CoCl₂ reinforced polymeric nanocomposites of conjugated polymer (polyaniline) and its conductive properties

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Abstract. Polyaniline (PANI) was synthesized by chemical oxidative polymerization of aniline using ammonium persulphate as an oxidant in acidic aqueous medium. Cobalt chloride hexahydrate (CoCl₂·6H₂O)-doped PANI composite was synthesized by *in-situ* oxidative polymerization process by using various concentrations of CoCl₂. Its chemical, structural and morphological properties were examined by X-ray diffraction, energy-dispersive X-ray spectroscopy, Fourier transform infrared spectroscopy and field-emission scanning electron microscopy techniques. These results confirmed the successful formation of PANI and CoCl₂-doped PANI nanocomposites. The morphology of CoCl₂-doped PANI nanocomposite was found to be spherical in nature. The dielectric properties were examined using LCR-HITESTER in the frequency range 50 Hz–5 MHz. The optical properties were examined by UV–visible spectroscopic techniques in the wavelength range of 200–800 nm. The high dielectric properties and alternating current conductivity of the composite was studied in the temperature range 313–373 K. It was found that the synthesized polymeric nanocomposite owned fairly suitable dielectric and optical properties for its application in actuators, conductive paints and for many other purposes.

Keywords. Polyaniline; cobalt chloride hexahydrate; SEM spectroscopy; dielectric properties; AC conductivity.

1. Introduction

In recent times, conjugated polymers have been recognized as an attractive area of research interest among research community due to its salient features for electrical, optical and thermal properties. These polymers do not carry any mobile charge and have low electronic excitation in the UV region. These polymeric materials become conductive by oxidation and reduction of charges, which conduct electricity and have wide range of applications in electrolyte membrane, electromagnetic interference (EMI) shielding, rechargeable batteries, chemical, biological and gas sensors, anti-corrosion protection coatings and microwave absorption.^{1–7} These polymeric materials have low charge carrier mobility as well.^{8–13} Among these polymeric materials, polyaniline (PANI) is recognized as one of the most commonly known candidates on account of its selective, electrochemical and tunable properties.^{14,15} It is quite inexpensive, highly environment stable, easy for synthesis¹⁶ and has high degree of conductivity. It is known to exist in different oxidation forms such as leucoemeraldine base, emeraldine base, pernigraniline base and emeraldine salt. Emeraldine salt is the important form of PANI, which is electrically conductive due to the presence of cation radicals in the structure.

Further, the addition of inorganic fillers in the polymeric chain of PANI enables to improve the electrical, optical and tunable properties to greater extent. Nowadays, numerous inorganic fillers such as SnO₂, TiO₂, Co₃O₄, ZnO and PdCl₂,^{17–21} etc. are employed as inorganic fillers to enhance the desirable properties. Cobalt chloride (CoCl₂) is one of the important class of inorganic fillers and is supplied in the form of hexahydrate (CoCl₂·6H₂O). It has been utilized for electroplating, catalyst preparation, painting on glass and porcelain and also for the manufacture of vitamin B₁₂. It is also used as water indicator, additive in fertilizer, invisible ink, computer memory devices, silica gel, printing ink, paint, etc.

Studies on PANI and its composites have been conducted extensively including PANI–Mn₃O₄, PANI–ZnFe₂O₄, PANI–ZnO, PANI–Ce(NO₃)₃·6H₂O, PANI–NaVO₃,^{22–26} etc. Ozkazanc *et al*²⁷ synthesized the PANI doped with different dopants like CuCl₂ and ZnCl₂ in aqueous HCl medium and measured their structural and dielectric properties. Gupta *et al*²⁸ synthesized PANI–CoCl₂ nanocomposite by the wet chemical method for direct current (dc) electrical transport properties. They discussed the dc conductivity in terms of variable range of hopping theory. Gupta *et al*²⁹ also synthesized CuCl₂- and CoCl₂-doped PANI through the chemical oxidation method. They found that doped PANI had more thermal stability and crystallinity than undoped PANI. They also studied

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magnetic and alternating current (AC) transport properties. Dhibar *et al*³⁰ synthesized CuCl₂-doped PANI as an electrode material for supercapacitor applications. They found that it showed higher thermal stability aimed for potential application in supercapacitor as well as in other electronic device fabrication. Thus, PANI nanocomposites are reported to be credited with huge number of studies and investigations in relation to their synthesis, characterization and properties aimed for useful application. In the present communication, the synthesis, characterization and properties of PANI–CoCl₂ nanocomposite are reported. PANI was synthesized in the form of emeraldine salt by chemical oxidative polymerization of aniline monomer and was doped by various concentrations of CoCl₂·6H₂O. Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD), energy-dispersive X-ray spectroscopy (EDX) and scanning electron microscopy (SEM) techniques were used for their characterization. Optical and dielectric properties were investigated and discussed in detail.

2. Experimental

Aniline (Merck), hydrochloric acid (35% Merck), ammonium persulphate (LOBA Chemie) and cobalt (II) chloride hexahydrate (Merck) were procured. Acetone (Merck), ethanol (Merck) and other organic solvents (Merck) were used for chemical synthesis of CoCl₂-doped PANI nanocomposite. These chemical reagents were used without any further processing and purification. Polyaniline was synthesized by chemical oxidative polymerization of aniline in aqueous acidic medium. Firstly, 2 ml aniline monomer was dissolved in 1.5 M HCl and 70 ml distilled water and the solution was stirred continuously. On the other hand, 4 g ammonium persulphate as an oxidant was dissolved in 20 ml distilled water and it was added drop wise into the above monomer solution. The whole solution was stirred at constant speed for 4 h at the temperature 0–5°C. For polymerization, the solution was kept at rest in refrigerator for 24 h. Dark green PANI precipitate was collected on a filter paper and it was washed successively with distilled water and HCl to remove the excess oxidant and monomer. The resultant precipitate in solid phase was dried in vacuum oven at 60°C for 24 h. Lastly, it was grinded using mortar pestle to obtain the PANI hydrochloride powder (emeraldine salt). An schematic reaction has been shown below.

CoCl₂-doped PANI nanocomposite was prepared by *in-situ* polymerization process. For this purpose, 2 ml of aniline was dissolved in 1.5 M HCl, 70 ml distilled water and varying amount of cobalt chloride hexahydrate (2, 5, 10, 15 and 20%) duly dissolved in 5 ml distilled water. These were mixed and vigorously stirred for half an hour. On the other hand, 4 g ammonium persulphate was dissolved in 20 ml of 1.5 M HCl solution and it was kept for half an hour at 0°C and then slowly added to the above solution. The solution was constantly stirred at the temperature of 0–5°C. For polymerization, the solution was kept at rest in refrigerator for 24 h. Consequently, dark green precipitate was collected on a filter paper and it was successively washed with ethanol, acetone and distilled water to remove oligomer, monomer and excess oxidant. Finally, the dark green precipitate was collected and dried in vacuum oven at 40°C and it was preserved for further studies. The schematic structure of the synthesized matrix has been shown below.

The polymeric matrix of CoCl₂-doped PANI nanocomposites were characterized by XRD, FTIR, EDX and field-emission SEM (FESEM) techniques to confirm the presence of CoCl₂ in the polymeric chain of PANI. XRD studies were carried out in the angular range of 10–90° using X-ray diffractometer (Model: Brooker D8) with CuKα ($\lambda = 1.5406 \text{ \AA}$) radiation. FTIR spectrum (Model: Perkin Elmer RXI) were studied in the frequency range of 400–4000 cm⁻¹ using KBr pellet. The pellet was prepared by mixing KBr and CoCl₂-doped PANI nanocomposite (1 : 20), duly pressed with 5 t of load for 1 : 30 min. Morphological studies of PANI and CoCl₂-doped PANI nanocomposite were carried out using FESEM (FESEM model: ZEISS, Supra 55 spectrometer) duly operated at 5 kV. The presence of C, Cl, Co and N was confirmed by EDAX analysis. Dielectric measurements of PANI and CoCl₂-doped PANI nanocomposites were carried out by LCR meter (Model: HIOKI-3532-50) in the frequency range of 50 Hz–5 MHz. The real and imaginary parts of permittivity, loss factor and AC conductivity were also estimated for the PANI and CoCl₂-doped PANI nanocomposites. UV–vis spectroscopy (Agilent Cary 5000) was used in the wavelength range of 200–800 nm. The optical bandgap for pure PANI and CoCl₂-doped (2, 5, 10, 15 and 20%) PANI nanocomposites were estimated to be 1.86, 1.86, 1.81, 1.78, 1.76 and 1.71 eV, respectively.

3. Results and discussion

3.1 FTIR analysis

Figure 1 shows the FTIR spectra for pure PANI and CoCl₂ (2, 5, 10, 15 and 20%)-doped PANI nanocomposites. The IR characteristic peaks for PANI were observed at 505.73, 596.40, 810.97, 1146.82, 1240.11, 1305.41, 1398.71, 1492.60, 1572.96, 2342.41 and 2371.75 cm⁻¹. The peak assignments at 1146.82 and 810.97 cm⁻¹ were attributed to the plane bending vibrations of C–H, which belonged to quinone- and benzene rings, respectively. The band at 1240.11 cm⁻¹ was attributed to the stretching vibration of C–H in the benzenoid ring. The band at 2371.75 cm⁻¹ was assigned to N–H bending vibration, whereas the bands at 1572.96 and 1492.60 cm⁻¹ corresponded to C–C stretching vibration of quinoid ring and C=N stretching, respectively. The band at 1398.71 cm⁻¹ was the characteristic vibration mode of C–H bonding of

aromatic nuclei. The CoCl₂-doped PANI nanocomposite showed that the band at 1305.41 cm⁻¹ was attributed to C–N stretching vibration shifted to 1294.53 cm⁻¹ when CoCl₂ was added in the reaction system. This indicated that the Co²⁺ interacted with the nitrogen atoms in the polymer chains. All the bands of CoCl₂-doped PANI nanocomposites were slightly shifted. This implied that the interaction between Co²⁺ and nitrogen atoms in the PANI chains was partially affected by the concentration of CoCl₂ in the reaction solution. The detailed characteristic peaks for FTIR spectra are shown in table 1.

3.2 XRD analysis

Figure 2 shows the XRD spectra for pure PANI and CoCl₂ (2, 5, 10, 15 and 20%)-doped PANI nanocomposites. The XRD pattern of pure PANI showed four diffraction peaks centred at 8.9°, 15.0°, 20.3° and 25.4°. ³¹

Figure 1. FTIR spectra for (a) pure PANI, (b) PANI–20% CoCl₂, (c) PANI–15% CoCl₂, (d) PANI–10% CoCl₂, (e) PANI–5% CoCl₂ and (f) PANI–2% CoCl₂ nanocomposites.

Figure 2. XRD spectra for (a) PANI, (b) PANI–2% CoCl₂, (c) PANI–5% CoCl₂, (d) PANI–10% CoCl₂, (e) PANI–15% CoCl₂ and (f) PANI–20% CoCl₂ nanocomposites.

Table 1. FTIR spectral data of pure PANI and CoCl₂-doped PANI nanocomposites.

Band assignments	Wavenumbers (cm ⁻¹) for PANI and CoCl ₂ -doped PANI composites					
	Pure PANI	2% CoCl ₂	5% CoCl ₂	10% CoCl ₂	15% CoCl ₂	20% CoCl ₂
C–H bending vibration	810.97,	–	801.64,	790.75,	790.75,	790.75,
	1146.82	1117.28	1107.95	1117.28	1107.95	1107.95
C–H benzenoid ring vibration	1240.11,	–	–	1238.56,	1238.56,	1238.56,
	1398.71	1387.82	1387.82	1387.82	1387.82	1387.82
C–C stretching vibration	1572.96	1563.52	1563.52	1572.85	1572.85	1563.52
C=N stretching vibration	1492.60	1471.79	1462.46	1471.79	1471.79	1471.79
C–N stretching vibration	1305.41	1305.41	1294.53	1294.53	1294.53	1294.53
N–H stretching vibration	–	2343.21,	2342.25,	2342.49,	2343.20,	2342.87,
	2371.75	2375.29	2371.81	2373.74	2373.23	2375.20

This occurred due to the scattering from PANI chains at interplanar spacing. These peaks revealed the semicrystalline nature of the pure PANI and CoCl_2 -doped PANI nanocomposites. From figure 2 it was observed that the presence of CoCl_2 in PANI chain was less effective, because meagre amount of Co^{2+} ion interacted with nitrogen in polymeric materials. Figure 2 did not represent any peak for cobalt, as very small amount of cobalt ion interacted with PANI chain in comparison to polymer.

3.3 FESEM and EDX analysis

Figure 3 shows the morphological behaviour of pure PANI and CoCl_2 (2, 5, 10, 15 and 20%)-doped PANI nanocomposites. From figure 3 it was observed that the morphology of CoCl_2 -doped PANI nanocomposites were spherical in its nature. This morphology was probably due to the reason that one Co^{2+} ion interacted with more than one nitrogen atom in PANI chain. Figure 4 shows

Figure 3. SEM micrographs (a) for pure PANI, (b) PANI–2% CoCl_2 , (c) PANI–5% CoCl_2 , (d) PANI–10% CoCl_2 , (e) PANI–15% CoCl_2 and (f) PANI–20% CoCl_2 nanocomposites.

Figure 4. EDX spectra for (a) pure PANI and (b) 20% CoCl₂-doped PANI nanocomposites.

Figure 5. Schematic curves for real part of dielectric constant for (a) pure PANI, (b) PANI–2% CoCl₂, (c) PANI–5% CoCl₂, (d) PANI–10% CoCl₂, (e) PANI–15% CoCl₂ and (f) PANI–20% CoCl₂ nanocomposites.

the EDX analysis of pure PANI and 20% CoCl_2 -doped PANI nanocomposites which indicates the presence of elements of Cl, N, C and Co. However, the EDX spectra for 2% CoCl_2 , 5% CoCl_2 , 10% CoCl_2 and 15% CoCl_2 have not been shown here because of the limiting approach of the communication.

3.4 Dielectric analysis

3.4a Dielectric constant and dielectric loss: The dielectric constant has been discussed in two separate parts. The complex part of dielectric constant was calculated by using the relation; $\varepsilon = \varepsilon' + i\varepsilon''$, where first term

represents the real part of the dielectric constant and the second term represents the imaginary part of the dielectric constant. The real part describes the stored energy and imaginary part describes the dissipated energy and both of them are frequency (ω) dependent. The real part of dielectric constant was measured experimentally by using the relation

$$\varepsilon' = \frac{c_p d}{\varepsilon_0 A},$$

where c_p is the capacitance of the specimen in Farad (F), d the thickness of the specimen in metre (m), ε_0 the

Figure 6. Schematic curves for imaginary part of dielectric constant for (a) pure PANI, (b) PANI-2% CoCl_2 , (c) PANI-5% CoCl_2 , (d) PANI-10% CoCl_2 , (e) PANI-15% CoCl_2 and (f) PANI-20% CoCl_2 nanocomposites.

dielectric permittivity in vacuum and A the surface area in m². The imaginary part of the dielectric constant was calculated by using the relation

$$\varepsilon'' = \varepsilon' \tan(\delta),$$

where $\tan(\delta)$ is the loss factor. By using the dielectric constant and dielectric loss, the AC conductivity of the specimen is calculated with the help of the below equation

$$\sigma_{AC} = \omega \varepsilon' \varepsilon_0 \tan(\delta),$$

where ω is the angular frequency.

Figures 5 and 6 show the variation of real part of dielectric constant and dielectric loss in the frequency range 50 Hz–5 MHz and in the temperature range 313–373 K for pure PANI and CoCl₂ (2, 5, 10, 15 and 20%)-doped PANI nanocomposites. The value of dielectric constant and dielectric loss decreased with the increase in frequency for CoCl₂-doped PANI nanocomposites due to dielectric relaxations. On the other hand, the movement of dipoles and charge carriers were slowed down due to the alternating applied field. It was found that the dielectric constant and dielectric loss were quite high at low frequency and decreased at higher frequency. At low frequency, dielectric constants and dielectric loss increased

Figure 7. Schematic curves for AC conductivity (S m^{-1}) as a function of frequency at different temperatures for (a) pure PANI, (b) PANI–2% CoCl₂, (c) PANI–5% CoCl₂, (d) PANI–10% CoCl₂, (e) PANI–15% CoCl₂ and (f) PANI–20% CoCl₂ nanocomposites.

Figure 8. (a) UV-vis spectra and (b) optical bandgap for pure PANI and CoCl_2 (2, 5, 10, 15 and 20%)-doped PANI nanocomposites.

up to temperature 353 K and then decreased due to orientation polymerization. At higher frequency, these two were frequency independent as the dipoles in the system could not reorient themselves. The real and imaginary part of dielectric constant of the pure PANI did not depend upon the temperature, as shown in figures 5a and 6a, respectively. For 20% of CoCl_2 content in PANI nanocomposite, dielectric constant and dielectric loss were observed to be higher in comparison to the other nanocomposites.

3.4b AC Conductivity: Figure 7 shows the variation of AC conductivity as a function of frequency at different temperatures for the pure PANI and CoCl_2 (2, 5, 10, 15 and 20%)-doped PANI nanocomposites. The AC conductivity was calculated in the frequency range 50 Hz–5 MHz and in the temperature range 313–373 K. The AC conductivity of all the specimens showed dispersion behaviour of the curve. At low frequency, the AC conductivity dropped either due to the interfacial impedance or space charge polarization. At high frequency, the AC conductivity increased due to trapped charges, which were active only in the higher frequency range. However, conductivity of pure PANI was not adversely affected for the varying range of temperature, as shown in figure 6a.

3.5 UV-visible spectroscopy

Figure 8a shows the absorbance spectra for pure PANI and CoCl_2 (2, 5, 10, 15 and 20%)-doped PANI nanocomposites. According to figure 8 we observed the two absorption peaks for all specimens. The characteristic absorption bands for (a) pure PANI was found at 344.20 and 633.94 nm, which occurred due to π – π^* transition and the transition of benzenoid rings into quinoid rings. The absorption peaks due to π – π^* transition for curves (b), (c), (d), (e) and (f) for CoCl_2 -doped PANI

nanocomposites shifted at 317.28, 323.67, 299.68, 290.09 and 319 nm, respectively. The absorption peak due to quinoid ring transition of curves (b), (c), (d), (e) and (f) appeared at 635.53, 635.53, 627.54, 633.94 and 635.53 nm, respectively. The absorption peak for nanocomposites due to π – π^* transition and quinoid ring transition was shifted from that of the absorption peak of pure PANI. This indicates that the cobalt ion prefers to interact with the nitrogen atoms of the quinone rings. This is in good agreement with the literature.³²

3.6 Optical bandgap

The optical bandgaps of all the specimens were directly calculated from the UV-visible spectra, for which the photon absorption obeyed the Tauc relation³³ as shown below

$$\alpha h\nu = B(h\nu - E_{\text{opt}})^n,$$

where α is the absorption coefficient, $h\nu$ the incident photon energy, B the constant and n the distribution of the density of states. The values of n equal to 1/2 and 2 corresponded to the direct bandgap and indirect bandgap, respectively.³⁴ In the present investigation, the optical bandgap of pure PANI was estimated around 1.86 eV. Figure 8b shows the bandgap of pure PANI and CoCl_2 (2, 5, 10, 15 and 20%)-doped PANI nanocomposites. After doping with CoCl_2 (2, 5, 10, 15 and 20%), the bandgap of the CoCl_2 -doped PANI nanocomposites were decreased to 1.81, 1.78, 1.76 and 1.71 eV, respectively. The optical bandgap of 2% CoCl_2 -doped PANI nanocomposite was not affected because of the low content of CoCl_2 . The reduction in the optical bandgap of CoCl_2 -doped PANI nanocomposites occurred due to the incorporation of CoCl_2 in the polymer chain, which is known to increase the density of states preferably in the visible region of the electromagnetic spectrum.³⁵

Table 2. Optical bandgap for pure PANI and CoCl₂ (2, 5, 10, 15 and 20%)-doped PANI nanocomposites.

Polymeric materials	Bandgap (eV)
Pure PANI	1.86
PANI-2% CoCl ₂	1.86
PANI-5% CoCl ₂	1.81
PANI-10% CoCl ₂	1.78
PANI-15% CoCl ₂	1.76
PANI-20% CoCl ₂	1.71

4. Conclusions

CoCl₂-doped PANI nanocomposites were synthesized by *in-situ* oxidative polymerization process. The FTIR studies showed that the structure of backbone chains of PANI-CoCl₂-doped PANI nanocomposites were changed weakly in comparison to the pure PANI. The FESEM studies showed that the morphology of CoCl₂-doped PANI nanocomposites were spherical in nature. The XRD patterns of pure PANI and CoCl₂-doped PANI nanocomposites showed a meagre effect on the semicrystalline nature of pure PANI. At low frequency, dielectric constant and dielectric loss increased with the increase in temperature up to 353 K and then it decreased at 363 and 373 K. The AC conductivity for CoCl₂-doped PANI nanocomposites increased up to 353 K and decreased at 363 and 373 K. The AC conductivity for CoCl₂-doped PANI nanocomposites increased at higher frequency due to the mechanism of hopping action. The AC conductivity, dielectric constant and dielectric loss of the CoCl₂-doped PANI nanocomposites showed higher values in comparison to the values for pure PANI. The studies showed encouraging results aimed towards its use in conductive paints, rechargeable batteries, actuators, etc.

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