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Polyaniline Conducting Electroactive Polymers: Thermal and Environmental Stability Studies

REZA ANSARI* and M. B. KEIVANI

*Chemistry Department, Faculty of science,
Guilan University, Rasht, Iran, POB 41335-1914.
Iranian Academic Center for Education, Culture & Research (ACECR)
Guilan Branch, Rasht, Iran
E mail: ransari@guilan.ac.ir

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Abstract: In the current studies, polyaniline (PANi) was prepared both chemical and electrochemically in the presence of different bronsted acids from aqueous solutions. The effect of thermal treatment on electrical conductivity, and thermal stability of the PANi conducting polymers were investigated using 4-point probe and TGA techniques respectively. It was found that polymer prepared by CV method is more thermally stable than those prepared by the other electrochemical techniques. In this paper we have also reviewed some fundamental information about synthesis, general properties, diverse applications, thermal and environmental stability of polyaniline conducting polymers.

Keywords: Polyaniline, conducting polymer, electroactive, thermal and environmental stability

Introduction

Thermal studies of PANi conducting polymers are particularly important when one considers the use of elevated temperatures to process PANi and its blends into technologically useful forms. In any practical application, knowledge of the stability and degradation mechanism of this class of conducting polymers is also of primary importance. For many practical applications of polyaniline conducting polymers such as battery applications, the thermal stability of the material is very important. Among conducting polymers, a great deal of researches have been devoted to PANi due to its unique electrical, electrochemical properties, high environmental stability, easy polymerization and low cost of monomer¹⁻¹⁰.

Furthermore, the superior processibility of PANi stimulated several investigations for potential applications of this intrinsically conductive polymer. However, melt processing is not possible, since the polymer decomposes at temperatures below its softening or melting point. Polyaniline can be synthesised by the oxidative polymerisation of aniline in aqueous acidic media using a variety of oxidising agents such as $(\text{NH}_4)_2\text{S}_2\text{O}_8$, KIO_3 and $\text{K}_2\text{Cr}_2\text{O}_7$. For large scale production the chemical method is more convenient because the scale of products in electrochemical synthesis depends on the size of electrode¹¹⁻¹⁸. Polyaniline films can also be easily synthesised by electrochemical deposition employing potentiostatic, potentiodynamic or galvanostatic methods¹⁹⁻²¹ through oxidation of aniline in bronsted acid medium. A major problem however is the production of the conducting form of polyaniline. Therefore, it becomes necessary to critically control all the process parameters involved in a particular deposition technique so as to obtain the deposit only with the particular oxidation state of interest²¹. For example, cyclic potential sweep deposition produces films with better morphology, conductivity and structural integrity than potentiostatic deposition²⁰.

Polymer synthesised using chemical methods is a powdery material and the properties of chemically synthesised polyaniline from aqueous solutions are determined by a wide variety of synthesis parameters, such as *pH*, aniline/oxidant ratios, polymerisation temperature and time, type/ concentration of oxidising agents and protonic acids¹⁴. It has been reported that the aniline/oxidant ratio has a minor effect on the electrical conductivity of the polyanilines produced. By contrast, the polymer yield was strongly dependent on this ratio. Polyaniline in its base form (by treatment with dilute aqueous alkali e.g. 0.1M NH_4OH) is insoluble in water and soluble in several aqueous and non-aqueous solvents such as concentrated sulphuric acid, acetic acid (%80), formic acid, dimethylsulfoxide (DMSO), dimethylformamide (DMF), and 1-methyl 2-pyrrolidinone (NMP)¹⁵.

Large flexible films of emeraldine base can be cast from NMP solution which can be thermally stretch-aligned at $\sim 140^\circ\text{C}$ up to 4.5 times their original length. Conductivities of about 400 S/cm with significantly greater tensile strength ($\sim 145\text{MPa}$) and crystallinity can be obtained upon doping with HCl after stretching⁷. This permits it to be solution processed to produce large, flexible, free standing films of the emeraldine base polymer which can be protonated (doped) with a non-oxidising protonic acid such as HCl to films having conductivities of $\sim 10\text{ S/cm}$ ¹⁶. On the basis of conductivity, and stability of the product, HCl and H_2SO_4 are the best dopants for protonation of PANi. The electrochemical polymerisation of aniline is believed to proceed via the cation radical according to the following scheme²². It has been found that the growth mechanism of PANi is autocatalytic²³. It is not due to a simple buildup of layers on the surface like PPy. The oxidation process is accompanied by the insertion of anion to maintain the charge neutrality. Polyaniline has been reported to have the following idealised structure (Figure 1)²⁴.

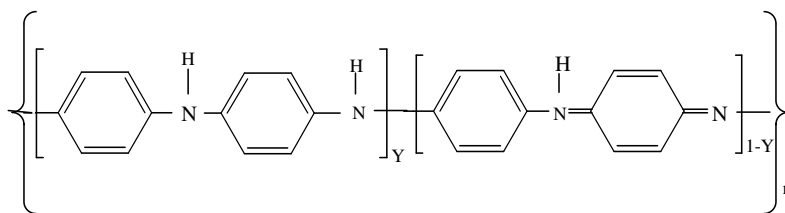


Figure 1 The general structure of PANi conducting polymers

The structure containing Y reduced (benzenoid diamine) and (1-Y) oxidised repeat groups(quinoid diamine) where the oxidation state can be defined by the value of (1-Y). Y can in principle be varied continuously from one (the completely reduced material), to zero (the completely oxidised polymer). The completely reduced material (Y = 1) is called Leucoemeraldine and the completely oxidised form (Y = 0) is termed pernigraniline. Intermediate oxidation states where Y = 0.75 and 0.25 are called protoemeraldine and nigraniline¹⁷. The true emeraldine oxidation state y = 0.5 of polyaniline in which 50% of the nitrogen atoms are protonated (consists of equal numbers of reduced and oxidised repeat units) is the most highly conducting (metallic) form of the polymer⁶. The relative content of the benzenoid and quinoid forms depends on the acid concentration and the degree of oxidation of the polymer²². It can be protonated by aqueous acids with a concomitant increase in conductivity of almost 10 orders of magnitude (to a maximum conductivity of 10¹-10² S cm⁻¹), forming a polysemiquinone radical which contains a delocalized half-filled broad polaron energy band²⁵. Of the different oxidation states of polyaniline (Figure 2), the emeraldine salt (50% oxidised) is the only electrically conducting form while all other forms are insulating^{26,27}. Each oxidation state can exist in the form of its base or its protonated form (salt) by treatment of the base with acid (Figure 2). These forms may be interconverted by chemical and/or electrochemical oxidation or reduction²⁶.

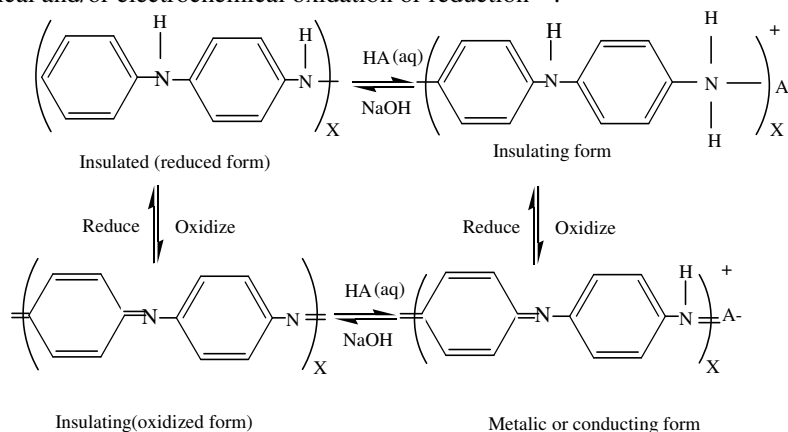


Figure 2 . Four redox forms of polyaniline

Electrical conductivity

Polyaniline is one of the conducting polymers in which the transition between the insulating and conducting states may involve only migration of a protons a polaron hopping mechanism has been suggested¹¹. Cyclic resistometry analysis shows that PANi is less conductive in the fully reduced and fully oxidised states. It is conductive when it is partially oxidised and is the most conductive state when it is 50% reduced and 50% oxidised. Electrical conductivity of the polyaniline is strongly sensitive to most synthesis variables and post-treatments¹². The conductivity of polyaniline, unlike all other conducting polymers depends on two variables, namely the degree of oxidation (electrochemical doping) and the degree of protonation (acid doping) of the material²⁸. To a lesser extent, it is also dependent on the type of anion present²⁹. However, It has been found that the nature of anion can have an important effect on the properties and molecular structure of the polymer³⁰. The conductivity of the electrochemically prepared polyaniline increases with decreasing solution pH of and polymerisation temperature²².

A maximum conductivity up to 500 S/cm at room temperature for oriented PANi films prepared chemically and cast from NMP solvent has been achieved³¹. The conductivity of PANi without doping (*pH* 6.3) at room temperature is only 10-10 S/cm. With decreasing *pH*, the conductivity increases with a jump at *pH* 3-4³². It has also been found that moisture acts as a plasticizer and also improves conductivity¹⁷. It has also been found that drying the polymer under vacuum in order to remove the residual traces of water decreases the conductivity of the polymer while upon exposure to water vapor the conductivity increases³³.

Electroactivity

In many applications of polyanilines eg. in batteries³⁷ sensors⁴¹, chemically modified electrode sensors⁴² and *pH* sensors⁴³, membranes for separation⁴⁴ and electrochromic devices⁴⁵, the application relies on the electroactive switching properties of polyanilines. All of these applications require that the material have a highly reversible and rapid switching rate while maintaining chemical stability. The switching properties of polyaniline are affected by the nature of the acid electrolyte⁴⁶, *pH*⁴⁷, anions⁴⁸ and the solvent⁴⁹. Polyaniline at *pH* 6, for example, becomes essentially electrochemically inactive, but regains electroactivity in a completely reversible manner when placed in a more acidic electrolyte⁸. Depending upon the proton content of the polyaniline film and the availability of protons in the medium, one can obtain completely resistive and electroinactive films or electroactive and conducting films⁴⁹. Using cyclic voltammetry (CV) experiments it has been indicated¹³ that the chemically prepared PANi has properties very similar to the electrochemically prepared PANi. The oxidising agent type or concentration has little effect on the electroactivity and the conductivity of the chemically prepared material. The redox reaction of the film is accompanied by colour changes where the film changes from a blue color when the electrode potential is positive of +0.20V to a transparent yellow when it is negative of 0.0V, and yellow at -0.20V (neutral form)⁵⁰.

Experimental

A three electrode electrochemical cell was used to prepare PANi conducting polymers used in these studies⁴. Electropolymerisation of polyaniline was carried out using 0.4M of freshly distilled aniline in a solution of 1M selected acids. A constant potential (0.80 V versus Ag/AgCl) and potentiodynamic method (scanning the potential between -0.20 and +0.90 V, scan rate 20 mV/sec) was employed. Platinum plate was employed as working electrode, platinum (gauze) was used as the auxiliary electrode, and an Ag/AgCl in 3M NaCl electrode was used as the reference throughout this work. Electropolymerisation was carried out at RT. Polymer powder was removed from the electrode and washed completely with distilled water. The samples dried under ambient conditions before TGA. The chemical polymerization was carried out using freshly distilled aniline and ammonium persulfate as oxidant. The details of the procedure can be found in our previously published work⁵³.

Instrumentation

For the potentiodynamic (CV) growth of PANi, electropolymerisation was carried out using a BAS CV-27. Alternatively, a Princeton Applied Research (PAR) Potentiostat/Galvanostat (Model 363) was employed for potentiostatic deposition of PANi. Thermal Gravimetric Analysis (TGA) was carried out using a Rigaku Thermal Analyzer instrument. The analyses were conducted on 10 mg samples of polymer heated from room temperature to 500°C.

Results and Discussion

Synthesis of Polyaniline conducting polymers

Polyaniline can be synthesised either chemically or electrochemically in aqueous and non-aqueous solvents. The overall polymerisation reaction of PANi can be simply shown in Figure 3.

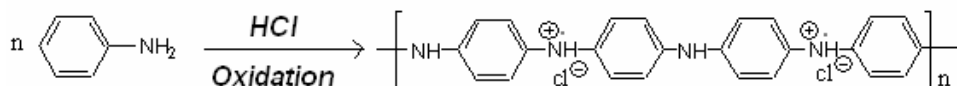


Figure 3 polymerisation reaction of polyaniline

The oxidation process is accompanied by the insertion of anions of acid electrolyte in order to maintain the charge neutrality of the final polymer. However, PANi in contrast to polypyrrole conducting polymers could not be prepared as free standing film electrochemically. Electrochemically prepared PANi has lower conductivity, a powdery appearance and easily wipes off the electrode surface. For electrochemical deposition of PANi, the growth potential of polyaniline was first determined using CV method as shown in Figure 4. Polymer samples were prepared employing the potentiostatic or CV methods because of the greater control which can be achieved over the electrode potential. From the CV recorded during electrodeposition, it was found that a suitable potential for potentiostatic growth of polymer was found 0.8 V (see Figure 4). Below this potential, the rate of oxidation was too low. Anodic polarization at potentials more than 0.85V causes oxidation leading to gradual degradation of polymer film.

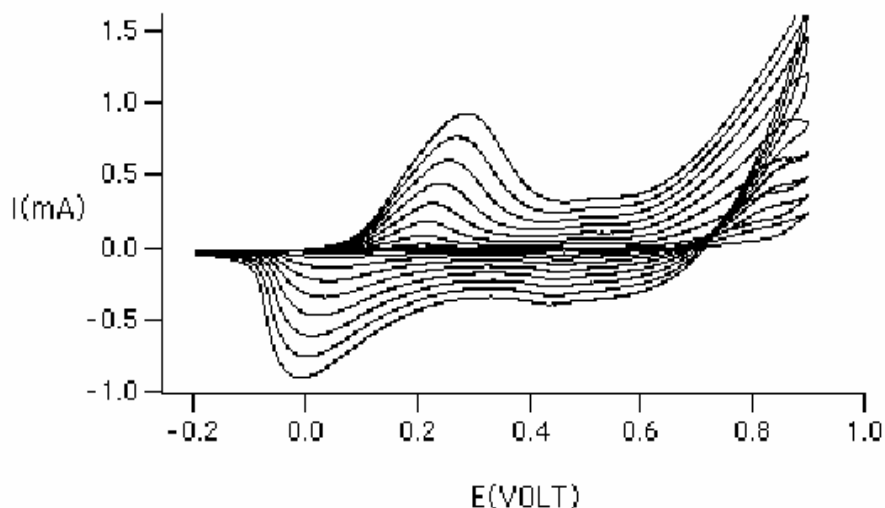


Figure 4. Cyclic voltammograms (CV) recorded during growth for polyaniline. Scan rate= 20mV/sec. Electropolymerisation was carried out using a solution of 0.4M aniline in 1 M HCl.

A typical CV of a polyaniline sample prepared electrochemically is shown in Figure 5.

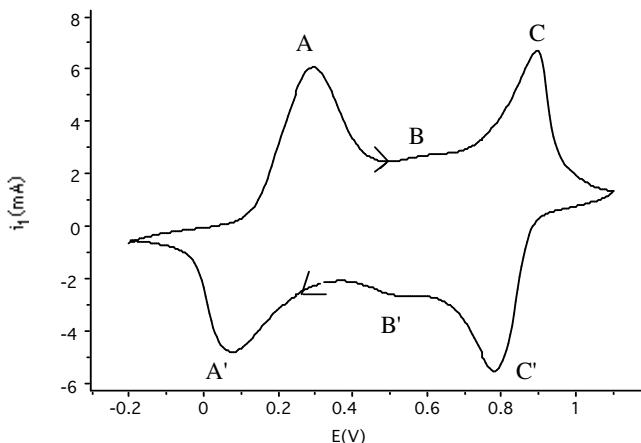


Figure 5. Typical cyclic voltammogram (CV) of Polyaniline synthesised electrochemically ($E_{app} = 0.80$ V versus Ag/AgCl) from a solution of 0.4M aniline and 1M HCl. CV was recorded after growth in 1M HCl as supporting electrolyte. Glassy carbon was used as the working electrode. Scan rate was 20 mV/s.

The responses observed (A/A') and C/C') are due to the reactions described in the following equations(Figure 6)

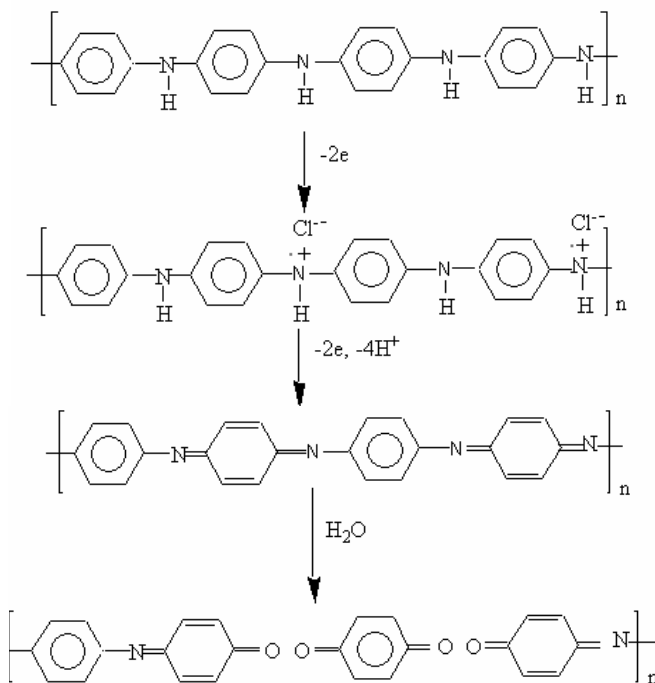
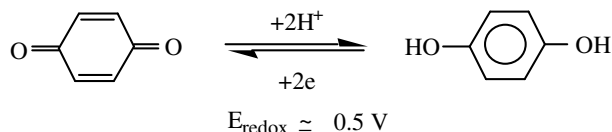


Figure 6. Redox reactions of PANi

Electroneutrality is maintained by the incorporation of anions from solution. Initial electrochemical responses occur without loss or gain of protons, however, the second electrochemical response involves protonation and deprotonation. The middle peak (B/B') \sim 0.5V in the cathodic scan can be related to the formation of quinones (mostly benzoquinone) as a consequence of a hydrolysis reaction in water.



It has been reported that the CV analysis of PANi prepared electrochemically in the presence or absence of aniline suffers from degradation when the potential exceeds +0.85V and below this potential, it is stable and the redox reaction of the film is reversible. This has been attributed to hydrolysis of the imine to form benzoquinone. Upon electrochemical doping, delocalized positive charges form along the PANi chains. Using quartz crystal microbalance (QCM) technique it has been shown⁵¹ that the loss of electrochemical responses is accompanied by a large frequency increase which indicates that the hydrolysis (changing imine into benzoquinone) products of the oxidised film are soluble and leave the surface. Because of the pH dependence of the second oxidation process the maximum potential which can be attained without film degradation is also pH dependent⁵¹. The rate of electrochemical reversibility of polyaniline prepared in aqueous solution with various acid electrolytes depends on the acidity of the solution but is independent of the nature of counterion⁵². The films are also electroactive in non-aqueous solvents containing both organic salt and protic acid electrolyte.

Effect of thermal treatment on electroactivity of PANi

We have shown⁵³ that the electroactivity of polyaniline starts to decrease after 70°C but then shows little further deterioration until 150°C. This seems to be almost independent of the drying atmosphere, although the inert one is slightly better than air. The electroactivity of polyanilines doped with HCl prepared chemically or electrochemically both in reduced and oxidized and fully oxidized forms are unstable at T > 150°C in air but keep their electroactivity up to 300 °C under nitrogen. Since the thermal stability of the polyaniline is greatly dependent on the type of the dopant acid employed during synthesis. By contrast, the exposure to an oxygenated environment at elevated temperatures at 200 °C resulted in a total loss in electroactivity. It may be concluded that the rate of decay of electroactivity was much faster when samples were heated in air at T > 150 °C. This is probably due to chemical reaction of O₂ with the highly conjugated PANi system. This was not observed when the polymer was exposed to this temperature in an inert atmosphere. A major irreversible loss in electroactivity was observed at T > 200 °C in air and T > 300 °C in nitrogen⁵³. Some changes in polymer structure such as crosslinking³⁵ or chlorination³⁸ of aromatic rings at high temperature are likely reasons for the loss of electroactivity after thermal treatment under nitrogen at temperatures below the decomposition temperature. In air, however, the chemical reaction of oxygen with the polymer seems to be responsible for the electroactivity decay.

Effect of thermal treatment on conductivity of PANi prepared chemically

In order to measure conductivity of PANi, the polymer was synthesized chemically and then used solvent cast method⁵³, since electrochemically prepared PANi is powdery form. The Effect of thermal treatment on dry state electrical conductivity of polyaniline membranes has been summarized in Table 1.

Table 1. Effect of thermal treatment on dry state electrical conductivity of polyaniline membranes prepared chemically and casted from NMP

T (°C)	As grown	100	150	200	300	350
σ^T (1) (S/cm)	25 ± 3	0.2	0.03	i	i	i
$\sigma^T(\text{HCl})(2)$ (S/cm)	25 ± 3	25 ± 3	20	5	4	i

Note: The dimensions of samples prepared 5mm(width) × 60mm(length) × 30 ± 3 μm(thickness). The room temperature dry state conductivity of the polymer films in their doped state (σ^0) was 25 ± 3 S/cm. The other data obtained are the average of three tests for each temperature.

(i) The conductivity was too low to be measured by the 4-point probe method.

(ii) σ^T is the conductivity of polymer after thermal treatment at temperature T

(iii) $\sigma^T(\text{HCl})$ is the conductivity after soaking thermally treated polymers in solution of 1 M HCl for 24 h at room temperature.

As our data show (Table 1), conductivity decreased after even mild heat treatment and the loss in conductivity observed after thermal treatment up to 100 °C could be fully recovered after soaking in acid. The loss in conductivity up to 100 °C is most likely due to simple dehydration of the polymer and evaporation of free dopant, HCl. After treatment at 150 °C the conductivity could be recovered as much as 80% by exposing to the acid media. However, thermal treatment at higher temperatures than 150 °C caused more irreversible loss in dry state conductivity. It seems that exposure of PANi to elevated temperatures (up to about 150-200 °C) can have an annealing effect on chemically prepared polyaniline. With thermal treatment under inert atmosphere the regularity of the polymer chains can be increased without any structural changes in the polymer backbone such as ring opening. This is thought to lead to a phase change to a looser packed ordered system. However, in an oxygenated atmosphere a range of reactions are possible including introduction of substitutions along the polymer chains and subsequent loss of conjugation and conductivity. At temperature exceeding 200 °C conductivity of the polymer decreased rapidly and polymer becomes an insulator.

It has also been reported³³⁻³⁷ that the irreversible conductivity decay of thermally treated PANi at temperatures below the thermal decomposition has been attributed to changes in morphology, crosslinking, possible structural rearrangements or other chemical reactions such as chemical interactions between dopant or solvent with the polymer, and irreversible conversion of ionic chlorine to covalent chlorine. Crosslinking reactions and morphological changes may be responsible for decrease in the re-protonation after the thermal ageing.

The conductivity changes observed with exposure to temperatures up to 150 °C in air were very close to the data obtained in nitrogen. However, at temperatures greater than 150 °C the conductivity decay after treatment in air was more irreversible than after treatment in nitrogen. At higher temperatures, thermal degradation is a predominant factor. The decrease in σ is also dependent on sample form, environment, dopant, time and temperature of exposure³⁸⁻⁴⁰. Spectroscopic studies revealed that the doping process of an HCl - doped film of PANi could be thermally reversed at 180 °C under N₂ without any indication of major changes in the structure of the polymer backbone, but the possibility of substitution of the aromatic rings and cross linking of the polymer chains that could lead to decrease in the conjugation length can not be excluded⁴⁰. Other workers have reported that thermal treatment at up to 150 °C is favorable to the crystallisation of both doped and undoped PANi

and heating at more extreme temperatures crystallinity decreases and the polymer becomes more amorphous. X-ray photo electron spectroscopy (XPS) experiments on thermally treated PANi-HCl samples indicate that the irreversible conversion of ionic chlorine to covalent chlorine becomes significant at temperatures greater than 100 °C³³.

Thermal Gravimetric Analysis (TGA)

The technique of TGA has been found one of the most useful techniques for evaluating the onset of thermal decomposition temperature and determining thermal stability of conducting polymers. The TGA results obtained from PANi^{35,53} show that the method of synthesis is important in determining the thermal stability of the polymer but the oxidation state of the polymer is not very important. A three step decomposition process for the protonated conducting form has been proposed by previous workers. They suggest that the initial stages of weight loss are due to the volatilization of water molecules, then at higher temperatures the protonic acid component of the polymer is lost and finally at more extreme temperatures the degradation of the polymer can lead to production of gases such as acetylene and ammonia. The thermograms (a plot of mass vs. temperature) obtained for PANi/HCl prepared by constant potential (CP) and cyclic voltammetry methods (CV) are shown in Figures 5 and 6 respectively.

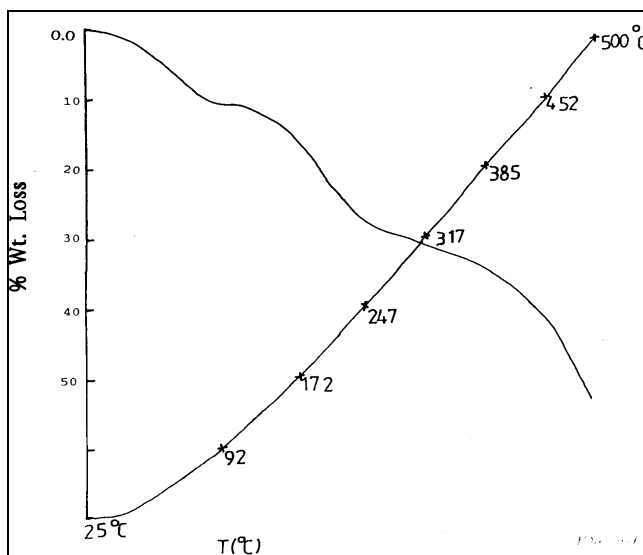


Figure 5. TGA of PAN prepared potentiostatically at 0.8 V. A heating rate of 10 °C/min was employed throughout this work unless otherwise stated. The experiments were performed under nitrogen atmosphere. The flow rate of N₂ gas over the samples 80 ml/min.

A three step decomposition process for the protonated conducting is observed for both potentiostatic and CV produced acid doped polymers, three separate stages of weight loss were observed under N₂. The first continues weight loss that is observed above room temperature may be attributed to loss of moisture, free HCl and unreacted monomer. The second may be attributed to loss of dopants from deeper sites in the material. At more extreme temperatures (the third weight loss) degradation of the polymer backbone is occurred.

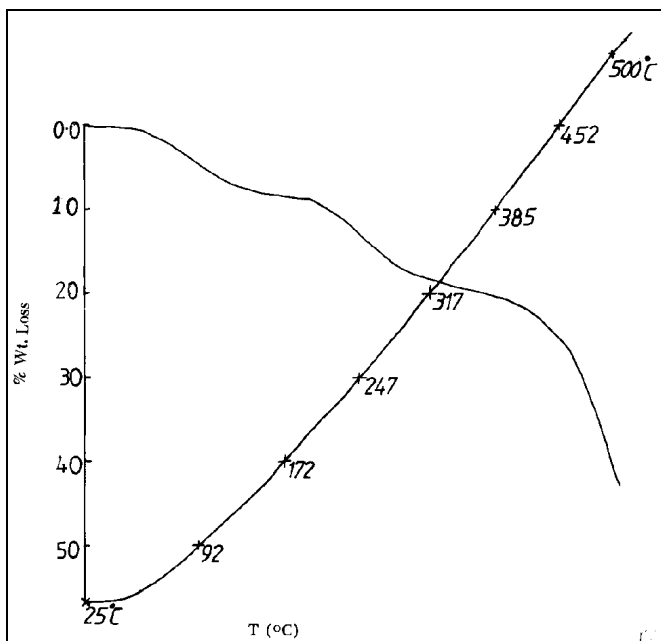


Figure 6. TGA of PANi/HCl prepared by CV method. The TG analysis conditions were the same as used in Figure 5.

According to our TGA results, the temperature required for degradation were slightly higher for samples prepared using the CV method. It may be concluded that PANi conducting polymers synthesised by CV method is more thermally stable than those prepared by CP methods. It was also observed that cyclic potential sweep deposition produces more adherent films with higher structural integrity than potentiostatic deposition. As our TGA show, continuous weight loss was observed above room temperature although this may be broken down into three steps. Up to a temperature of 150 °C, may be attributed to evaporation of moisture, unreacted monomer, free HCl and probably some low molecular weight polymer segments formed during chemical polymerisation. The major component of the volatiles seems to be water molecules. The major weight loss of chemically synthesised PANi/HCl at around 200 °C in the TGA curves was attributed to HCl loss. The major mass loss occurred at 380 °C is due to polymer backbone degradation. The thermograms (TG) obtained for PANi/H₂SO₄, and PANi/HPTS are shown in Figures 7 and 8.

The initial weight loss observed in TGA of PANi/H₂SO₄ (Figure 7) from 50 to 100 °C can be attributed to loss of moisture. The higher moisture content of this polymer compared to PANi/Cl may be due to the hygroscopic properties of the dopant acid (H₂SO₄). The larger mass loss (compared to PANi/HCl) occurred at temperatures between 200 and 320 °C. This is most probably due to the evaporation of acid bound to the polymer chain as protonating dopant. PANi/HPTS showed higher thermal stability than PANi doped with HCl or H₂SO₄ acids (see Figure 8).

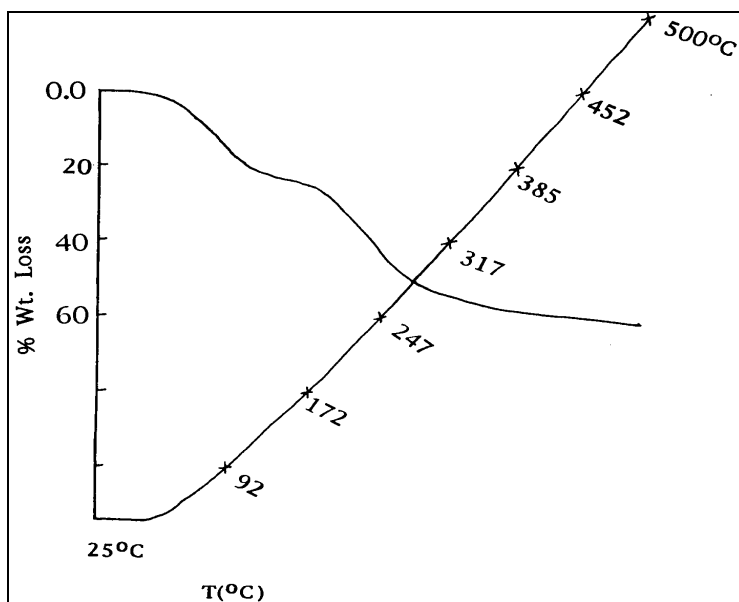


Figure 7 Thermogram of PANi/H₂SO₄. The TGA experimental conditions were the same as used in Figure 5.

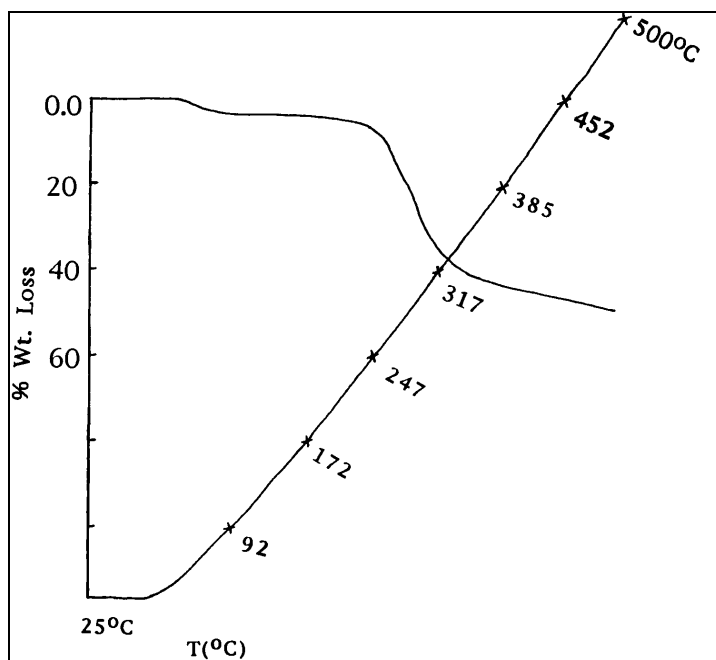


Figure 8. Thermogram of PANi/HPTS. The TGA experimental conditions were the same as used in Figure 5.

The major weight loss in PANi/HPTS occurred at temperatures between 250 °C and 320 °C. The initial weight loss observed at 110 °C may be attributed to solvent evaporation (water). The second weight loss observed at 250 °C is probably due to the evaporation of the dopant. The polymer backbone seems to be thermally stable up to 500 °C. Differences were observed between polyaniline grown by a sweep potential (CV) method than those grown by constant potential method. Weight losses were greater and more rapid with the latter. This may be due to a lower amount of impurities in the polymer from the CV method. There was little difference between the stability of the reduced and oxidised states of PANi⁵³. Thermal stability of electrochemically reduced form of PANi measured by TGA was very similar to the oxidised form of polymer, but showed lower stability than oxidised form, when TGA were carried out in air. It was also found that the doped polymers are significantly less thermally stable than the chemically undoped polyaniline (EB). The thermogram obtained from EB form of polyaniline has been shown in Figure 9. As the TG of EB shows, emeraldine base (EB) powder synthesised chemically is the most thermally stable form of polyaniline (Figure 9).

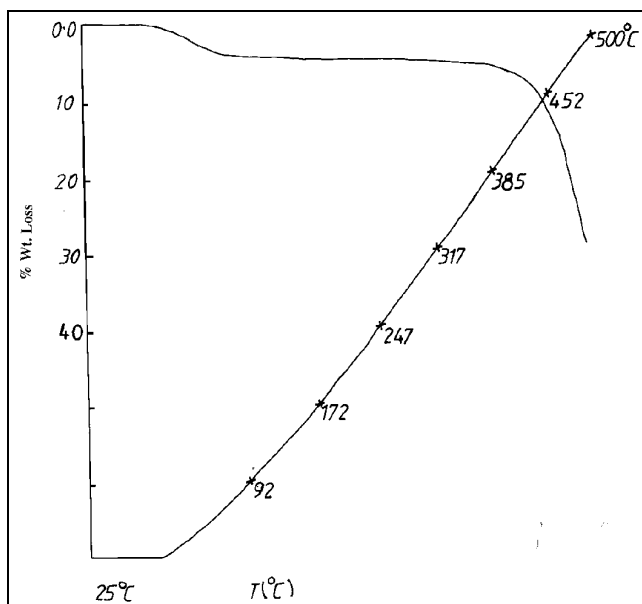


Figure 9. TGA on emeraldine base (EB) powder. The TGA experiment was carried out at using the same conditions given in Figure 5

As our TG analysis show (Figure 9), after the initial weight loss (5%) observed at 100°C minimal mass loss was observed until the temperature was 400 °C. The major weight loss was observed at 420 °C. The total weight loss at T=500 °C was 29%. After 600 °C polymer decomposition is almost complete. TGA profiles confirmed that the polymer material was stable to at least 300 °C. Emeraldine base (EB) form of polyaniline was found to be the most thermally stable form of polyaniline. TGA results indicated⁵⁷ that undoped polyaniline samples (EB) show lower weight losses before the thermal breakdown of the polymer backbone and thermal stability of the intrinsically oxidized PANi is dependent to dopant acid and is generally poor.

It has been reported^{59,60} that longer heat treatment time of PANi-EB leads to more pronounced cross-linking which in turn lead to reduced solubility of the polymer and to reduced conductivity recovering after post treatment in acids. This originates in fewer imine N atoms being available for reprotonation. From TGA, IR spectroscopy and elemental analysis, it has been found that in air, oxidation and possible structural rearrangements lead to loss in conductivity (because of loss in conjugation, not dopant) at temperatures below thermal decomposition³⁴. It was also noted that the structural integrity of doped PANi, as probed by infrared spectroscopy, was maintained during thermal ageing at temperatures at or below 200°C³⁵. Neoh *et al.*³³ have reported that when PANi/Cl is heated in air at 150 °C, the total Cl content changes little but it is transformed to a deprotonated structure accompanied by Cl substitution at the aromatic ring. The TG data obtained in air or N₂ is consistent with the theory that the formation of covalent chlorine makes it more stable to heat above 250 °C than the mainly ionically bonded chlorine present in the protonated structure. The rapid weight loss observed in air for temperatures greater than 350 °C is due to formation of volatile products resulting from the oxidation of the polymer. Thermal stability of polyaniline conducting polymers is also dependent upon some important factors such as, acid dopant, oxidation state of the polymer, monomer substitutions, atmosphere of heat treatment, exposure time and preparation conditions. PANi-EB is the most stable among polyaniline.

Crystallinity of PANi

It has been found that doped PANi is remarkably crystalline. It becomes almost amorphous when it is undoped with NH₄OH. Heat treatment at up to 150°C is favourable to the crystallisation of both doped and undoped PANi. The structure of annealed PANi up to 150°C becomes more regular and ordered⁵⁴. Heating at higher temperatures destroys the crystalline structure. Elemental analysis and IR spectroscopy of initial and 150 °C annealed PANi (under N₂) showed no significant differences³⁹. In this study, X-ray diffraction analysis also supported the increasing regularisation and crystallinity of PANi annealed at 150 °C.

It is interesting to note that the weight loss of the re-doped samples could be lower than the unaged polymer, which might be responsible for the incomplete recovery of the conductivities by re-doping. Therefore, there must be other processes involved during the thermal ageing below and at 200 °C besides the loss of water and HCl. Wei *et al.*³⁵ suggested that crosslinking reactions along with the morphological changes could take place during the thermal aging. The aged polymer samples at 100 and 200°C were also found to have lower solubility than the unaged ones in NMP. Wang and Rubner⁵⁵ obtained spectroscopic evidence which suggests that in the case of polyaniline thermal dedoping occurs due to disordering of the polymer backbone through chemical modifications (substitution of aromatic rings/crosslinking) or changes in molecular reorganisation (thermal disruption of crystalline or paracrystalline regions). They also point out, however, that even spectroscopic studies are limited in that minor structural changes would not be detected and yet these could have a major impact on physical properties. In the later case, the thermal disruption of crystalline or polycrystalline regions of the film could disrupt the ability of the backbone electrons to achieve a high level of delocalisation. In addition, they emphasize the importance of film thickness and the form of the sample (Powder, pressed pellet) on thermal properties, although spectroscopy can only be carried out on thin films. Mattes *et al.*⁵⁶ also reported that thermal treatment of polyaniline films at 125 °C for three hours makes the polymer a very dense material which decreases its permeability and increases its selectivity

for gas separations. Therefore, thermal treatment may also be used to modify the properties of conducting polymers make them desirable for some specific applications. Previous workers³⁹ have reported that thermal treatment at up to 150 °C is favourable to the crystallisation of both doped and undoped PANi and heating at more extreme temperatures crystallinity decreases and the polymer becomes more amorphous. These previous observations are in good agreement with the data reported above. We have also reported⁵³; showing an increase in tensile strength after heating, confirm that cross linking reactions occur in the course of thermal treatment.

Environmental stability of PANi conducting polymers

Polyaniline conducting polymers the same as other reactive and conducting organic materials suffer from their poor thermal stability in air because of the chemical reaction of oxygen with the highly conjugated system of PANi. In contrast to most conducting polymers which are less stable in humid environments, polyanilines are very stable. This clearly indicates that the conductivity stability of PANi is enhanced in the presence of humid air. It was also reported that the water vapour in the air appeared to be an essential factor in the recovery process of conductivity since the sample cooled in the dessicator shows only minimal recovery. It has been reported⁴⁸ that prolonged storage of polyaniline in water or working electrolyte (without polarisation) leads to an irreversible decrease of its electrochemical activity, but when stored dry, its activity is preserved. Polyaniline can be left standing in air and the electroactive properties are not destroyed. Storage in air, however, does alter the film and produces an anodic shift in the peak positions¹⁹. Pasquali *et al.*¹⁰ have indicated that after storage of polyaniline in distilled water (open circuit) a hydrolysis reaction as evidenced by the appearance of the anodic peak at ~ 0.5 V occurs. Degradation of the polymer was higher when stored in a solution of 1M H₂SO₄ (even after one day). The dissolved O₂ in H₂O and impurities contained in the film can favour the deprotonation of polymer, then the rapid degradation.

Conclusions

Bulk preparation of polyaniline conducting electroactive polymers powder can be achieved using simple chemical method without need to any special equipment. Highly conducting coating or polymer membranes (PANi or composites) with high mechanical properties of polyaniline can be prepared using solvent cast method. The electrical properties, thermal and environmental stability of PANi Films is highly dependent on the nature and the size of its dopant acid. The thermal stability of the acid doped PANi was in the order of PANi/HPTS > PANi/ H₂SO₄ > PANi/HCl. The undoped form of PANi (EB) is the most soluble and more thermally stable than the other forms of PANi. The loss in conductivity and electroactivity of PANi conducting polymers are mostly reversible when thermally treated below 150 °C in air or nitrogen atmospheres.

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