and new applications, it is becoming increasingly important to understand the relationships between the elevated temperature and the time-dependent behaviour of polymer composites.[14−16] In this study, accelerated ageing of PANI/Ag nanocomposites has been conducted, using activation energy from heatflow calorimetry (HFC), at elevated temperature of 120 °C to simulate a storage period of 2 years at 25 °C. The effect of ageing on the electrical properties of these

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nanocomposites has been investigated.

## 2. Experiment

The PANIEB was prepared by oxidative polymerization of aniline using ammonium persulfate (APS) as an oxidant.[12] The silver nanoparticles synthesized by using inert gas condensation were added in the NMP solutions of PANIEB in different concentrations, such as 0.25%, 0.5% and 1.0% by weight, to cast PANI silver nanocomposite films. Details have been described elsewhere.[12] These films were aged at elevated temperature of 120 °C to simulate a storage period of 2 years at 25 °C.

The heatflow data of PANI/Ag nanocomposites were obtained with a TAM III microcalorimeter from Thermometric AB, Sweden. Details of the system have been given elsewhere.[17] Measurements were made in the temperature range of 110–140 °C. Impedance measurements of all aged PANI samples were performed using an Alpha-N Analyzer from Novocontrol (Germany) in the frequency range of $0.1 \leq f \leq 10^7$ Hz at room temperature. The WINDETA software had been used for data acquisition, which had been fully automated by interfacing the analyzer with a PC. Before the impedance experiments, the dispersive behaviour of the leads had been carefully checked to ensure the absence of any extraneous inductive or capacitative coupling in the experimental frequency range. The alternating current (ac) signal amplitude used for all these studies was 0.5 V. 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 $Z = Z' + \mathrm{j}Z''$ and the modulus as $M = M' + \mathrm{j}M'$, where $Z'$, $M'$ and $Z''$, $M''$ are the real and the imaginary parts of the impedance and the modulus, respectively. The relationship between $M$ and $Z$ is given by $M = \mathrm{j}\omega C_\mathrm{c} Z$, where $\omega = 2\pi f$ and $C_\mathrm{c}$ is the capacitance of the measuring cell.[18]

## 3. Results and discussion

### 3.1. Isothermal heatflow microcalorimetry

#### 3.1.1. Oxidation study

In order to study the oxidation processes occurring in PANI/Ag nanocomposites, three experiments were conducted for 0.5% Ag films (∼0.1 g) in sealed 3 ml glass ampoules at 110 °C. In the first experiment, the sample was flooded with oxygen gas; in the second experiment, nitrogen gas was flushed through the sample; whereas, the third experiment was performed in air. Figure 1 show the normalized heatflow $\rho$ (μW/g) and the normalized heat energy as a function of time for 0.5% Ag films at 110 °C.

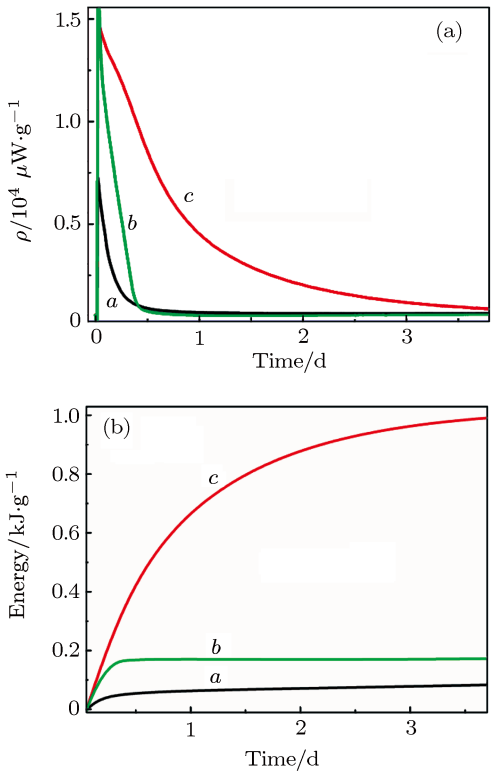



**Fig. 1.** (colour online) Normalized heatflow and normalized energy vs time for 0.5% Ag film in *a*, nitrogen, *b*, air and *c*, oxygen at 110 °C: (a) normalized heatflow, (b) normalized energy.

A strong heatflow signal in oxygen is observed in all samples, which indicates the occurrence of oxidation process in nanocomposites. This strong exotherm is followed by a decrease in heatflow due to gradual consumption of the limited amount of oxygen available in sealed ampoules. The normalized energies measured after 3 days of reaction at 110 °C increases from 83 J/g for nitrogen to 964 J/g for oxygen with 238 J/g in air.

The heatflow signal of nanocomposite samples in nitrogen decays sharply and then becomes almost stable after 1 day. The heatflow signal and its decay can be partially associated with the presence of some traces of oxygen that are difficult to remove during flushing of sample with nitrogen. Additionally, various oxygen-independent processes like thermal degradation can also contribute to the heatflow signals

measured in nitrogen saturated samples. The same heatflow contributions also exist in heatflow curves recorded in the presence of oxygen.

Figure 2 shows the effect of various concentrations of silver nanoparticles on the heatflow curves of nanocomposites in air at 110 °C. It can be observed that all samples show a prominent oxidation peak in the initial part of exotherm, which decays with time due to the depletion of oxygen in the ampoules and then reaches a relatively constant, non-zero level indicating oxygen independent chemical activity in the sample. This constant level is not attained even after 72 hours (h) in the pure PANI film, whereas heatflow curves of the 0.25% Ag, the 0.5% Ag and the 1.0% Ag films turn out to be almost stable after 36, 14 and 8 h, respectively. It indicates that the increase in concentration of silver nanoparticles in nanocomposites represses the oxidation process of PANI. It has been observed that annealing of NMP plasticized PANI films at elevated temperature results in the evaporation of NMP molecules hydrogen bonded to the macromolecular chains.[19] In addition, the crosslinking reaction is proceeded by the formation of radicals at the imine nitrogen, making a chemical bond with the quinoid ring of another PANI chain and forming a 2-dimensional $N$, $N'$-diphenylphenazine polymer structure.[20,21] The macroradicals formed can react with oxygen to form hydroperoxides, which themselves are unstable and decompose to produce alkoxy and hydroxy radicals. These radicals usually react with the polymer backbone to produce water molecules.[22] The oxidation at elevated temperature may cause chain scission and opening of quinoid and benzoid rings thus forming oxime groups and nitrile groups.[20] The presence of silver nanoparticles in nanocomposites may reduce the mobility of polymer chains which suppresses the inter-chain transfer of radicals formed during degradation of nanocomposites at elevated temperature. Consequently, the oxidative degradation of nanocomposite will be reduced.

The energies of various samples can be compared by plotting the evolved heat energies as a function of time, which is shown in Fig. 3. In the pure PANI film, the energy increases sharply even after 3 days of reaction; whereas in nanocomposites it increases initially and then becomes almost stable, indicating entire consumption of the oxygen available in the ampoule. The constant level of heat energy is achieved in less time by increasing the concentration of silver nanoparticles in the nanocomposites. These energy values for all nanocomposites after ∼3.6 days of reaction are given in Table 1. We note that the increase in the concentration of silver nanoparticles from 0.25% to 1.0% results in 26 times decrease in the energy value of the nanocomposite. Energy of oxidation $\Delta H_{ox}$ can be calculated using the un-normalized heat energy (11 J) and the amount of oxygen available in ampoules with air ($n \approx 2.4 \times 10^{-5}$ mole) as $11/2.4 \times 10^{-5} = 458$ kJ/mole $O_2$. From these results we can infer that $\Delta H_{ox}$ is independent of the amount of nano-filler in the polymer.

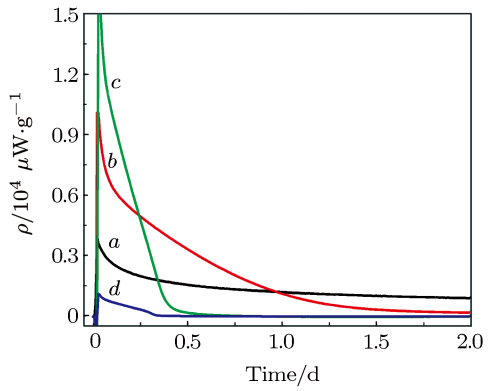



**Fig. 2.** (colour online) Normalized heatflow vs time for $a$, pure PANI film, $b$, 0.25% Ag film, $c$, 0.5% Ag film and $d$, 1.0% Ag film at 110 °C in air.

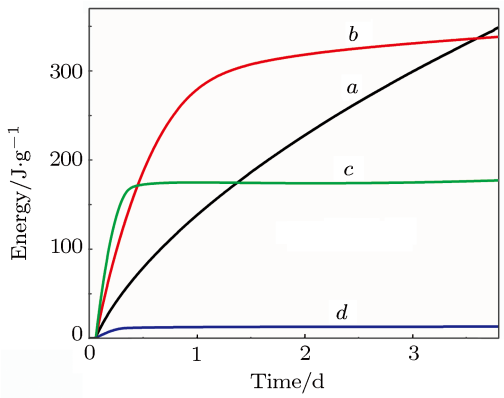



**Fig. 3.** (colour online) Normalized energy vs time for $a$, pure PANI film, $b$, 0.25% Ag film, $c$, 0.5% Ag film and $d$, 1.0% Ag film at 110 °C.

**Table 1.** Normalized energy and % degradation of pure PANI and nanocomposite films after 3.6 days at 110 °C.

| Samples | Energy/J·g$^{-1}$ | Degradation/% |
|---|---|---|
| Pure PANI film | 341 | 7.7 |
| 0.25% Ag film | 337 | 7.6 |
| 0.5% Ag film | 177 | 4.0 |
| 1.0% Ag film | 13 | 0.3 |

### 3.1.2. Thermal stability beyond oxidative degradation

In Fig. 2, the strong peak observed in the initial part of the exotherm indicates that the oxidation process is followed by an almost non-zero constant level of heatflow. It provides the information of thermal stability of the sample. Based on the heatflow curves, we can point out the following sequence of long term thermal stabilities: 1.0% Ag film > 0.5% Ag film > 0.25% Ag film > pure PANI film. The reason of the greater thermal stability of the nanocomposite with higher concentration of Ag nanoparticles is due to the reduced mobility of polymer chains, which slows down the degradation process. These findings support the thermogravimetric analysis results previously presented for PANI/Ag nanocomposites.[12]

### 3.1.3. Influence of temperature

The microcalorimetric measurements of all samples were performed at different temperatures, such as 110 °C, 120 °C and 140 °C. Figure 4 shows the influence of temperature on the heatflow and the energy curves of the 0.5% Ag film in air. It is observed that the curves are shifted towards longer time and lower levels at lower temperatures.

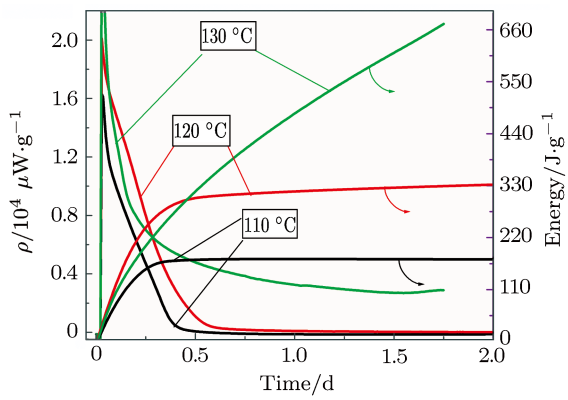



**Fig. 4.** (colour online) Normalized heatflow and normalized energy for 0.5% Ag film at various temperatures.

The influence of temperature on a reaction is determined by the activation energy ($E_a$). The relation between $E_a$ and the rate constant ($k$) of a reaction is given by the following Arrhenius equation:

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

where $A$ is the pre-exponential factor, $E_a$ is the activation energy, $R$ is the gas constant (8.314 J·mol$^{-1}$·K$^{-1}$) and $T$ is the absolute temperature (K). The rate of a reaction at some natural storage temperature ($T_1$) can be calculated from the rate at some elevated temperature ($T_2$) by means of the acceleration factor ($k_T$),[23] which is defined as

$$k_T = \exp\left[\frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)\right]. \tag{2}$$

The $E_a$ is usually calculated from an Arrhenius plot of the natural logarithm of heatflow versus $1/T$, although the fundamental theory makes use of the natural logarithm of rate constant. Activation energies and acceleration factors for samples are summarized in Table 2. It has been observed that the 1% Ag film has a lower value of activation energy as compared to the pure PANI film, even though it is the more stable composite. It indicates the absence of any direct relationship between the activation energy and the thermal stability of PANI/Ag nanocomposites. Using Eq. (2) with natural storage temperature $T_1 = 298$ K (25 °C) and accelerated temperature $T_2 = 393$ K (120 °C) yields the acceleration factors listed in Table 2. Such information has been used for the design of temperature-accelerated ageing of PANI/Ag nanocomposites at elevated temperature of 120 °C to simulate 2 years storage at 25 °C. The aged samples are named as aged pure PANI, aged 0.25% Ag, aged 0.5% Ag and aged 1.0% Ag films.

**Table 2.** Kinetic parameters calculated for pure PANI and nanocomposites using isothermal calorimetric data at 110 °C. The $E_a$ is the activation energy and $k_T$ is the acceleration factor. The $T_{120}$ is the time required to age samples at 120 °C to simulate a period of two years at 25 °C.

| Samples | $E_a$/kJ·mole$^{-1}$ | $k_T$ (25 °C/120 °C) | $T_{120}$/h |
|---|---|---|---|
| Pure PANI film | 127 | $2.38\times10^5$ | 0.07 |
| 0.25% Ag film | 89 | $5.85\times10^3$ | 3.00 |
| 0.5% Ag film | 89 | $5.85\times10^3$ | 3.00 |
| 1.0% Ag film | 117 | $8.98\times10^4$ | 0.20 |

### 3.1.4. Degradation study

Microcalorimetric data can be used to calculate the percent (%) degradation of the samples. The following equation is used to convert energy to % degradation of nanocomposite as

$$d(X) = \frac{100E(t_o)M_X}{\Delta H_X S_X}, \tag{3}$$

where $E(t_o)$ is the total energy (J/g) of the sample released at time $t_o$, $M_X$ is the molecular weight (g/mol) of the repeating unit in the polymer, $\Delta H_X$ is the degradation reaction enthalpy (J/mol) and $S_X$ is the number of reactive sites per repeating unit. Realistic values can generally be assigned to $M_X$ and $S_X$ provided that the chemistry of the degradation reaction is known. The $\Delta H_X$ can be calculated theoretically from reactants and reaction products by means of Hess' law, provided that all products are known. Crude $\Delta H_X$ values can be used for rough estimations of sample degradation. We have used $\Delta H_X = 400$ kJ/mole, $M_X = 90.5$ g/mole and $S_X = 1$ to calculate % degradation of pure PANI and PANI/Ag nanocomposites at energy ($E$) obtained after 88 h of reaction at 110 °C; these results are given in Table 1.

The ageing of PANI films involves the loss of NMP solvent, crosslinking reactions resulting from the coupling of two neighbouring quinoid groups to produce two benzoid groups through a link of nitrogen with its neighbouring quinoid rings to form phenazine heterocycles and chain scissions to form oxime and nitrile groups.[20] From Table 1, it is observed that the incorporation of 1.0% Ag nanoparticles in the polymer matrix decreases the degradation from 7.7% to 0.3%. This decrease is due to the reduced mobility of PANI chains in the nanocomposites thus slowing the transfer of radicals through inter-chain reactions which in turn leads to the slowdown of the degradation process.

## 3.2. Modulus/impedance spectroscopy

The electrical properties of materials are strongly affected by ageing. Figure 5 shows the comparison of imaginary part of modulus plotted as a function of frequency $f$ for unaged and aged pure PANI and nanocomposite films.

A single relaxation peak is observed in Figs. 5(a) and 5(b), whereas a small peak below 5 Hz appears in Figs. 5(c) and 5(d).

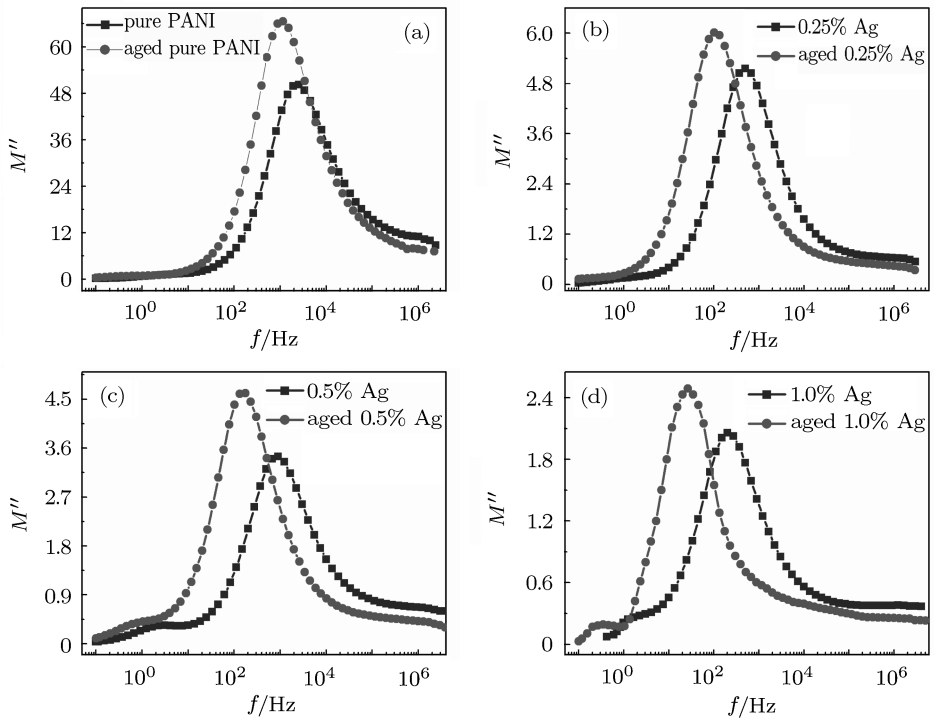



**Fig. 5.** Comparison of $M''$ vs $f$ of unaged and aged samples: (a) pure PANI film, (b) 0.25% Ag film, (c) 0.5% Ag film, (d) 1.0% Ag film.

In addition, this peak becomes more pronounced by increasing the concentration of silver nanoparticles from 0.5% to 1.0%. From Fig. 5, we can see that the ageing of samples causes an increase in the peak height with a shift of the peak to lower frequencies, indicating that the aged samples are less conducting than the unaged ones as suggested by Mellander and Albinsson.[24] The two characteristic relaxation frequencies corresponding to oxidized and reduced repeat units in aged PANI films were not resolved well in modulus plots similar to those in unaged ones; however they are resolved well in impedance plots as discussed below.

The $Z'$ and the $Z''$ versus frequency plots for unaged and aged samples are shown in Figs. 6 and 7 respectively. The behaviour of the real part of impedance of aged samples is similar to that of unaged samples; both spectra show the existence of a strong peak corresponding to the phase of oxidized repeat units at low frequency and a weak peak corresponding to the phase of reduced repeat units at high frequency. The comparisons of $Z'$ and $Z''$ values of unaged and aged samples are given in Table 3, which indicate that in aged samples both phases have high resistivity when compared with unaged ones. From the imaginary part of the impedance (Fig. 7), the relaxation peaks of both phases observed in aged samples are enhanced and shifted towards lower frequency. These results point out that the conductivity of the samples decreases with time, which is consistent with the previous study of Mellander and Albinsson.[24]

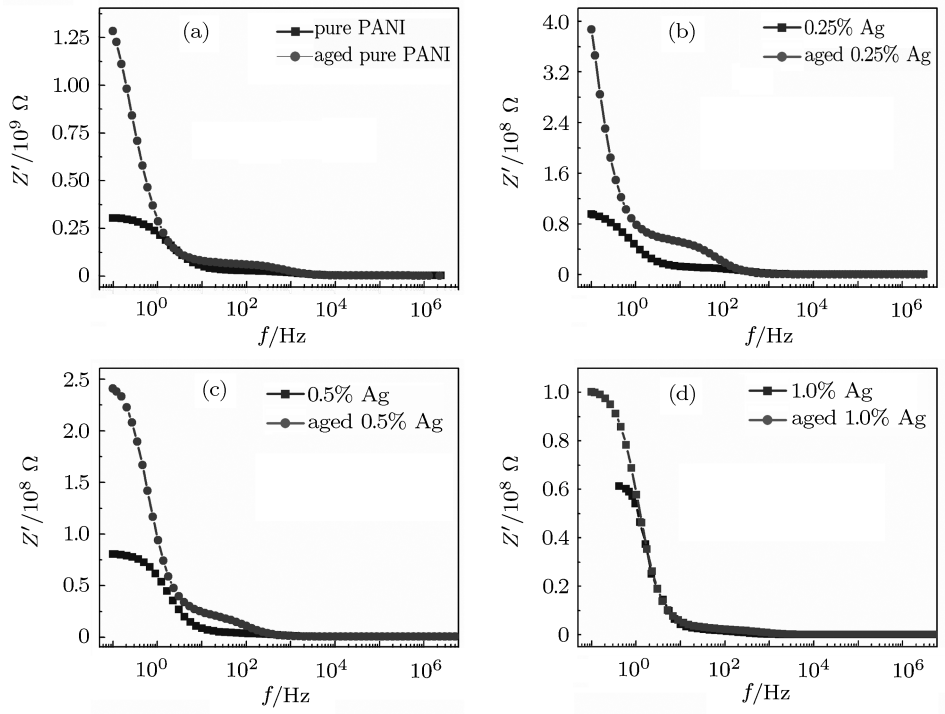



**Fig. 6.** Real part ($Z''$) vs $f$ of unaged and aged samples: (a) pure PANI film, (b) 0.25% Ag film, (c) 0.5% Ag film, (d) 1.0% Ag film.

**Table 3.** Comparison of $Z'$ and $Z''$ values of phases of unaged and aged samples.

| Samples | Phases | Impedance | Pure PANI film | 0.25% Ag film | 0.5% Ag film | 1.0% Ag film |
|---|---|---|---|---|---|---|
| Unaged samples | oxidized phase | $Z'/\Omega$ | $3.0\times10^8$ | $9.5\times10^7$ | $7.9\times10^7$ | $6.1\times10^7$ |
| | | $Z''/\Omega$ | $-1.1\times10^8$ | $-3.7\times10^7$ | $-3.5\times10^7$ | $-3.1\times10^7$ |
| | reduced phase | $Z'/\Omega$ | $1.9\times10^7$ | $8.8\times10^6$ | $2.9\times10^6$ | $2.0\times10^6$ |
| | | $Z''/\Omega$ | $-1.0\times10^7$ | $-4.6\times10^6$ | $-1.7\times10^6$ | $-1.0\times10^6$ |
| Aged samples | oxidized phase | $Z'/\Omega$ | $1.3\times10^9$ | $3.9\times10^8$ | $2.4\times10^8$ | $1.0\times10^8$ |
| | | $Z''/\Omega$ | $-6.7\times10^8$ | $-2.7\times10^8$ | $-1.0\times10^8$ | $-4.6\times10^7$ |
| | reduced phase | $Z'/\Omega$ | $5.1\times10^7$ | $4.5\times10^7$ | $1.7\times10^7$ | $2.1\times10^6$ |
| | | $Z''/\Omega$ | $-2.7\times10^8$ | $-2.3\times10^7$ | $-1.0\times10^7$ | $-1.2\times10^6$ |

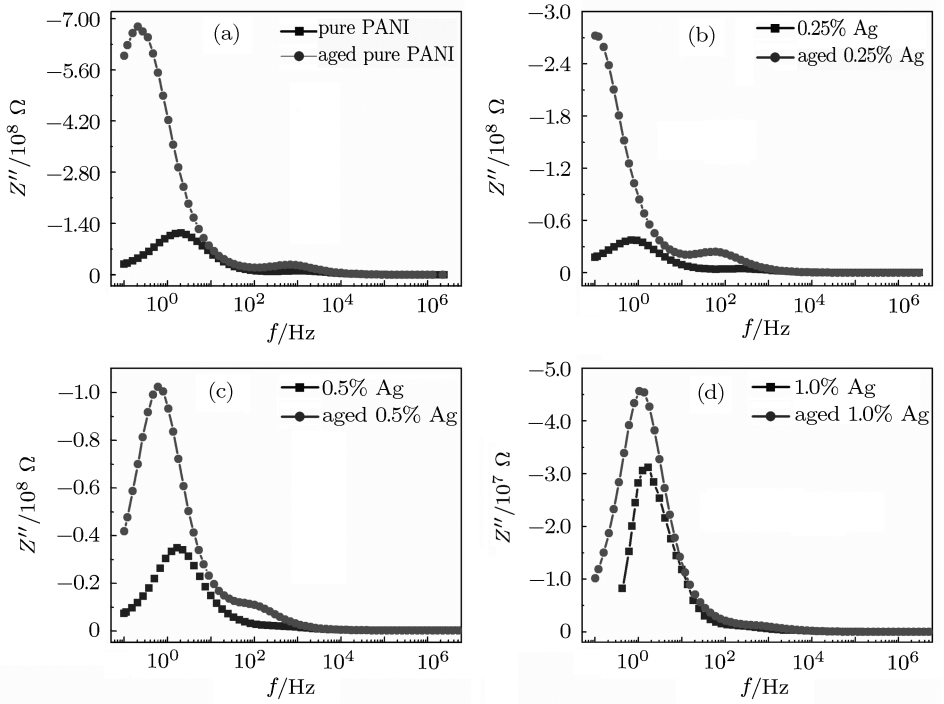



**Fig. 7.** Imaginary part ($Z''$) vs $f$ of unaged and aged samples: (a) pure PANI film, (b) 0.25% Ag film, (c) 0.5% Ag film, (d) 1.0% Ag film.

Impedance plane plots of unaged samples have been investigated previously (Fig. 8);[12] in the present study we have aged these samples to simulate a storage period of 2 years at 25 °C and investigate their electrical properties. Here we compare the impedance plane plots of unaged samples (Fig. 8) with that of aged samples (Fig. 9).

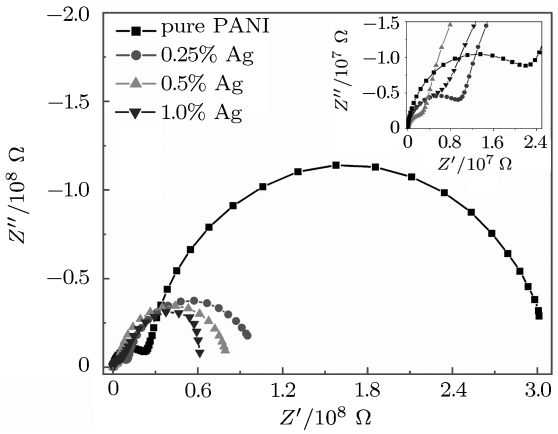



**Fig. 8.** Impedance plane plots of PANI/Ag nanocomposite films. Insert is enlarged portion of the impedance plane plots of the 1st small arc.[12]

We observe a clear resolution of two arcs corresponding to the two phases in NMP plasticized films; which are similar in unaged and aged samples. By comparing Figs. 8 and 9 for unaged and aged samples, it is clear that the sizes of both arcs increase with ageing. The phenomenon can be attributed to the crosslinking of the PANI films during ageing thereby obstructing the charge transfer between PANI and silver nanoparticles. As a result, the resistivity is increased.

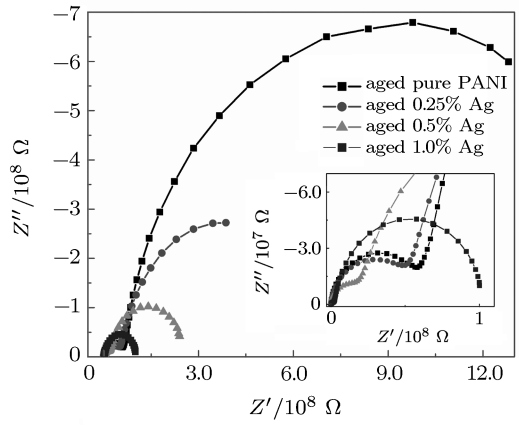



**Fig. 9.** Impedance plane plots of aged pure PANI and aged nanocomposite films. Insert is enlarged portion of the 1st small arc of the impedance plane plots.

Impedance data is analyzed by fitting it to an equivalent circuit model. It has been observed that the best fitting of impedance data is achieved by employing the equivalent circuit configuration presented

in Fig. 10. That is ($R_r$, $CPE_r$) and ($R_o$, $CPE_o$) for reduced phase and oxidized phase respectively, where subscripts "r" and "o" indicate the phases of reduced and oxidized repeat units respectively. The fitting parameters of the equivalent circuit for aged film (0.25% Ag) are presented in Table 4. When these values are compared with those for unaged film (0.25% Ag); we note an increase in the resistance of reduced and oxidized repeat units ($R_r$, $R_o$) from $9.01\times10^6$ Ω and $9.32\times10^7$ Ω to $4.83\times10^7$ Ω and $7.38\times10^8$ Ω respectively, after 2 years ageing. This increase is more significant in oxidized phase than that in reduced phase due to the occurrence of crosslinking in oxidized phase.[25] However, the *CPE* parameters of aged samples decrease with ageing. Ageing process decreases the values of $n_r$ and $n_o$ of both phases, signifying that aged samples show more heterogeneity when compared with unaged ones.

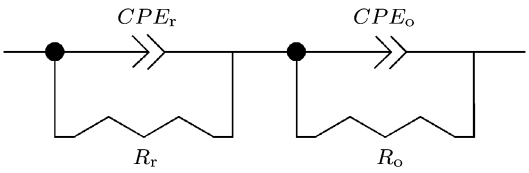



**Fig. 10.** Equivalent circuit model used for fitting impedance data of unaged and aged pure PANI and PANI/Ag nanocomposite films.

**Table 4.** Fitting parameters calculated from the equivalent circuit model.

| Parameters | 0.25% Ag film | Aged 0.25% Ag film |
|---|---|---|
| $CPE_r$/F | $6.30\times10^{-11}$ | $6.08\times10^{-11}$ |
| $n_r$ | 0.96 | 0.95 |
| $R_r/\Omega$ | $9.01\times10^6$ | $4.83\times10^7$ |
| $CPE_o$/F | $2.93\times10^{-9}$ | $2.23\times10^{-9}$ |
| $n_o$ | 0.86 | 0.85 |
| $R_o/\Omega$ | $9.32\times10^7$ | $7.38\times10^8$ |

The accelerated ageing of NMP plasticized PANI films at 120 °C for simulating 2 years causes the evaporation of NMP, which is more serious in reduced phase than in oxidized phase, followed by the crosslinking in the phase of oxidized repeat units. In case of nanocomposites, the crosslinking hinders the conduction mechanism (as discussed earlier) between silver nanoparticles and PANI chains. Consequently, there is a decrease in conjugation and an increase in the barrier height for charge transport, thus increasing the resistivity of aged nanocomposites.

## 4. Conclusions

Silver nanoparticles, prepared by using inert gas condensation were incorporated in PANI solution to cast PANI/Ag nanocomposite films. HFC data of these samples was used for their accelerated ageing at elevated temperature of 120 °C to simulate a storage period of 2 years at 25 °C. Aged nanocomposites showed microphase separations into reduced and oxidized repeat units. Resistivities of aged nanocomposites were larger than those of unaged ones; reason can be attributed to the crosslinking of the PANI films during ageing, which obstructs the charge transfer between PANI chains and silver nanoparticles.

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## References

[1] Gul V E (Ed.) 1996 *Structure and Properties of Conducting Polymer Composites* (Utrecht, The Netherlands: VSP)

[2] Huang J, Virji S, Weiller B H and Kaner R B 2003 *J. Am. Chem. Soc.* **125** 314

[3] Trivedi D C and Dhawan S K 1992 *J. Mater. Chem.* **2** 1091

[4] Kelly K L, Coronado E, Zhao L L and Schatz G C 2003 *J. Phys. Chem.* B **107** 668

[5] Lin J C and Wang C Y 1996 *Mater. Chem. Phys.* **45** 136

[6] Gould I R, Lenhard J R, Muenter A A, Godleski S A and Farid S 2000 *J. Am. Chem. Soc.* **122** 11934

[7] Tian Z Q, Lian Y Z, Wang J Q, Wang S J and Li W H 1991 *J. Electroanal. Chem.* **308** 357

[8] Kitani A, Akashi T, Sugimoto K and Ito S 2001 *Synth. Met.* **121** 1301

[9] Khanna P K, Singh N, Charan S and Viswanath A K 2005 *Mater. Chem. Phys.* **92** 214

[10] Kang Y O, Choi S H, Gopalan A, Lee K P, Kang H D and Song Y S 2006 *J. Non-Cryst. Solids* **352** 463

[11] Karim M R, Lim K T, Lee C J, Bhuiyan M T I, Kim H J, Park L S and Lee M S 2007 *J. Polym. Sci. Part* A *Polym. Chem.* **45** 5741

[12] Afzal A B, Akhtar M J, Nadeem M, Ahmad M, Hassan M M, Yasin T and Mehmood M 2009 *J. Phys.* D: *Appl. Phys.* **42** 015411
[13] Martin R (Ed.) 2008 *Ageing of Composites* (Cambridge:Woodhead Publishing Ltd)
[14] Wingard C W 2000 *Thermochimica Acta* **357–358** 303
[15] Tuukkanen I, Brown S D, Charsley E L, Goodall S J, Rooney J J, Griffiths T T and Lemmetyinen H 2004 *Thermochimica Acta* **417** 223
[16] Roy P K, Surekha P, Rajagopal C, Chatterjee S N and Choudhary V 2005 *Polym. Degrad. Stab.* **90** 577
[17] Afzal A B, Akhtar M J and Svensson L G 2010 *J. Therm. Anal. Calor.* **100** 1017
[18] Macdonald J R (Ed.) 1987 *Impedance Spectroscopy* ( New York: John Wiley & Sons)
[19] Rodrigues P C, Souza G P D, Neto J D D M and Akcelrud L 2002 *Polymer* **43** 5493
[20] Trchova M, Matejka P, Brodinova J, Kalendova A, Prokes J and Stejskal J 2006 *Polym. Degr. Stab.* **91** 114
[21] Scherr E M, MacDiarmid A G, Manohar S K, Masters J G SY, Tang X, Druy M A, Glatkowski P J, Cajipe V B, Fischer J E, Cromack K R, Jozefowicz M E, Jinder J M, MacCall R P and Epstein A J 1991 *Synth. Met.* **41–43** 735
[22] Pielichowski K 1997 *Solid State Ionics* **104** 123
[23] Svensson L G 1997 *J. Therm. Anal. Cal.* **49** 1017
[24] Mellander B E, Albinsson I 1996 In: Chowdari B V R, Dissayanke M A K L and Careem M A (Eds.) *Solid State Ionics: New Developments* (Singapore: World Scientific) p. 83
[25] Lee H T, Chuang K R, Chen S A, Wei P K, Hsu J H and Fann W 1995 *Macromolecules* **28** 7645