SPECTRAL AND ELECTRICAL INVESTIGATION OF POLYANILINE BASED CONDUCTIVE POLYMERS

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ABSTRACT

Conductive polymers are highly nanostructured materials formed by organic building blocks. The presence of delocalized molecular orbitals in these polymers makes them conductive. Present work deals with the study of polyaniline based conductive polymers synthesized by bulk oxidative chemical polymerization using ammonium per sulfate as an oxidant. The conductive polymeric materials were investigated by thermo gravimetric analysis (TGA), UV-visible studies confirmed the structure of synthesized polymers. TGA studies shows that polymeric materials are thermally stable upto about 150°C, above this temperature degradation of polymeric material starts. Slight structural and morphological changes are observed in TEM images with change in substituent in monomer units.

Key words: Ammonium per sulfate, Scanning electron microscopy, Morphological changes, Emeraldine salt.

INTRODUCTION

Discovery of polymer has given a new dynamic dimension to the present era. Polymer materials have long been known to be good insulators of because their covalent bonds exhibit low conductivity. However, in the last five decades polymers are evolved as the most important classes of material. This is due to versatility, good mechanical properties, low cost, environmental stability, conductivity and good processability. A range of commodity polymers provide a spectrum of products such as fibers, nanotubes, elastomers and thermosetting resins[1-3]. The importance of conducting polymers was rewarded in the form of the 2000 Nobel prize in Chemistry to MacDiarmid, Heeger and Shrikawa[4]. This was most exciting because it has created a new field of research on the opportunities between the boundary of chemistry and condensed matter physics. The conducting polymers are known as organic metals. These are highly engineered nanostructured materials made from organic

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building blocks. The family of conducting polymers differs from the conventional polymers by processing the particular chemical structure with the extended π-conjugated system formed by the overlap of carbon Pz orbitals and alternating single-double bond along the polymer chains. These particular conjugations in polymer chain give rise to distinct electronic properties of non doped conducting polymers. The unpaired Pz electrons may contribute to electrical transport of the system. The electrical conductivity of polymers can be examined by several parameters like chain properties, interchain interactions, interaction between chain and dopants, structural disorder, sample morphology.

Interest in these conducting polymers stems from the fact that many different rings and nitrogen substituted derivatives can be synthesized and each of these derivatives can exist in several different oxidation states, which can be doped by various dopants either by non redox process or by partial chemical or electrochemical oxidation[6]. Conductive polymers are organic polymers that conduct electricity. Such material is either metallic conductors or semiconductors. Plastics are conductive polymer which is organic in nature and posses mechanical properties, toughness, elasticity, malleability, flexibility etc. with high electrical conductivities. The properties of conducting polymer can be fine tuned with the equizite methods of organic synthesis[7]. The common feature of conducting polymer is its extended π system along its backbone, which confers the possibility of movement of an electron along the chain, i.e. conduction. The conjugated polymers are either semiconductors or insulators in their undoped state and have energy gap more than 2eV, which is too great for thermally activated conduction. Hence, the undoped conjugated polymers like polythiophens; polyacetylenes possesses low electrical conductivity about 10^{-10} to10^{-8} S/cm.

EXPERIMENTAL

Polymer preparation – All chemicals are of analytical grade used for synyhesis.

Synthesis of polyaniline, poly o-toludine, poly m-toludine, polynitro aniline was done by procedure reported earlier[8].

Characterization

The synthesized polymeric materials were characterized by TGA, UV-vis, XRD, TEM, techniques. TGA was performed on Perkin-Elmer, dimond model instrument within temperature range 25-500°C at a heating rate of 10°C/min. FTIR spectrum of all polymers were taken on FTIR spectrophotometer (Bruker make, Germany Model) in the region 400-4000 cm^{-1}. Morphology of synthesized polymers were studied by Field Emission Gun Scanning Electron microscopes (FEG SEM). Model-JSM-7600F, Resolution 1.0 nm (15 kv.)

RESULTS AND DISCUSSION

Thermogravimetric analysis

TGA serves as an analytical technique to quantify amount of organic matter. Thermogravimetric analysis was used to investigate the thermal stability of synthesized polymers within the temperature range 25-500°C. The polymer powder pellets were heated at rate 10°C/min. Polymers showed a small weight loss below 100°C, presumably caused by the loss of solvent, moisture and low molecular weight volatile impurities.

Thermo gravimetric analysis of polyaniline

Fig. 1 shows the thermogram for emeradine base form of polyaniline. Fig. 1 shows a weight loss of 3% weight loss upto 100°C, a weight loss of 32% from 100-500°C possibly due to decomposition of polymeric backbone. Our data are found in good agreement with data reported in literature[10]. For polyaniline three mass losses could detected in the temp range 25-500°C. The first weight observed at 100-150°C was essentially due to desorption of water absorbed on the polymer. The weight loss at 150-250°C can be related to the expulsion of the doped HCl from PANI. The thermal loss at 250 to 500°C can be assigned to thermal degradation of skeletal polyaniline chain structure. This curve also indicats that there is a sharp weight loss near 200°C and continues until 500°. The total weight loss of PANI at the temperature range from 25-500°C is about 35%.
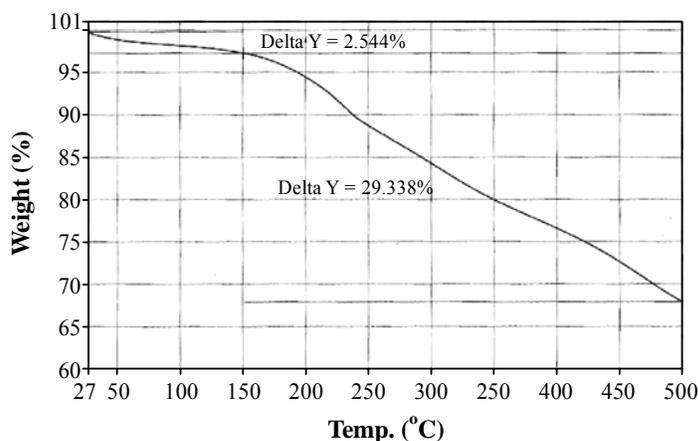

Fig. 1: TGA curve of polyaniline

TGA of poly m-toludine

Fig. 2 shows the thermogram of poly m-toludine. The TGA analysis of poly m-toludine obtained with two transitions at 160°C and 350°C. The weight loss was observed from

27-500°C. m-toludine shows small weight loss up to 100°C, presumely caused by the loss of solvent, moisture and low molecular weight volatile impurities.
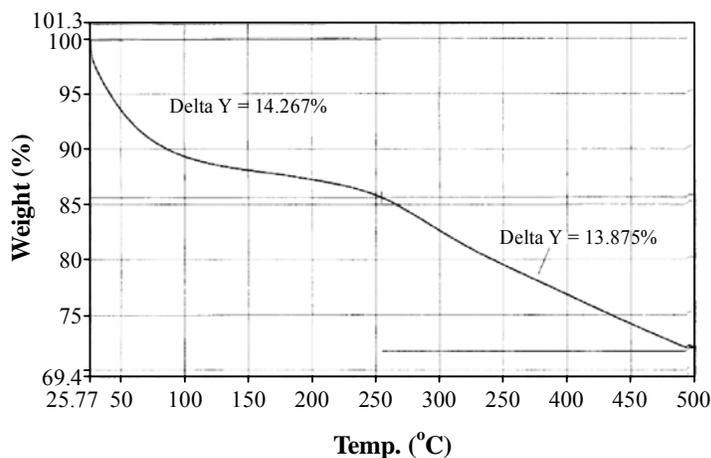

Fig. 2: TGA curve of poly m-toludine

TGA of poly o-toludine

Fig. 3 shows the thermogram of poly o-toludine. It shows a weight loss of 4% at 26-4% and 14% weight loss at 200-500°C. It is possibly due to degradation of poly o-toludine matrix. This indicate that base form of polyaniline is thermally more stable than undoped poly o-toludine and substitution at ortho position. The weight loss in first stage at 25-200°C is assigned to the loss of moisture and residual HCl, the further weight loss is due to degration of polymer matrix.
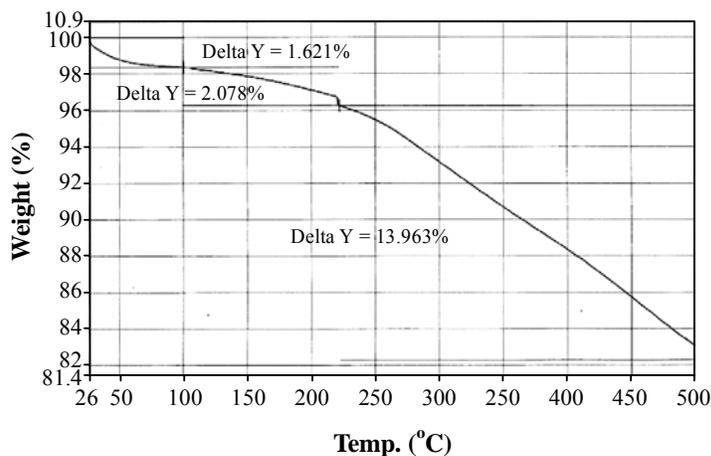

Fig. 3: TGA curve of poly o-toludine

Poly o-toludine in base form shows a negligible weight loss upto 500°C (14%), which is due to degradation of poly o-toludine backbone. The lesser weight loss as compared to thermogram of PANI is possibly because of lower steric hindrance of the CH_3 group of toludine present in ortho position.

TGA of poly nitro aniline

Fig. 4 shows the thermogram of poly nitoaniline. It shows the weight loss at 25-500°C. Initially 8% weight loss is observed upto 100°C. Negligible weight loss is observed from 100-250°C (12%) and 14% in the temperature range 250-500°C. The lesser weight loss as compared to PANI is possibly due to nitro group substitution.
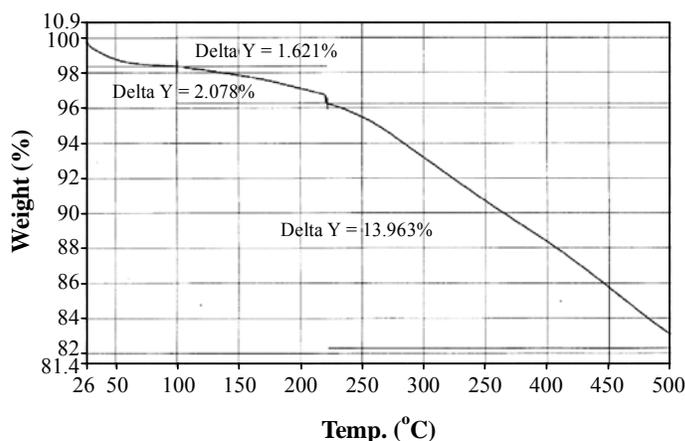

Fig. 4: TGA curve of poly nitroaniline

Fig. 5 shows FTIR spectra of polyaniline. The principal absorption band was observed at 3265 cm^{-1} corresponds to then N-H stretching mode of secondary amine. The band in the region 1600-1450 cm^{-1} this region is assigned for N-H deformation, aromatic ring breathing, C=N stretching. 1, 4 substituted benzene ring may give absorption at 1600-1580 cm^{-1}. The peaks at 1582 cm^{-1} and 1548 cm^{-1} is assigned to the benzenoid and quinoid form of PANI backbone[11,12]. 1400-1200 cm^{-1} is C-N stretching region for aromatic amines. 1200-500 cm^{-1} is the region for in plane and out of plane bending of C-H in aromatic ring. Peak at 1302 cm^{-1} is assigned to C-N oscillations in benzene ring. The peak at 1173 cm^{-1} corresponds to C-H in plane oscillations.

Fig. 6 shows the FTIR spectra of m-toludine. The broad band observed in spectra at 3182 cm^{-1} is assigned to N-H stretching mode. The characteristic band at 2918 cm^{-1} show vibrations of –CH_3 group. The peak at 1595 cm^{-1} and 1493 cm^{-1} are assigned to the stretching vibrations of benzenoid and quinoid ring. The peak appearing at 1402 cm^{-1}

indicates the symmetric deformation of -CH_3 group. 1301 cm^{-1} and 1230 cm^{-1} corresponds to the C-N vibration. The peak at 1153 cm^{-1} is assigned to C-H stretching of benzenoid ring. The 1108 cm^{-1} peak is assigned to C-C stretching vibrations of methyl substituted benzenoid and quinoid structure. The prominent peaks at 941, 877, 810 cm^{-1} assigned to an out of plane C-H vibrations and 1, 2, 4 substituted benzenoid ring and in plane C-H vibrations quinoid ring. The peak at 692 cm^{-1}. C-H bending and 615 cm^{-1} indicate aromatic ring deformation. The peaks at 569, 514 and 439 cm^{-1} corresponds C-C stretching in benzenoid ring, C-C stretching and C-N stretching in benzenoid and quinoid structures, respectively.
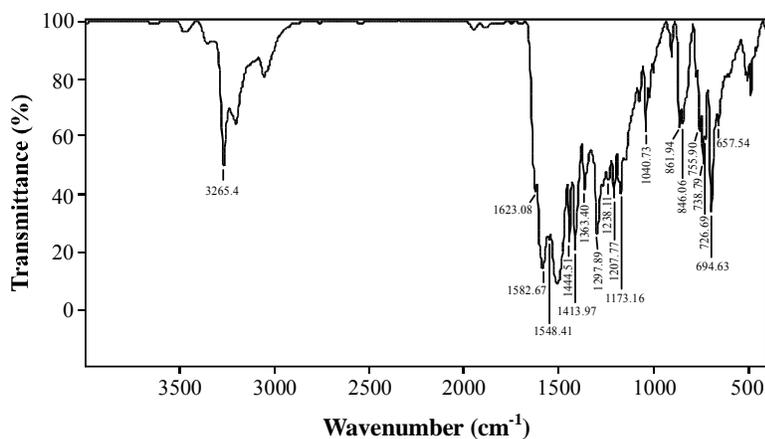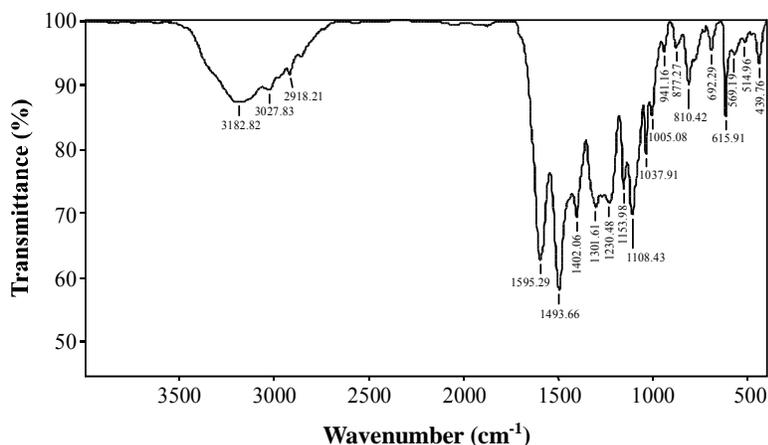

Fig. 5: FTIR spectrum of polyaniline

Fig. 6: FTIR spectrum of poly m-toludine

Fig. 7 shows the FTIR spectra of poly o-toludine. 3355 cm^{-1} is assigned to N-H stretching. Peak at 2917, 2855 cm^{-1} corresponds to the C-H stretching due to substituted

methyl group. 1596 cm^{-1} peak indicate C-N stretching of quinoid structure. 1376 cm^{-1} peak is assigned to C=N+ stretching vibrations[13]. 1305 and 1242 cm^{-1} peaks corresponds to C-N vibrations in alternate units of quinoid-benzenoid-quinoid ring. C-H stretching vibrations in benzenoid ring vibration mode. Peak at 1110 cm^{-1} is assigned to methyl substituted benzenoid and quinoid ring. 940, 879, 750 cm^{-1} corresponds to C-H out of plane vibrations. C-C stretching vibrations of benzenoid ring are indicated by peak at 568 cm^{-1}.[12] 440 cm^{-1} peak is assigned to C-N stretching in benzenoid and quinoid ring.
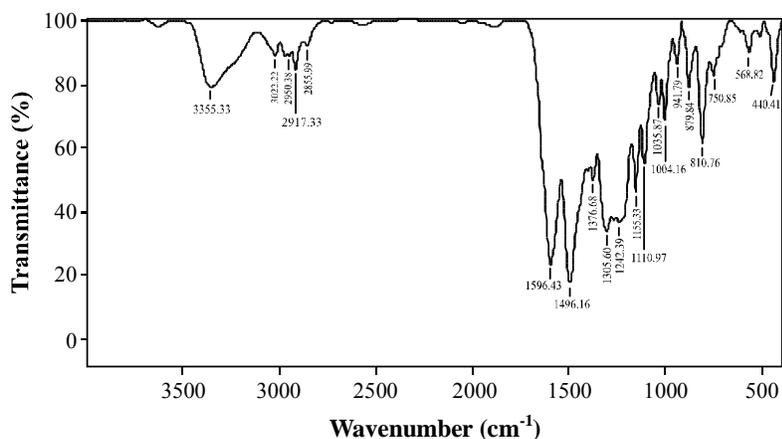

Fig. 7: FTIR spectrum of poly o-toludine

Fig. 8 shows the FTIR spectra of polynitro aniline. Peak at 3420 cm^{-1} indicate N-H stretching. The characteristic peaks at 1597, 1495 cm^{-1} corresponds to asymmetric and symmetric stretching vibrations in NO$_2$ group.
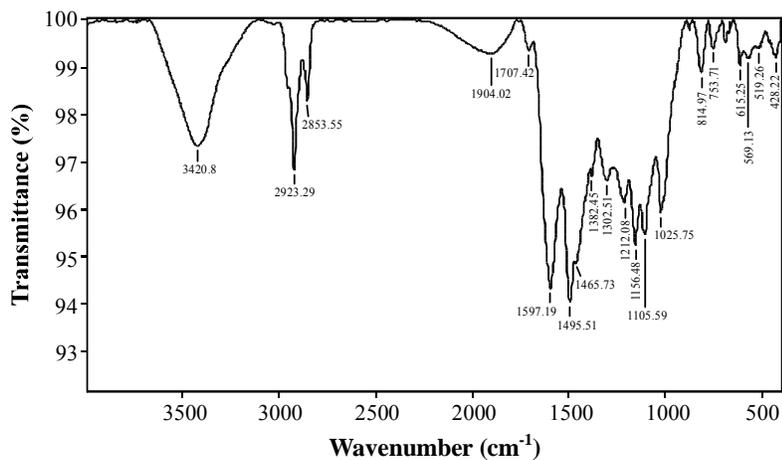

Fig. 8: FTIR spectrum of poly nitroaniline

The absorption band at 1302 cm^{-1} indicate C-N vibrations in alternate units of semiquinoid and quinoid ring. 1212-428 cm^{-1} is the region of in plane and out of plane C-H bending in aromatic ring. 753 cm^{-1} corresponds to in plane bending of C-NO$_2$. 615 cm^{-1} peak is assigned to aromatic ring deformation.

Fig. 9, 10, 11, 12 shows the SEM images of polyaniline, poly m-toludine, poly o-toludine, poly nitroaniline, respectively. Characterization of synthesized polymers was also carried out using scanning electron microscopy (SEM).
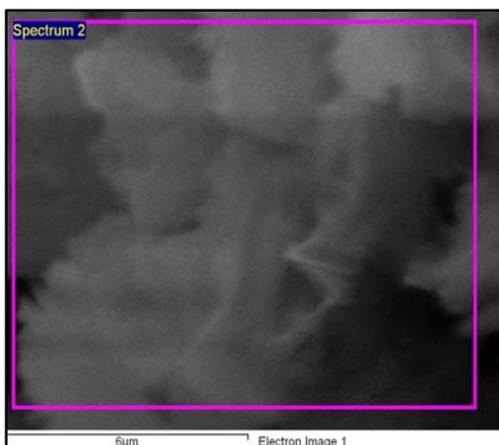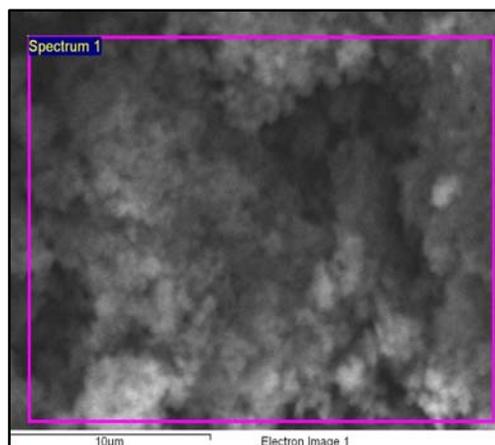

Fig. 9: SEM image of polyaniline
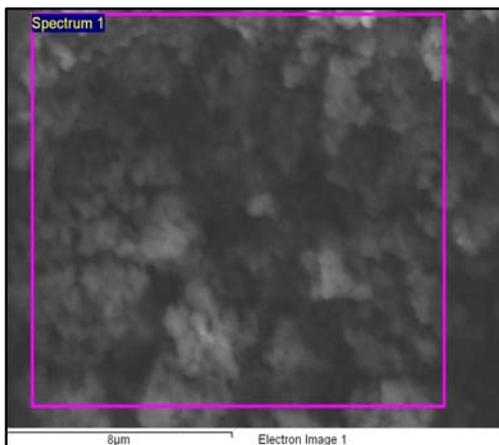

Fig. 10: SEM image of poly m-toludine
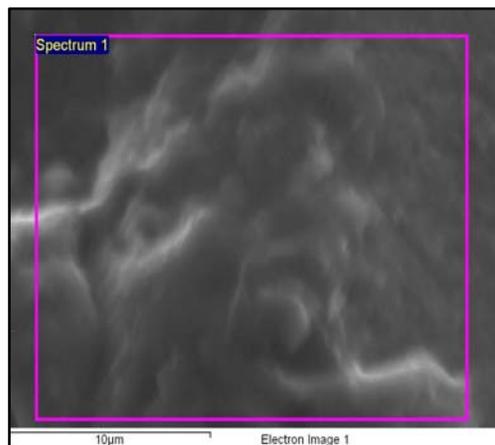

Fig. 11: SEM image of poly o-toludine

Fig. 12: SEM image of poly nitroaniline

All electron micrographs were obtained from the powdered form of polymers. SEM micrograph of polymers in base form gives a smooth and homogeneous appearance. SEM images show the differences in morphologies of the polymers.

CONCLUSION

Polyaniline based polymer have been successfully prepared by bulk oxidative polymerization method. TGA analysis shows that the synthesized polyaniline based polymers are thermally stable upto 200°C, which can find applications in the formation of conductive polymers with the conventional thermoplastics. The TGA curves of polyaniline, poly m-toludine, poly o-toludine, poly nitro aniline show the weight loss in three stages. The first stage is due to loss of absorbed moisture and solvent from room tempeture to around 100°C. The second stage weight loss is due to loss of acid dopant in polymers in the temperature range 100-350°C. The third final stage indicate the weight loss due to degradation of polymer backbone occurs above 350°C. The FTIR spectra of synthesized polymers are in agreement with FTIR characterization reported in literature. FTIR spectral study confirms the formation of polyalniline, poly m-toludine, poly o-toudine, poly nitroaniline. SEM images obtained indicate the amorphous nature of polymeric material. SEM studies shows the homogeneous and smooth morphology. Slight differences observed in SEM images are due to nature and position of substituent groups in monomer.

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