Synthesis, Characterization and Conductance Properties of Cobalt Chloride Doped Polyvinyl Alcohol / Polythiophene (PVA-Co-Pth) Nanocomposite Films

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ABSTRACT
Polyvinylalcohol-Co-polythiophene (PVA-Co-Pth) composite polymer films were produced by chemical polymerization. Cobalt chloride CoCl2.6H2O was applied on various levels, i.e., 0.2, 0.4, 0.6 and 0.8g. The produced films were characterized by TEM (transmission electron microscopy), UV-Visible spectroscopy, IR (Infra red spectroscopy), SEM (scanning electron microscope), XRD (X-ray diffraction), d.c electrical conductivity, and dielectric constant measurements. The optical properties of all investigated films were analyzed, when the optical absorption of the prepared films reduces with raising the amount of CoCl2.6H2O in UV (200–400nm) & VIS (500–700nm) regions. It is evident from the XRD patterns of the PVA-Co-Pth samples that the intensity of the peaks of diffraction rises with the rise in cobalt chloride content owing to the semi crystalline of the resulting Co (II) doped PVA/PTh compositions. These findings are comparable with morphological variations seen in the PVA-Co-Pth samples, as per the TEM and SEM analysis. The increase in conductivity with increase in Co (II) concentration up to 0.8g of CoCl2.6H2O has been observed in PVA-Co-PPy composites and the dielectric constant tends to increase with the increment infrequency as well as with enhancement in Co (II) composition.

KEYWORDS
PVA-Co-Pth Nano composite X-ray diffraction SEM, TEM Dielectric constant

Introduction
Naturally, nanotechnology is very wide, covering the fields such as micro-fabrication, semiconductor physics, molecular biology, surface science, etc. Synthetic polymers are human-made polymers, they are often found in a range of consumer items like super glue, money, and so on [1]. Polyvinyl alcohol is odorless and white (colorless). Polyvinyl alcohol has good film-forming, adhesive and emulsifying properties [2]. PVA has a melting point at 180 °C (356 to 374 °F) and 230 °C for the partially hydrolyzed. PVA is almost incompressible. Polythiophenes become "organic metals" electrically conductive after partial oxidation. Thiophene was found to be a benzene contaminant. Thiophene was the novel heterocyclic compound [3]. Polythiophene was frequently utilized in ecologically as well as thermally conjugated polymers like transistors, solar cells, polymer electronic interconnects, DNA detection, molecular devices, light-emitting diodes, and displays, photovoltaic devices, optical and chemical sensors.

In recent decades, because of its better flexibility, stability and cost-efficiency, the usage of conductive polymer composites has been taken into account for the manufacture of display and sensing equipments [4]. Comprehensive investigations on gas sensing characteristics of PANI composites [5,6] and polypyrrole (PPy) composites were noted for different oxidation and gas reduction [7,8]. But, to resolve their solubility constraints and electrochemical properties of the conducting PANI composites are mostly owing to the polymerization methods, non-homogeneous composite formation, as well as doping dedoping properties of the conducting polymers, further more to increased process ability as well as mechanical properties, there is required to produce a real composite of conducting polymers with fundamental properties of the conductive polymers. The enhancement of these properties could be obtained through the formation of pyrrole copolymers or the forming composites PPy or through mixing with commercially available inorganic materials or polymers that provide better optically as well as mechanical characteristics, stability, and processing capacity [9,10] thus polypyrrole blends with an isolating polymer has good mechanical characteristics [11,12]. Electrochemical or chemical polymerization may be used to create polymer composites. Substantial influence on the electrical and optical characteristics of PVA polymers, like transition metal salts [13, 14, 15]. In this work, the host material PVA is integrated into the conductive composite polymer consisting of "polythiophene" (PTh). In this study, the PVA: "polyvinyl alcohol" was utilized as an isolating polymer and blended with PTh by applying chemical polymerization to enhance the PTh properties. To examine the effect of doping compositions on the structural, optical as well as electrical characteristics of the composite polymer, the doping concentration, particularly hydrous cobalt chloride, was changed.

Experimental
Thiophene monomer, anhydrous iron (II) chloride (FeCl3), polyvinyl acetate (PVA), methanol, and CoCl2.6H2O from SD
Fine Chemicals (AR grade) were utilized in the current study. The monomer of thiophene was utilized as received. Composite PTh/PVA prepared according to by chemical oxidative polymerization method. These synthesized PVA-Co-PTh composite films with various content of Co (II), For these films morphology and the structures were studied by “TEM JEOL JEM-1230” and “scanning electron microscopy” (SEM, JSM-6360LV, Japan) operating at 120 kV. The X-ray diffraction patterns of the powders were taken using the “Philips XPERT diffractometer” utilizing Cu Kα radiation (λ = 1.54 Å). The FTIR - Perkin Elmer make-model RXI Spectroscopy was used to analyze the chemical bonding. UV-Visible measurements were conducted on the “Perkin Elmer make-Lambada” 35 model, as well as absorption spectra, were found by depositing the film PVA-Co-PTh on a glass substrate. The AC conductivity of all the composites with different Fe:O3 content was studied in the range of frequency 0.2 to 10 MHz by using LCR-Q meter (Wayne Kerr, 4300) analyzer.

Preparation

Polythiophene nanoparticles are synthesized by in situ polymerizations where the thiophene monomer, cobalt chloride is dispersed in the PVA matrix. In one beaker, 3g of PVA with MW = 7000, dissolves fully in 100ml purified water under continuous agitating. The combination was heated for 1 hour at 90 degrees Celsius and cooled to the temperature of the room. In a cooled combination, 30ml were combined with 1.0g of thiophene (Th) monomer already dissolved in 20 ml of chloroform solution and 2ml of FeCl3 solution. Five minutes later, the blend was stirred. In a composite mixture, the 0.2 g cobalt chloride (CoCl2·6H2O) was finally utilized for doping and agitated for a further 10 minutes. As mentioned above various amounts of cobalt salt (x =0.2, 0.4, 0.6 and 0.8) were applied, there by producing distinct samples. Thick films were formed using a casting procedure, where the material was placed into a glass Petri dish for the individual samples and allowed to dry 120 hours later on at room temperature, after this period, the films were ready for characterization in appropriate portions.

Results and Discussion

X-ray diffraction studies:

Fig.1. Indicates the pure PVA/PTh composite XRD patterns along with CoCl2·6H2O salt range doping at 0.0, 0.2, 0.4, 0.6 as well as 0.8. The PVA/PTh shows large peaks approximately 20 values of 15.6⁰ and 8.9⁰ showing the amorphous structure and is owing to the scattering on the inter planar spacing from PVA/PTh chains. Rather than large peaks showing amorphous nature [16, 17, 18], PVA’s amorphous nature arises from the strong intermolecular connection of PVA chains via the intermolecular hydrogen bonding in pure PVA-PTh composite film with sulphur thiophene ring of PTh. After complexation with fillers CoCl2·6H2O salt range from 0.0, 0.2, 0.4, 0.6 and 0.8g, the composite samples of PVA-Co-PTh show strong as well as narrow peaks at 31.24⁰, 32.3⁰, 34.6⁰, 37.0⁰ and 38.15⁰. The appearance of these extra peaks is clear evidence of the Co²⁺ substitution in PVA/PTh blend and complexation through the oxygen of –OH groups of PVA via deprotonation.

FTIR spectroscopic studies:

The spectrum from FTIR showed characteristic peak at 3469 cm⁻¹ because of O–H stretching frequency of PVA/PTh blend, but in the IR spectra of PVA–Co-PTh
Moreover, the vibration peaks higher frequencies due to complexation through $S$ of composite morphology study: when fillers are added to limit the growth of PVA/PTh spherical particle agglomeration such as shaped in the shown that composite morphology shows nano previous findings. Production of such ordered structures validates conductivity. The SEM analy lead to increased electron transfer between the flacks conductive networks inside the PVA/PTh chains, which more ordered structure helps to organize electricity distribution within the PVA/PTh mat higher flakes are seen that show homogeneity in Co(II) concentration of Co (II) doping to the greatest level, medium level of doping Co(II). Increasing the SEM images generating a large particles appear to merge into the adjacent particles, rises to the medium. Doping Co(II) shows that the SEM images of PVA/PTh and the PVA-CoCl2 samples all these bands slight shifted to higher frequencies due to complexation through $S$ of thiophene ring of PTh in PVA-Co-PTh composite samples. Moreover, the vibration peaks obtained in the range of 550 cm$^{-1}$ & 770–710 cm$^{-1}$ may be assigned to (M-O) and (C-S), here M = Co$^{2+}$ that showed that the doping was polymer matrix complexes Due to the group vibration of CH3: many bands were found at the level 2935–2810 cm$^{-1}$ [21]. At 1632 cm$^{-1}$absorption was given to the thiophene stretching of the C=C ring [22]. The characteristic PVA absorption bands which are 1765, 1410, 1130, 920 & 820 cm$^{-1}$ were found for each spectrum with certain changes owing to the Co$^{2+}$ doping formation and PVA–PTh composite. These bands are allocated to CH rocking of PVA, C–O, (CH-OH), C–H band of CH3:group $^*$and Co-O, respectively [23,24]. The presence of the band at 1560 cm$^{-1}$ shows that a tiny conjugated polyyne sequence is formed that is probably responsible for doping of Co$^{2+}$with PVA--PTh blend.

**Morphology study:**

The SEM images of PVA/PTh and the PVA-Co-PTh composites with different weights of fillers 0.2, 0.4, 0.6 and 0.8g of CoCl$_2$6H$_2$O were shown in Fig.3. The SEM image of PVA/PTh visualizes the presence of an equal ratio of secondary phase (PThs) which was randomly distributed and get adhered to on PVA matrix [25,26]. PVA-Co-PTh Sample surface morphology is significantly altered by increasing the concentration of Co (II). Surface morphology exhibits globular structures for the PVA-Co-PTh sample with the lowest Co(II) concentrations. The samples’ morphology varies significantly from that of PVA/PTh, as the concentration rises to the medium. Doping Co(II) shows that the particles appear to merge into the adjacent particles, generating a large-scale structure that can be found in the SEM images of the PVA-Co-PTh samples on a medium level of doping Co(II). Increasing the concentration of Co (II) doping to the greatest level, higher flakes are seen that show homogeneity in Co(II) distribution within the PVA/PTh matrix. This form of more ordered structure helps to organize electricity conductive networks inside the PVA/PTh chains, which lead to increased electron transfer between the flacks and hence contribute to high levels of electrical conductivity. The SEM analysis indicates that with the rise in Co(II) concentration, the samples are structurally ordered. Based on the XRD studies, the production of such ordered structures validates previous findings.

Fig.4 shows PVA/PTh composite TEM images which are processed with cobalt fillers. For pure PVA/PTh it may be shown that composite morphology shows nanospherical particle agglomeration such as shaped in the 50-60 nm range. The size of particles reduced to 4 nm when fillers are added to limit the growth of PVA/PTh composite polymerization process by complexity with the filler ratios $x = 0.2$, 0.4 as well as 0.6 g Figure. 4. 0.2 and 0.6g. [27]. The nanoparticles tend to create a higher agglomeration, with a further increase in filler (0.8g).

**UV-Visible absorption studies**

Figure 5 indicates the UV–VIS spectrum of the examined sample, the spectrum of pure PVA/PTh, and that doped at various concentrations of cobalt chloride salt ($x = 0.2$, 0.4, 0.6 as well as 0.8g). The optical absorption of the produced films rises with rising the $x$ value of CoCl$_2$6H$_2$O in UV (200–400nm) and VIS(500–700nm) regions and the PVA/PTh with one spectral band on 340 nm [28]. With increased CoCl$_2$6H$_2$O contents the intensity of the bands rises which is evidence for the integration of Co$^{2+}$ into PVA/PTh matrix when its positions are slightly changed to a greater wavelength. The octahedral structure around the Co(II) ion is characterized by two absorption bands of about 550 and 625 nm. The appearance of Co$^{2+}$ ions fully as six
coordinated. The impact of Jahn–Teller may be linked to their asymmetry. This distortion was observed progressively decreased by increasing the CoCl₂·6H₂O concentration, indicating a tendency to local order via cobalt chloride additions in the amorphous polymer structure [29].

![Image](59x47 to 534x69)

**Figure 5:** The absorption spectra in the UV–VIS region for films of PVA/PTh and that doped with 0.2, 0.4, 0.6 and 0.8g of CoCl₂·6H₂O

### DC Electrical Conductivity:

Conductivity variation with temperature for the various composites PVA-Co-PTh is indicated in Fig.6. Conductivity increased by increasing temperature, which shows that semiconducting nature, these results agree with the findings reported by other comparable systems[30].

![Image](60x89 to 293x707)

**Figure 6:** Temperature dependence of electrical conductivity of composites, PVA-Co-PTh and that doped with 0.2, 0.4, 0.6, and 0.8g of CoCl₂·6H₂O

The measured room temperature conductivity for PVA/PTh, and that doped with (0.2, 0.4, 0.6, and 0.8g of CoCl₂·6H₂O, PVA-Co-PTh. Composites are 0.56x10⁻⁴ (Ωm)⁻¹, 0.66x10⁻⁴ (Ωm)⁻¹, 0.78x10⁻⁴ (Ωm)⁻¹, 0.89x10⁻⁴ (Ωm)⁻¹, as well as 1.08x10⁻⁴ (Ωm)⁻¹. These values are 2 orders of magnitude less than the reported values for individual pure PVA and PTh. This indicates that conductivity increases with the integration of Co⁺⁺ in PVA-PTh. The increase in conductivity with an increase in Co(II) concentration up to 0.8g of CoCl₂·6H₂O has been observed in PVA-Co-PTh composites [31]. The conducting data with temperature was matched to conductivity expression originated under Mott’s small polaron hopping model [32]. Under this model, conductivity is provided in the non-adiabatic region

\[
\sigma = \sigma_0 \exp \left(\frac{E_a}{K_B T}\right) \quad \ldots \ldots (1)
\]

Where \(\sigma_0\) indicates small polaron hopping activation energy and \(E_a\) signifies pre-exponential factor. The plots of ln (\(\sigma T\)) vs (1/T) were produced for all the composites according to equation (1). The least-square linear lines were fit to high-temperature data in the region in which the data was extracted linear and slopes. \(E_a\) (activation energy) of the relevant sample was determined using the slope of each line.

The variation in activation energy (\(E_a\)) as well as conductivity (\(\sigma\)) at 300K as functions of wt% of CoCl₂·6H₂O. It can be noted that \(E_a\) decreased and conductivity increased with the rise of wt% of CoCl₂·6H₂O content. The fact that the leading process is mused very easily by the appearance of Co(II) grains in between PVA-PTh grains could be causing an increase in conductivity by increasing the Co(II) content.

![Image](62x295 to 295x465)

**Figure 7:** Variation of activation energy, \(E_a\) at 300K as a function of weight in gms of CoCl₂·6H₂O in PVA-Co-PTh composites.

### Dielectric Properties:

The dielectric property of the material can be dependent on frequency. In this study, the dielectric property of the sample is evaluated by estimating different parameters such as capacitance \(C\), and \(\varepsilon'\) (Relative permittivity) & \(LP\) (loss factor) dielectric constant of the films at room temperature [33]. The dielectric behavior (\(\varepsilon'\)) as the variation for frequency for PVA-Co-PTh composites with varying Co(II) content. It may be observed that the "dielectric constant" \(\varepsilon'\) up to 4x10⁵ Hz for all the composites is constant. Later the dielectric constant tends to increase with the increment in frequency as well as with enhancement in Co(II) composition. Incorporation of Co(II) eventuated in a significant increment in the dielectric constant of the sample. The variation in the dielectric constant is generally specified to the concentration of Co⁺⁺ ions within the composites. Further, the increment in the dielectric constant can also be specified to increase in AC conductivity of the composites. This indicates that the better the dielectric constant, the higher is the capability of composites to store electric energy [34].

### Conclusions

Polyvinyl alcohol-Co-polythiophene (PVA-Co-PTh) composite polymer films have been produced using a chemical polymerization. The analysis of X-ray indicated an amorphous films structure PVA/PPy complexation with CoCl₂·6H₂O as filler. After complexation with fillers CoCl₂·6H₂O salt range from 0.0, 0.2, 0.4, 0.6 as well as...
0.8g, the PVA-Co-PTh composite samples show strong & narrow peaks on 27° & 38° with extra diffraction peaks on 31.24°, 32.3°, 34.6°, 37.9° & 38.15°. The appearance of these extra peaks is clear evidence of the Co²⁺ substitution in PVA/PTh blend and complexation through the oxygen of -OH groups of PVA via deprotonation and sulphur of thiophene ring. The FTIR spectra indicated a characteristic peak at 3469 cm⁻¹ owing to O-H stretching frequency of PVA/PTh blend, but in the IR spectra of PVA-Co-PTh composites films this absorption band was absent in all composite films of PVA-Co-PTh due to coordination of OH group of PVA to Co²⁺ ion via deprotonation. The SEM analysis demonstrated that with the rise in Co (II) content, the samples are structurally more ordered. The development of these ordered structures is based on the XRD investigations, which validate prior results. The TEM images showed that the size of particle declined with filler complexation at 0.0 to 0.6g in which excess filler addition inhibited the growth of PVA/PTh containing PVA/PPTh has a single optical absorption edge, whereas the X-ray diffraction CoCl₂·6H₂O has three edges of Co²⁺. The increase in conductivity with an increase in Co(II) concentration up to 0.8g of Co (II) has been observed in PVA-Co-PTh composites. It may be seen that E_a (activation energy) declined and conductivity raised with the rise of wt% of CoCl₂·6H₂O content. The dielectric constant tends to increase with the increment in frequency as well as with enhancement in Co(II) composition.

Acknowledgments:
We are thankful to Pooyja Dr.Sharanbashvasha Appa, President "Sharanshavareshwar Vidya varadhak Sangha, Kalaburagi", Dr. Anil Kumar Bidve, Registrar, and Registrar(Eval) Dr. Lingaraj Shastry, Dean, Dr. Basavaraj Kalaburagi, and Dr. Laxmi Patil Sharnhasa University Kalaburagi, Karnataka, for their constant encouragement and support during the process of performing this work.

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