

Structural, thermal and optical properties of Cu^{2+} and Co^{2+} : PVP polymer films

K Sivaiah, B Hemalatha Rudramadevi & S Buddhudu*

Department of Physics, Sri Venkateswara University, Tirupati 517 502, India.

and

G Bhaskar Kumar

Alternative Energy and Nanotechnology Laboratory, Department of Physics, Indian Institute of Technology Madras
Chennai 600 036, India.

and

A Varadarajulu

Department of Polymer Science, S.K.University, Anantapur 515 003, India

*E-mail: profsb_svuniv@hotmail.com

Received 19 April 2010; accepted 8 July 2010

Spectral characterization of Cu^{2+} and Co^{2+} : PVP polymer films has been carried out from the measurement of their absorption, excitation and emission spectra in order to understand their optical performance as the visible colour displaying luminescent materials. Transparent and very clear natured reference PVP polymer film has also been developed by employing a solution cast method to measure the profiles of XRD, FTIR and Raman spectra in exploring its structural details. Besides, we have also reported its thermal properties based on the measurement of TG-DTA profiles.

Keywords: PVP polymer films-characterization, FTIR, Raman spectra, X-ray diffraction, Absorption spectra

1 Introduction

In recent years, water soluble polymers such as PVA, PVP, etc, have been found to be more significant because of their possessing different applications. These polymers films have interestingly been found to be easily accepting various transition metal and rare earths as the dopant ions in required concentrations in their transformation as brightly luminescent polymer films of technical importance¹⁻³. Interactions between metal ions and water-soluble polymers such as polypeptides have been displaying significant influence on the behaviors of macromolecules⁴⁻⁶. Polyvinylpyrrolidone (PVP) has drawn a special attention amongst the conjugated polymers because of its good environmental stability, easy process situation and excellent transparency. PVP is a potential material having a good charge storage capacity and dopant-dependent electrical and optical properties. Chemically PVP has been bound to be inert, non-toxic and interestingly, it displays a strong tendency for complex formation with a wide variety of smaller molecules⁷⁻⁹.

Based on the identification of the importance and relevance of the PVP polymer as a suitable matrix, a couple of transition metal ions such as Cu^{2+} and Co^{2+}

ions have been chosen separately into the PVP polymer matrix, as luminescent ions to study their optical performance from the measurement of their absorption, excitation and emission spectra. Also the structural and thermal properties from measurement of XRD, FTIR, Raman spectra and TG-DTA profiles of the PVP polymer film have also been undertaken and the results are reported in the present work.

2 Experimental Details

PVP [polyvinylpyrrolidone $(\text{C}_6\text{H}_9\text{ON})_n$] possessing a molecular weight (MW) of 13,00,000 was purchased from M/s Sigma Aldrich Company. This PVP chemical was dissolved in a doubled distilled water of 50 cc in quantity and then it was mixed homogeneously by using a magnetic stirrer in a little warm condition of it; later this solution was cast into polymer films by employing flat and smooth surfaced dishes by means of a slow evaporation method in obtaining the reference or host PVP films in highly clean and more transparent form. Similarly, Cu^{2+} : PVP and Co^{2+} : PVP polymer films were developed by dissolving CuCl_2 and CoCl_2 salts each separately in double distilled water in a ratio of 1:9 of transition metal solution and the PVP solution. The Cu^{2+} and

Co^{2+} : PVP films, thus, prepared were cut in to different sized polymer films to carry out measurements on them accordingly.

The XRD profiles of both the reference PVP film and the Cu^{2+} or Co^{2+} : PVP polymer films were measured on a Shimadzu-XD 3A diffractometer with a Ni-filter and $\text{CuK}\alpha$ (1.542\AA) radiation with an operating voltage of 30 kV and current of 20 mA with a Si detector with the 2θ values at the rate of $2^\circ/\text{min}$. FTIR spectra of these samples were also carried out on a Nicolet IR-200 Spectrophotometer using KBr pellet technique in the range $4000\text{--}400\text{ cm}^{-1}$. In both XRD and FTIR measurements, it was noticed that doped and also the undoped PVP polymer films were showing similar natured profiles hence a specimen profiles of the reference PVP polymer film are shown in Figs 2 and 3, respectively. Thermo gravimetric (TG) and Differential Thermal Analysis (DTA) were performed for the precursor in N_2 atmosphere at a heating rate of $10^\circ\text{C}/\text{min}$ on a Netzsch STA 409 Simultaneous Thermal Analyzer. Raman spectrum was recorded on a high resolution Jobin Yvon Model HR800 UV system with a He-Ne laser (633 nm) as the excitation source with 15 mW as the output power having a laser beam spot size of $100\ \mu\text{m}$ through an appropriate lens system.

PVP polymer has not shown any characteristic absorption profile from its absorption spectrum, however, Cu^{2+} and Co^{2+} : PVP have shown absorption bands ($600\text{--}1500\text{ nm}$) and ($400\text{--}1800\text{ nm}$), respectively as shown in Figs 6 and 8. Both excitation and emission spectra of Cu^{2+} and Co^{2+} : PVP polymer films were recorded in the wavelength range $250\text{--}700\text{ nm}$, on a SPEX Fluorolog-2 Fluorimeter (Model-II) attached with a Xe-arc lamp (150W). This fluorescence system employs the Datamax software in acquiring spectral data of the samples used for the measured green emission (542 nm).

3 Results and Discussion

Figure 1 shows both the undoped (reference) and doped PVP polymer films (Co^{2+} and Cu^{2+}). The measured X-ray diffraction (XRD) profile of the PVP film is shown in Fig. 2, which confirms the amorphous nature of the prepared polymer film that is in conformity with the earlier reports in literature¹⁰.

Figure 3 shows the FTIR spectrum of the PVP polymer film in the range $4000\text{--}400\text{ cm}^{-1}$. Since both the PVP and Co^{2+} and Cu^{2+} : PVP polymer films have exhibited similar characteristic FTIR bands, therefore, for one specimen sample (reference PVP polymer

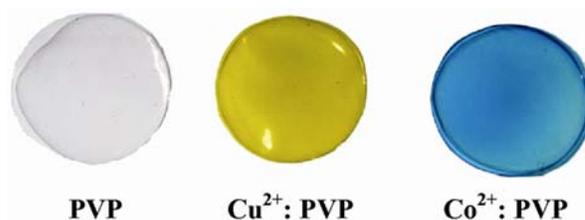


Fig. 1 — Reference PVP polymer film; Cu^{2+} : PVP and Co^{2+} : PVP polymer films

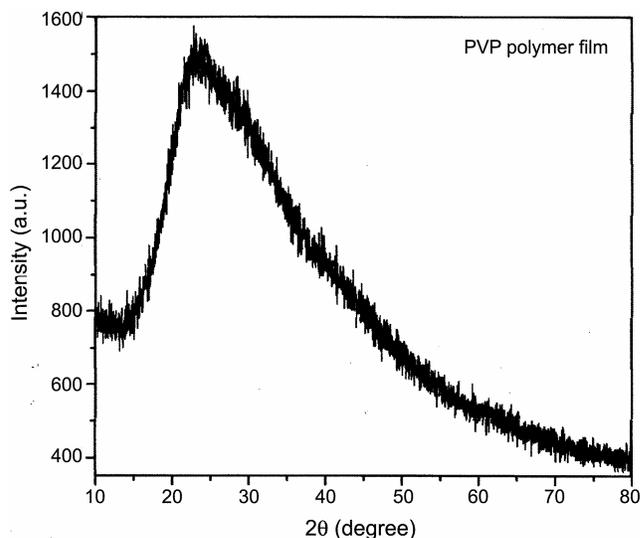


Fig. 2 — XRD profile of PVP polymer film

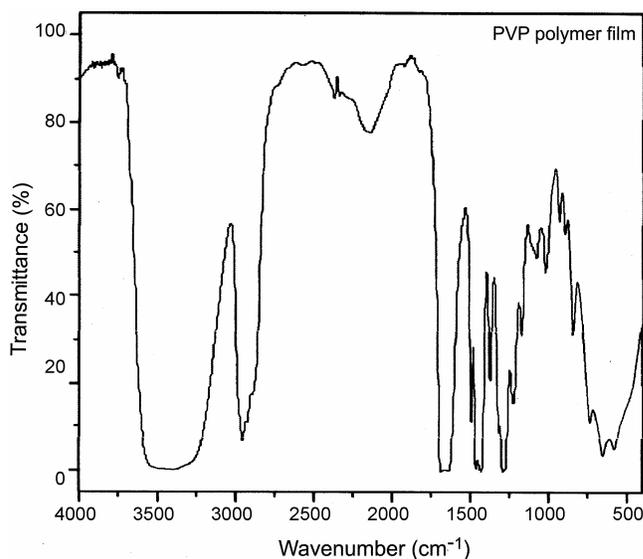


Fig. 3 — FTIR profile of PVP polymer film

film), the FTIR spectrum has been presented here. The obtained results from it, are in good agreement with the earlier reports in literature¹¹⁻¹⁵. A broad peak located at 918 cm^{-1} is due to the outer face vibration oscillation of the hydroxyl group ($\delta_{\text{O-H}}$), and the

strong peaks centered at 1447 cm^{-1} and 1286 cm^{-1} are assigned to the inner face bending vibrations of the hydroxyl group. We have also observed a broad band at 3400 cm^{-1} in the spectrum of PVP, and the vibration band of C=O group appears at 1665 cm^{-1} suggesting some H-bonding carbonyl groups exist in PVP. A broad and intense band in the range $3100\text{--}2500\text{ cm}^{-1}$ is ascribed to the stretching vibration of the associated hydroxyl group. The bands at 2900 and 1650 cm^{-1} are attributed to the characteristic stretching vibrations of C-H band respectively. Some researchers have proposed that a blue-shift of the C=O group in PVP can be attributed to the change of $p\text{-}\pi$ conjugation associated with the amide group of PVP arising from dissociation of PVP chains due to the incorporation of other species. It is possible that the interaction between the complexes and PVP leads to the dissociations of the aggregated PVP chains, resulting in the blue-shift of the C=O vibration band. From the summarized spectral features listed above, it can be seen that stronger super molecular interaction exists in these composites^{16,17}.

Figure 4 shows the Raman spectrum of PVP in the range $200\text{--}4000\text{ cm}^{-1}$. From the Raman spectrum, it has been observed that the intensity of the Raman band corresponding to the C-N vibration band at 758 cm^{-1} and C-C stretching vibration at 934 cm^{-1} . The bands at 1228 and 1421 cm^{-1} have been due to C-N stretching and C-H bending vibrations of pure PVP, respectively. The bands at 1663 cm^{-1} and 2928 cm^{-1} are attributed to C=O and C-H stretching vibrations, respectively^{19,20}.

Figure 5 shows the TG-DTA profiles of PVP polymer. The TGA thermogram has been plotted with

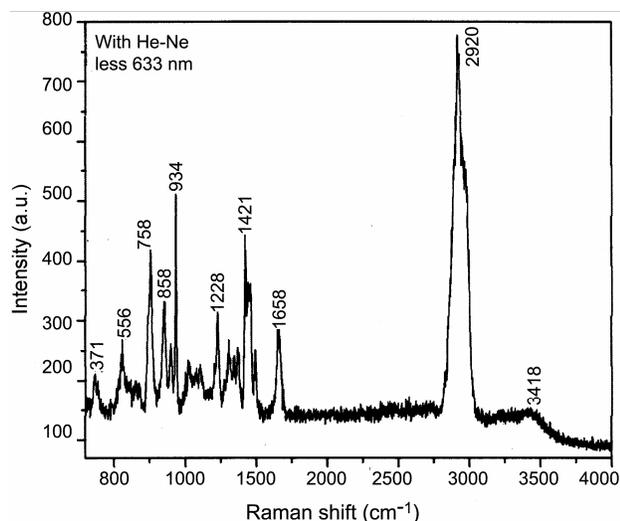


Fig. 4 — Raman spectrum of PVP polymer film

weight loss as a function of the temperature for the reference PVP precursor with a heating rate of $10^\circ\text{C}/\text{min}$ in the temperature range from 40 to 800°C . It is clear that the initial weight loss from the TG curve is 12% in the temperature range $40\text{--}103^\circ\text{C}$, is due to loss of OH content. In the DTA curve, two exothermic peaks were observed at 433° and 570°C , respectively. The sharp and strong exothermic peak at 433°C is due to the combined effect of combustion of organic residuals and the decomposition of PVP and which is well above the heating temperature employed in the present work. Correspondingly, the weight loss in TG curve is 18% between the temperatures^{13,18} from 470 to 605°C .

The optical absorption spectrum ($600\text{--}1450\text{ nm}$) of the Cu^{2+} : PVP polymer film is shown in Fig. 6 exhibiting a broad and intense absorption band which

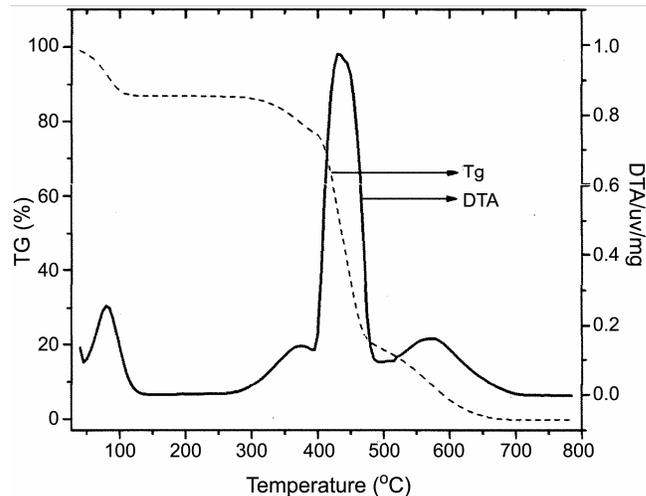


Fig. 5 — TG-DTA curves of PVP polymer precursor

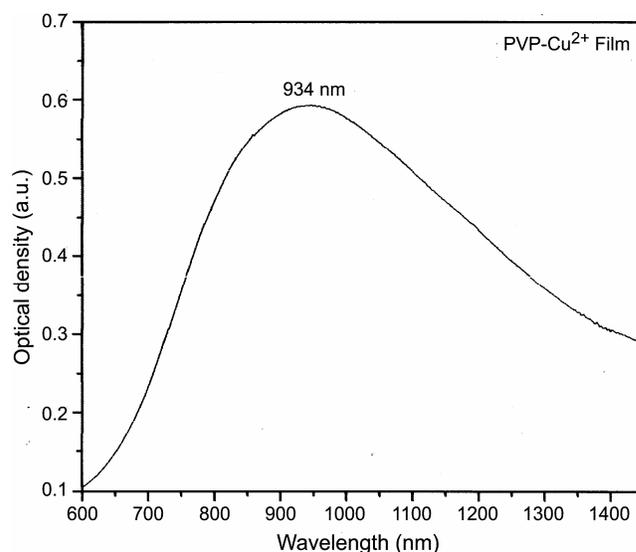


Fig. 6 — Absorption spectrum of Cu^{2+} : PVP polymer film

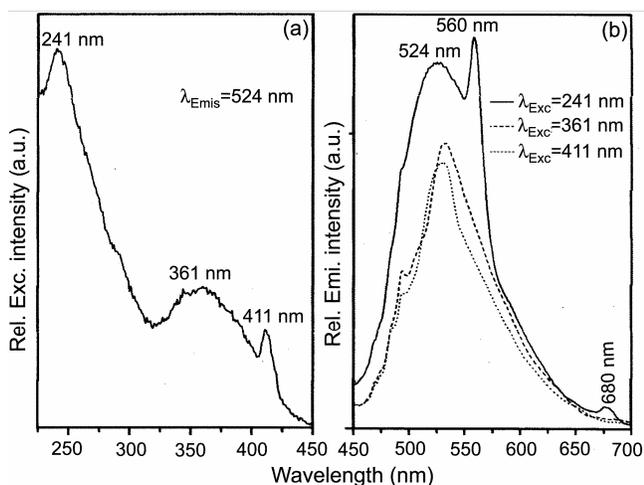


Fig. 7 — (a) Excitation and (b) Emission spectra of Cu^{2+} : PVP polymer film

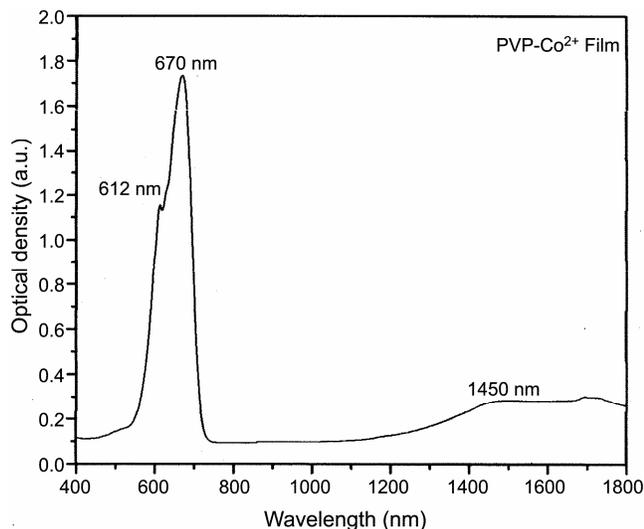


Fig. 8 — Absorption spectrum of Co^{2+} : PVP polymer film

is assigned to the $d-d$ transition of ${}^2\text{B}_{1g} \rightarrow {}^2\text{B}_{2g}$. Fig. 7 shows (a) excitation and (b) emission spectra of Cu^{2+} : PVP polymer film. It has earlier been reported that, chloride based polymer films could show charge transfer bands in the UV region, which normally fall in the wavelength range 225-450 nm. Accordingly, the Cu^{2+} : PVP polymer film has shown three excitation bands at 241, 361 and 411 nm. Emission spectrum shows a green emission at 524 nm that has been measured at three different excitation wavelength²¹ as shown in Fig. 7(b). The absorption spectrum of Co^{2+} : PVP Polymer film is shown in Fig. 8 revealing two bands are at 612 nm and 670 nm corresponding to the transitions of ${}^4T_1(F) \rightarrow {}^4T_2(F)$ and ${}^4T_1(F) \rightarrow {}^4A_2(P)$, respectively. A less intense band, however, in broader nature is located at 1450

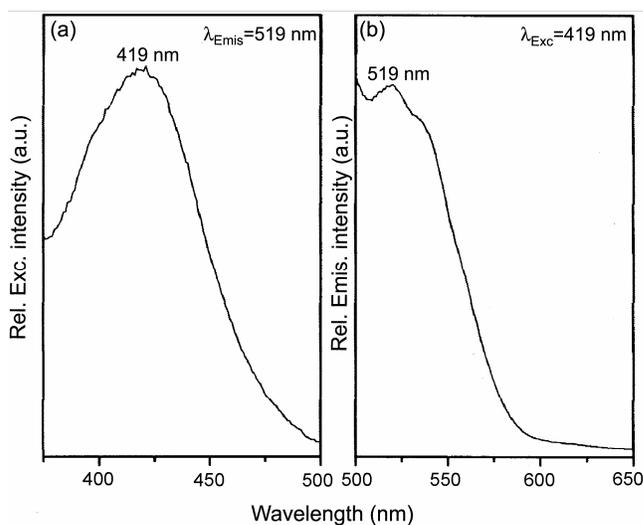


Fig. 9 — (a) Excitation and (b) Emission spectra of Co^{2+} : PVP polymer film

nm and it has also been assigned to the electronic transition ${}^4T_1(F) \rightarrow {}^4T_2(F)$ [22, 25]. Figure 9 shows the (a) excitation and (b) emission spectra of Co^{2+} : PVP polymer film. Figure 9(a) shows an intense excitation band²⁴ at 419 nm and Fig. 9(b) shows a bluish green emission at 519 nm which is assigned to the transition of $[{}^4T_1(F) \rightarrow {}^4A_2(F)]$.

4 Conclusions

It could be concluded that we have successfully developed Cu^{2+} and Co^{2+} : PVP polymer films and also a reference PVP polymer film by employing solution cast method. For the reference PVP, structural properties have been investigated based on the measurement of XRD, FTIR and Raman spectra. Optical characterization of Cu^{2+} : PVP and Co^{2+} : PVP polymers have been carried out from the measurement of their absorption, excitation and emission spectra. The results are encouraging to identify them as brightly visible colour luminescent materials.

References

- Díaz E, Valenciano R, Landa P, Arana J L & González J, *Polymer Testing*, 21 (2002) 247.
- Díaz E, Valenciano R B & Katime I A., *J Appl Polym Sci*, 93 (2004) 1512.
- Rzayev Z M O, Denizli B K & Denizli H, *J Appl Polym Sci*, 109 (2008) 903.
- Queiroz A A A D, Soares D A W, Trzesniak P & Abraham G A, *J Polym Sci, Part B: Polym Phys*, 39 (2001) 459.
- Hao C, Zhao Y, Dong X, Zhou Y, Xu Y, Wang D, Lai G & Jiang J, *Polym Int*, 58 (2009) 906.
- Rivas B L, Pereira E D & Villoslada I M, *Polymer Sci*, 28 (2003) 173.
- Wöhrle D *Macromolecular Metal Complexes: Materials for Various Applications Angew Chem Int Ed*, 44 (2005) 7500.

- 8 Majhi P R, Moulik S P, Burke S E, Rodgers M & Palepu R, *J Colloid Interface Sci*, 235 (2001) 227.
- 9 Wu H D, Wu I D & Chang F C, *Polymer*, 42 (2001) 555.
- 10 Razzak M T, Zainuddin Erizal, Dewi S P, Lely H, Taty E & Sukirno, *Radiat Phys Chem*, 55 (1999) 153.
- 11 Moharram M A & Khafag M G, *J Appl Polym Sci*, 105 (2007) 1888.
- 12 Dhanuskodi S, Mary P A A & Rao P S, *Spectrochim Acta, Part A*, 61 (2005) 721.
- 13 Zhenfeng C, Huijuan R, Guixia L & Guangyan H, *J Rare Earths*, 24 (2006) 724.
- 14 Abdelaziz M & Abdelrazek E M, *Physica B: Condensed Matter*, 390 (2007) 1.
- 15 Zheng S, Guo Q & Mi Y, *J Polym Sci, Part B: Polym Phys*, 37 (1999) 2412.
- 16 Zhang G, Zhang J, Zhou X & Shen D, *J Appl Polym Sci*, 88 (2003) 973.
- 17 Liu H G, Lee Y I, Qin W P, Jang K & Feng X S, *Mater Lett*, 58 (2004) 1677.
- 18 Ramya C S, Selvasekarapandian S, Savitha T, Hirankumar G & Angelo P C, *Physica B*, 393 (2007) 11.
- 19 Fini A, Cavallari C & Ospitali F *European J Pharmaceutics and Biopharmaceutics*, 70 (2008) 409.
- 20 Phoka S, Laokul P, Swatsitang E, Promarak V, Seraphin S & Maensir S, *Mater Chem Phys*, 115 (2009) 423.
- 21 Volk Y V, Malyarevich A M, Yumashev K V, Alekseeva I P, Dymshits O S, Shashkin A V & Zhilin, *J Non-Cryst Solids*, 353 (2007) 2408.
- 22 Stanescu G & Trutia A, *Optical*, 29 (2006) 332.
- 23 Zhang S, Xia H, Wang J & Zhang Y, *J Alloys Compd*, 63 (2008) 446.
- 24 Sun Z, Yuan D, Duan X, Wei X, Sun H, Luan C, Wang Z, Shi X, Xu D & Lv M, *J Cryst Growth*, 260 (2004) 171.
- 25 Rudramadevi B H & Buddhudu S, *Indian J Pure & Appl Phys*, 46 (2008) 825.