SYNTHESIS, CHARACTERIZATION AND EVALUATION OF CONDUCTING COPOLYMERS FOR CORROSION INHIBITION AND ANTISTATIC APPLICATIONS

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By

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ABSTRACT

The thesis describes the synthesis, characterization and evaluation of conducting copolymers for corrosion inhibition and antistatic applications. Homopolymers of aniline (AN), o-alkyl anilines [o-methyl aniline (MA), o-ethyl aniline (EA), o-isopropyl aniline (IPA)] and 1-amino-2-naphthol-4-sulphonic acid (ANSA) were synthesized in the presence of different dopants [dodecylbenzene sulfonic acid (DBSA)/ 5-lithiosulpho-isothalic acid (LiSIPA)/ p-toluene sulphonic acid (PTSA) / oxalic acid] by chemical oxidative and electrochemical polymerization method. Various copolymers were prepared by varying the molar ratio of monomers (AN: MA/EA/IPA) and dopants (DBSA/LiSIPA) during synthesis. The homopolymers and copolymers thus obtained were characterized i.e. structural (NMR, FTIR, UV-visible, X-ray photoelectron spectroscopy), thermal (TGA & DSC), electrical conductivity (four probe method), morphology (SEM and TEM) and electrochemical (cyclic voltammetry) methods.

In the first part, chemical and electrochemical synthesis of homopolymers of aniline, o-alkyl anilines and their copolymers of various feed ratio (i.e. 90:10, 80:20, 70:30, 60:40 and 50:50) in presence of two different dopants like DBSA and LiSIPA has been described. The effect of alkyl group and its molar ratio in copolymer feed on thermal and electrochemical properties of conducting polyaniline has been discussed. Thermal stability of DBSA and LiSIPA doped homopolymers and copolymers were in the range of 175 °C-250 °C and the conductivity was in the range of 4.9 S/cm to 5.25 x 10^{-7} S/cm depend on the nature of dopant/copolymer composition). The homopolymers and copolymers based on aniline (AN) and o-isopropyl aniline (IPA) when doped with LiSIPA showed not only the good conductivity and thermal stability but also showed good solubility as compared to DBSA doped copolymers and homopolymers. ^{1}H-NMR was used to determine the copolymer composition. The solubility of conducting

polyaniline could be enhanced by the use of bulkier substituent i.e. substituted aniline as comonomers and their higher feed ratio in polymer matrix. The use of polyaniline and its copolymers with o-alkyl aniline in varying molar ratio has been discussed for two different applications i.e. corrosion inhibition and antistatic applications. Evaluation of homopolymers and copolymers for corrosion inhibition of iron in highly acidic medium like 1.0 M HCl was investigated by electrochemical impedance spectroscopy (EIS), Tafel extrapolation and linear polarization resistance methods (LPR). The corrosion inhibition efficiency of iron in highly acidic medium like 1.0 M HCl was found to increase with increasing molar ratio of o-isopropyl aniline (IPA) in the copolymer feed which was further increased by using LiSIPA as a dopant. Corrosion inhibition efficiency of iron in highly acidic medium with the addition of 80 ppm of DBSA doped copolymer [aniline and IPA in 50:50 molar ratio] was 70 % while LiSIPA doped copolymers at same molar ratio showed 80 % inhibition efficiency at the same concentration.

For antistatic applications, the method used to evaluate the static decay time and static charge on the surface of copolymers/LDPE blown film has been described in this thesis. For evaluation of such conducting polymers in the field of antistatic or electrostatic charge dissipation (ESD) application, blends of conducting copolymers at 1.0 % and 0.5 wt. % loading with insulating polymers like LDPE were prepared. ESD performance of DBSA doped LDPE/copolymers based on AN and IPA was found to be better up to 70:30 molar ratio of AN: IPA at 1.0 % wt. loading. While LiSIPA doped copolymer /LDPE blends showed better ESD performance upto 60:40 molar ratio of AN:IPA at same loading level. ESD performance of LDPE/ LiSIPA doped copolymer films decreased with increasing amount of o-isopropyl aniline in copolymer feed due to the

decreased conductivity of copolymers with increasing amount of o-isopropyl aniline in the copolymer.

In the second part of the thesis, an attempt has been made to evaluate and improve the antistatic and corrosion inhibition performance of conducting copolymers. in order to achieve the better solubility, optimum conductivity, better ESD and corrosion inhibition performance, a new conducting homopolymers and copolymers based on aniline and 1-amino-2-naphthol-4-sulphonic acid (ANSA) were synthesed by varying the ratio of AN: ANSA (90:10, 80:20 and 50:50) with and without use of p-toluene sulphonic acid (PTSA) as an external dopant by chemical oxidative polymerization method. Structural characterization of PTSA and self doped copolymers carried out using ^{1}H-NMR, ^{13}C-NMR, FTIR and XPS spectra revealed the involvement of -OH/ -NH_2 in the polymerisation. Conductivity of PANI-PTS was 1.72 S/cm and the conductivity of resultant copolymer decreased from 1.72 S/cm to 9.40×10^{-3} S/cm depending on the molar ratio of ANSA in the copolymer feed and type of dopant. TGA analysis of PTSA and self doped copolymers revealed that they were stable in the temperature range of 180 °C to 200 °C. Formation of nanoparticles/nanotubes was confirmed by morphological characterization using SEM and TEM of copolymers.

PTSA and self doped copolymer/LDPE films (1.0 % w/w) showed static decay time in the order of 0.1 to 0.31 sec. at 10 % cut-off. When the loading level of copolymers in LDPE was reduced to 0.5 wt. %, only the copolymers with tubular morphology showed good performance to ESD protection while the copolymer with granular morphology was not able to show the effective antistatic response. Better antistatic behavior shown by these copolymers at very low loading in LDPE was investigated by their nanotubular morphology.

PTSA doped copolymers of AN and ANSA were insoluble in methanol/ethanol. Hence only self doped copolymers were used for corrosion study. The corrosion inhibition performance of soluble self doped copolymers of AN and ANSA (synthesized by chemical oxidative polymerization method) in 1.0 M HCl has been evaluated using Tafel Extrapolation method and electrochemical impedance spectroscopy (EIS) which was also used to propose the mechanism besides surface morphology. The results showed that the copolymer film exhibited a significant shifting in the corrosion potential and greater charge transfer resistance. The corrosion inhibition efficiency was found to increase from 50 % to 90 % by increasing the concentration of copolymer from 10 to 70 mg/l in HCl medium. Moreover, the corrosion inhibition performance of copolymers increased with increasing the molar ratio of ANSA in copolymer and these copolymer showed the larger degree of surface coverage onto the iron surface, reflecting the higher inhibition for corrosion of iron in highly acidic medium.

In the third and last part of the thesis, an attempt has been made to evaluate the corrosion inhibition performance of eletrochemically deposited copolymer film based on AN and ANSA. The copolymer film based on AN and ANSA in 80:20 molar ratio (PANSA2-OX) was electrochemically synthesized on the iron electrode by cyclic voltammetry using oxalic acid as a supporting electrolyte. Protective properties of copolymer film on the iron surface in 1.0 M HCl solution was investigated by chrono-amperometry, potentiodynamic polarization technique and electrochemical impedance spectroscopy (EIS). The results showed that the copolymer film showed a significant shift in the corrosion potential and greater charge transfer resistance. The coating had good protective efficiency which increased with increasing the number of cycles (deposition time) i.e. maximum of 92 % at 30 cycles and reduced to about 53 % after 12 h immersion in highly corrosive environment (i.e. 1.0 M HCl) confirming the improved

coating performance. on the other hand, PANI coated iron showed 85 % of protection efficiency at 30 cycles which reduced to 38 % after 12 h immersion in corrosive environment. Furthermore, the corrosion rate was found to be highest for uncoated iron in HCl medium and its values decreased from 11.0 mm/year to 1.01 mm/year for iron sample coated with copolymer. The mechanism of corrosion protection of iron by these copolymers was investigated by surface morphology and EIS techniques. In addition, by using scanning electron microscopy, the effect of morphology of copolymer on corrosion protection of metal was also investigated. The copolymer showed the larger degree of surface coverage onto the iron surface, reflecting the higher protection for corrosion of iron in acidic medium.

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