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Effects on the Physico-Chemical and Electrical Properties of *In Situ* Hcl-Doped Polyaniline Films to Water as Post-Polymerization Treatment

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ABSTRACT

Background: Polyaniline (PAni) has been one of the most promising materials for numerous practical applications because of its well-defined yet controllable redox states and doping level. However, the processability of pure PAni materials that is, either pure emeraldine salt or base is crucial since its properties are determined by the regularity of its structure which is also influenced by its parameter conditions as well as external stimuli like post-polymerization treatments. Water, for example is known to be included in the preparation of PAni films during and after synthesis. **Objective:** To determine the effect of water as post-polymerization treatment by washing on the physical, chemical, optical and electrical properties of HCl*in situ*-doped polyaniline films. The morphology and the elemental composition of the films were assessed by SEM and EDS, respectively. UV-Vis and FTIR spectroscopies were used to determine the absorption, band gap, purity and oxidation states of PAni films. Direct current conductance of films was determined via two-point probe method.**Results:**Formation of agglomerates on the surface of the films which gradually lessens in longer duration of water treatment was found. Both emeraldine salt and base states of polyaniline co-exist in standard treated film which was red-shifted with increasing water treatment time. Band gap energy values of water treated PAni films are lower than standard treated film which implies that the former are more conductive. The physical structure of PAni was not affected by water. Furthermore, the electrical conductance of water treated films was found to have higher values compared to standard treated film.**Conclusion:**PAni films have been successfully synthesized on glass substrates with lesser agglomerated morphology upon longer water treatment. Films treated with water at shorter time yields pure emeraldine salt PAni resulting to films having lower band gap and higher conductance values.

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INTRODUCTION

Conducting polymers has gained prodigious attention in research community because of their expanding applications in thin filmed sensor arrays (Jin *et al*, 2000; Jin *et al*, 2001), displays, transistors, energy storage and memory devices (Bhadra *et al*, 2009). Among them, polyaniline outshines due to its well-defined protonation and oxidation forms (Stejkal *et al*, 1996; MacDiarmid *et al*, 1987), high stability (Palaniappan and John, 2008; Li *et al*, 2010; Zhang *et al*, 2009; Trchová *et al*, 2009; Luo *et al*, 2011) and controllable conductivity (Sapurina and Shishov, 2012). Intrinsically, it exists in three oxidation states namely: (a) leucoemeraldine, (b) emeraldine and (c) pernigraniline where (b), which is the most conducting state of PAni, is subdivided again into two: the protonated emeraldine salt and its dedoped form emeraldine base (Dhand *et al*, 2011). The physicochemical properties of PAni is dependent on the regularity of the structure of the polymer chains which is concomitantly affected by its (1)synthesis parameters and its (2)reaction with external stimuli such as post-polymerization treatments on the films (Sapurina and Shishov, 2012). The effect of synthesis parameters on the structure of polymer chains has been elucidated through a number of studies already whereas only a handful of literatures have reported the influence of post treatments to the property of the films. Water is one of the compounds used in treating PAni which has distinct role in standard post treatment procedures used to eliminate excess oxidants.Recent study reported that adsorption of water has an adverse effect on the physico-mechanical properties of a polymer that would alter its features (Cotugno *et al*, 2001). For PAni, one study reported the significant frequency shifts that occur on the films as it is observed in the quartz crystal microbalance (QCM) when PAni is exposed in water (Ayad and Zaki, 2008). It was also found out that the conductivity of

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the PAni films doped with inorganic acids such as HCl tends to increase when there is a water vapour adsorption and that doped PAni adsorb greater amount of water (Lubentsov *et al*, 1991). With these literatures at hand, none, to the best of our knowledge has focused on the influences of water particularly on the purity of HCl *in situ*-doped PAni films. Doping is essential since it increases the magnitude of conductivity of PAni from $10^{-10} - 10^{4} S.cm^{-1}$ resultingfrom the presence of delocalized π - system in its backbone(MacDiarmid and Epstein, 1992).In most of the reported studies, dopant is introduced after polymerization of PAni takes place.

In this present work, PAni is synthesized through the conventional chemical oxidative polymerization of aniline and *in situ* doping of films has been simultaneously carried out using 0.4M hydrochloric acid. Post treatment water washing have been varied according to the extent of exposure. The surface morphology of the PAni films was investigated through SEM. UV Vis and FTIR characterizations of the films has been carried out to determine the absorption peaks, band gap, purity and oxidation states of PAni films produced. Furthermore, the conductance of the films was determined via two-point probe method.

1. *Methodology:*

The PAni films were synthesized on glass substrates through chemical oxidative polymerization. The monomer aniline (1.83ml) was first dissolved in 50 ml 0.4M HCl; the oxidant, ammonium peroxydisulfate (APS, 5.71g) was dissolved also in 50ml 0.4M HCl. After magnetic stirring for 30 mins, aniline hydrochloride was carefully transferred to a reaction vessel where glass slides are standing freely. Then APS-HCl solution was poured out into the same vessel where the phase of polymerization was monitored by temperature changes recorded every 5 s for 30 mins. The substrate coated with PAni films were then removed and washed with standard washing procedure using 0.2M HCl to remove adhering PAni precipitates, then with ethanol, and water for 10 s respectively. The remaining films were washed with water separately for 10 s, 20s, 30s, 30mins, and 1 hour as part of the post polymerization treatment. All the films were oven-dried at 60℃for10 mins.The morphology and elemental composition of the films were viewed throughJEOL JSM-6510LA Analytical Scanning Electron Microscopy (SEM). The absorption spectra of the PAni films deposited on glass substrates were recorded with a UV-Vis spectrometer Lambda 20 (Perkin Elmer, UK). The FTIR spectra of the samples were obtained by an UATR-FTIR spectrometer (Perkin Elmer, UK) and the conductivity of the films was calculated from IV curve characterization performed through NI-PXI IV tracer.

2. *Results:*

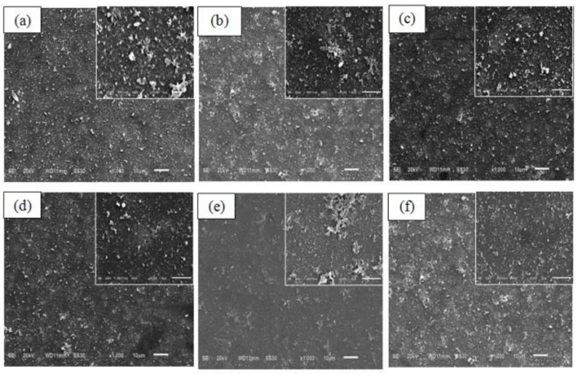

Fig. 1: SEM micrographs of HCl *in situ*-doped PAni films at 1000x that are post-treated with (a) standard procedure (W-st) and water only for (b) 10 seconds (W-10s), (c) 20 seconds (W-20s), (d) 30 seconds (W-30s), (e) 30 minutes (W-30mins) and (f) 1 hour (W-1hr). Inset images show magnified view of the films.

The surface morphology of standard and water treated HCl *in situ*-doped PAni films was viewed through scanning electron microscopy (SEM). Micrographs of standard and water treated PAni films (Fig.1) reveal the presence of agglomerates that are randomly distributed on its surface. The amount of agglomerations that are observed on the surface of the samplestends to lessen as the time of treatment is increased except for film treated with water only for 30 minutes.

In Figure 3, a broad absorption band initiated at ~500 nm is found in the spectra of standard treated film (W-st) consisting of peaks at ~600 nm and ~800 nm which are characteristic peaks of dedoped and doped PAni respectively (Stejkal *et al*, 2012; Sapurina *et al*, 2002).Specifically, these peaks are attributed to the exciton absorption of the quinoid ring and π^*- polaron transition in emeraldine base (EB) and salt (ES). High absorption spectra at 800 nm are observed in the spectra of water treated films for 10, 20 and 30 seconds treatment.

The band gap energy of the films were calculated using the Tauc relation (equation 1)

$$(\alpha h\upsilon)^2 = A(h\upsilon - E_g) \qquad \text{(Eq.1)}$$

where A is the energy independent constant, α is the absorption coefficient, h is the Planck's constant and υ is the frequency over 200-900 nm wavelength range. The absorbance coefficient is determined from the wavelength dependent absorbance which is computed from the normalized transmission spectra of the films. Then by extrapolating the linear part of the absorbance edge of the films, the band gap(Table 1) of the films is within the range of 1.87-2 eV.

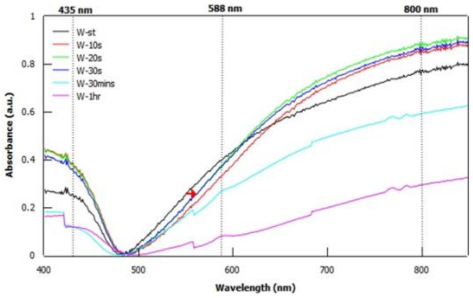

Fig. 3: UV-vis spectra water treated HCl *in-situ* doped PAni films.

Table 1: Band gap energy of water treated PAni films.

Samples	Band gap energy (eV)
Standard treatment (W-st)	2.09± 0.03
10 seconds (W-10s)	1.98± 0.02
20 seconds (W-20s)	2.03± 0.02
30 seconds (W-30s)	2.02± 0.02
30 minutes (W-30 mins)	1.87± 0.03
1 hour (W-1 hr)	1.77± 0.05

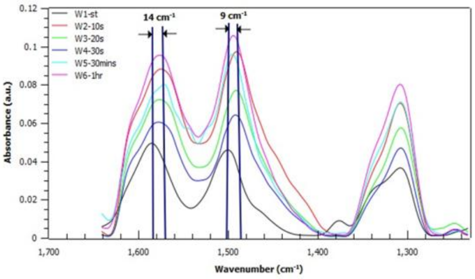

Fig 5: UATR-FTIR spectra of water treated HCl *in-situ* doped PAni films in 1700-1200 cm^{-1} region.

Figure 5 shows the main characteristic peaks of PAni emeraldine base at 1586 and 1502 cm^{-1} attributed to the C=C stretching vibrations of quinone and benzene units respectively in the spectra of standard treated (W-st) film. These peaks, however shift to lower wavenumber in the spectra of water treated PAni films.

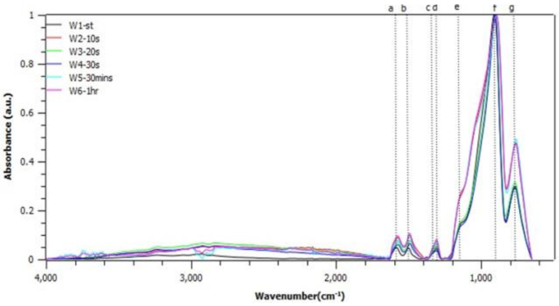

Fig. 4: UATR-FTIR spectra of water treated HCl *in-situ* doped PAni films with peaks at (a) 1586, (b) 1502, (c) 1332, (d) 1304, (e) 1154, (f) 902, and (g) 765 cm^{-1}.

Figure 4 shows the full vibrational spectra of standard and water treated HCl-*in situ* doped PAni films. The main absorption peaks at (a)1586and (b) 1502 cm^{-1} corresponds to the C = N stretching vibration of the quinoid ringand C = C stretching vibration of the benzenoid ring unit respectively.The peaks at (c) 1332 and (d) 1304 cm^{-1} is associated to the C – N stretching of the polaron units and the benzenoid ring structures of PAni respectively. The existence of the peak (d) further signifies that π-electron delocalization occurred in the polymer chain.The peak that is incident at (e) 1154 cm^{-1} is attributed to the vibration of $-NH^{+}=$structures that are usually formed upon the protonation of imine group. Moreover, the peaks of the PAni films located at (f) 902 and (g)765 cm^{-1}are the corresponding peaks of the glass substrates used.

Table 2: Conductance of water treated HCl *in situ*-doped PAni films.

Samples	Conductance (S)
Standard treatment (W-st)	$5.04 \times 10^{-07} \pm 1.02 \times 10^{-08}$
10 seconds (W-10s)	$2.06 \times 10^{-05} \pm 3.00 \times 10^{-07}$
20 seconds (W-20s)	$8.95 \times 10^{-06} \pm 1.02 \times 10^{-08}$
30 seconds (W-30s)	$4.42 \times 10^{-06} \pm 1.02 \times 10^{-07}$
30 minutes (W-30 mins)	$3.44 \times 10^{-06} \pm 6.88 \times 10^{-08}$
1 hour (W-1 hr)	$2.59 \times 10^{-04} \pm 1.02 \times 10^{-06}$

The electrical conductivity of PAni film samples are determined through two-point probe method. The conductance of standard and water treated films as summarized in Table 2 have the values 10^{-7} to 10^{-4} S belonging to the range of semiconductors and are observed to have an ohmic behavior.

Discussion:

The formation of agglomerations revealed in the SEM micrographs of standard and water treated PAni films in Figure 1 is caused by the adhesion and incorporation of PAni precipitates which are also responsible for the non-uniform surface morphology of the films. This is typical for a PAni that is synthesized using HCl through oxidative polymerization. The absorption spectra of standard treated films exhibitthe co-existence of emeraldine base and salt due to the existence of the typical peaks corresponding to two intrinsic redox states. The presence of EB peak is due to the OH ions in ethanol which interacted with the amine units of PAni.The shifting of the band,from lower to higher wavelength, whichoccurs in the UV-vis spectra of water treated filmsindicatesinteraction between water and PAni films. More specifically, this may be due to hydrogen bonding that may occur in the imine and amine regions of PAni.Moreover, high values of polaronic absorbance at 435 and 800 nm which is observed in the spectra of PAni films treated with water for 10 to 30 seconds (with 10 seconds increment) suggests that the films are more protonated than other films. This iscaused by the adsorption of H^{+} ions on the polymer backbone in the imine region.For the spectra of PAni films treated with water for 30 minutes and 1 hour, a peak at 600 nm is visible which is typical for dedoped form of PAni (Stejkal *et al*, 2012).The existence of this peak in the spectra of the films is due to the OH ions of water interacting with PAni in the amine region.The samples treated with water for 10, 20 and 30 seconds, 30 minutes and 1 hour are found to be more conductive than PAni film that has undergone standard treatment since they have lower band gap energy as shown in Table 1.

The changes in the morphology and molecular structure based on the analysis of SEM and UV-Vis are well supported by the vibrational spectra of standard and water treated PAni films. Some remarkable differences are observed in the spectrum within the range of 1700-1200 cm^{-1} (Fig.5). The red shifting of the peaks that is due to the stretching deformations of quinoid and benzenoid units suggests doping phenomenain the films (Stejskal *et al*, 2004). This noticeable changes could not be caused by the precision of the machine used since the shifts are too large, and thus, credited to the interaction of PAni and water explained in the UV-vis analysis of the samples.

A peak at 1377 cm^{-1} which is typical for emeraldine base PAni is very prominent in the spectra of standard treated PAni films. This peak also occurs in the spectra of water treated PAni films for 30 minutes and 1 hour, but not that noticeable compared to the standard treated PAni film which support the UV-vis results. The existence of the absorption bands at 1608-1611 and ~ 1245 cm^{-1}in the spectra of water treated PAni films which are strengthened during polymer chain protonation and polaron formation shows that the films are in the emeraldine salt form. The appearance of peak that signifies $\pi-$electron delocalization in the polymer chain is due to the protonation process through HCl-mediated polymerization. The degree of oxidation of the films calculated by the ratio of the integrated area of the fitted peak in the FTIR spectra that correspond to the quinoid rings to the respective integrated area of benzenoid rings of PAni approaches to ~ 50 % suggesting that the films are all in emeraldine state. Further investigation on the response of PAni films to water verifies that water does not affect the physical structures of the PAni film samples because no evident peak is located at 3500 cm^{-1} corresponding to the physical adsorption of water on the PAni films. This means that the interaction of water and PAni is on the molecular level as supported by the shifts that occur in the spectra of PAni films.

The values of the conductance for water treated films are greater compared to the standard treated film. This somehow supports the claim presented in UV-vis and FTIR analysis wherein water treated films becomes more protonated than standard treated sample.

Conclusion:

PAni films were successfully synthesized by chemical oxidative polymerization of aniline on glass substrates with *in situ* doping subjected to water washing post polymerization treatment. Agglomerations were found at the surface of the synthesized films which become less evident upon longer water treatment. The emeraldine base and salt form of PAni are found to co-exist in standard and water treated films for 30 minutes and 1 hour. Water treated PAni films were found to have lower band gap energy with high electrical conductance. Hence, it is recommended that for the preparation of polyaniline films of this type, water washing within 10 to 30 seconds should be done to produce PAni emeraldine salt films.

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