Abstract

Study of structure and properties of polymeric materials is necessary in order to understand the manner in which a modification of molecular structure affects properties of the material and thereby, help in developing new applications. The process of doping a polymeric material is known to improve electrical conductivity of polymeric materials, as well as modify its optical properties. The procedure of mixing two polymers to produce a blend can result in vastly improved properties in the resultant material. Further, on doping this blend with chemical agents (redox agents) or inorganic salts, a new field of applications has opened up. This includes battery and fuel cell applications, wherein the doped polymeric blend is used as a solid polymeric electrolyte.

This Ph.D. thesis describes the preparation, characterization, microstructural studies and investigation of physical properties (electrical, optical and thermal properties) of doped polymeric blends, including interpretation of experimental data. The samples selected for this comprehensive experimental study are films of cadmium chloride (CdCl$_2$) doped polyvinyl alcohol (PVA) – poly vinylpyrrolidone (PVP) blend, doped to different levels, namely, 0.0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.9, 1.4, 1.8, 2.2, 3.3, 4.3, 5.4, 6.3, 7.2, 8.4, 9.3, 10.2, 11.3, 12.1, 15.5, 21.5, 25.5, 30, 35, 40, 45 and 50.5 wt% (in weight percentage). PVA and PVP were taken in equal composition (by weight) and mixed; and by solution casting from aqueous solution, PVA-PVP blend films were prepared. The inorganic metallic salt, cadmium chloride (CdCl$_2$) was incorporated as a dopant in PVA-PVP blend solution, and then (after stirring to obtain a homogeneous solution), the mixture was cast on glass to obtain CdCl$_2$ doped PVA-PVP blend films. Doping levels (concentration of CdCl$_2$ in PVA-PVP blend) varying from 0.1 up to 50.5 weight percent (wt%) were achieved. Films doped to a total of thirty different doping levels were obtained, and many of them were selected for a comprehensive characterization and the study of physical properties. After preparation, the samples were studied using experimental techniques like Scanning Electron Microscopy (SEM), X-Ray Diffraction (XRD), Differential Scanning Calorimetry (DSC), Thermo-Gravimetric (TG) Analysis, Energy Dispersive X-Ray Spectrometry (EDS), Atomic Force Microscopy (AFM), Fourier Transform Infrared (FTIR) Spectroscopy, FT- Raman Spectroscopy, Fluorescence (Photo-
Luminescence or Emission) Spectroscopy, UV-Visible (Optical) Spectroscopy, Dielectric Relaxation Spectroscopy (DRS), DC electrical measurements and Doppler Broadening Spectroscopy (DBS). These experimental investigations yielded information about the microstructure, electrical (AC and DC), optical, spectroscopic and thermal properties of PVA-PVP blend films, doped with different levels (concentrations) of CdCl₂. Three different stages of structural changes: nano-phase, micro-phase and percolation effect are observed at different stages of doping of PVA-PVP blend with CdCl₂, as evidenced by SEM and AFM images, DSC scans and XRD spectra. SEM images revealed the presence of dopant induced nanostructures in PVA – PVP films doped with CdCl₂, from 0.1 wt% up to 6.3 wt%. This resulted in an enhanced degree of crystallinity of the doped polymeric blend at lower dopant levels (from 0.1 wt% up to 3.3 wt%), meso-scale and micro- scale structures at moderate levels (from 4.4 wt% up to 11.3 wt%), and the doped polymeric blend samples exhibited an amorphous nature (with homogeneous smooth surface) at higher dopant levels (that is, with increased concentration of CdCl₂, (in the dopant range varying from 15.5 wt% up to 50.5 wt%). The discussion on electrical parameters was complemented by SEM and XRD data. Optical parameters were extracted from UV-Visible spectra, and these show significant changes, highlighted by the observation of Localized Surface Plasmon Resonance (LSPR) peak due to cadmium (Cd) nanostructures in the polymeric blend (host). Results from photo-luminescence (fluorescence results) also revealed improved properties, such as an enhancement of fluorescence in PVA-PVP blend when compared to its components (PVA and PVP), whereas a ‘fluorescence quenching’ effect is noticed in most of the CdCl₂ incorporated PVA-PVP blend samples, when compared to the un-doped PVA-PVP blend film. Temperature and frequency dependent study of dielectric relaxation in pure PVA-PVP and CdCl₂ doped PVA-PVP blend films revealed prominent changes in these parameters due to doping of PVA-PVP blend with CdCl₂. Ten times improvement in AC conductivity and a smaller relaxation time is observed in the film doped to a level of 10.2 wt%, when compared to 0.0 wt% (un-doped) PVA-PVP blend sample, which indicates that there is an involvement of ions of the dopant (Cd²⁺ and Cl⁻) along with the polymer side chain ions, to enable improved AC conductivity. From DSC results, multi-crystalline domains of various thicknesses are found in the CdCl₂ doped PVA-PVP blend films. At lower and moderate dopant levels, the DSC scans showed multiple endotherm peaks of distinct intensity. Variation in melting
endotherm peak (around 150°C) is due to dopant nano-structures and agglomeration of these to form microstructures. Decrease in decomposition temperature reflects a decline in thermal stability of CdCl₂ doped PVA-PVP blends at higher dopant levels, and enhancement in amorphousness of these samples. Significant changes in morphology were observed in CdCl₂ doped PVA-PVP blend films, on exposing these films to Ultra- Violet (UV) light of wavelength 254 nm for different exposure times (from 30 minutes up to 180 minutes). These modifications resulted in significant changes in electrical and optical properties.