Arabian Journal of Chemistry (2016) 9, S1786–S1792

King Saud University

Arabian Journal of Chemistry

www.ksu.edu.sa
www.sciencedirect.com

REVIEW

Structural and optical properties of pure PVA/PPY and cobalt chloride doped PVA/PPY films

G.M. Elkomy [a,d], S.M. Mousa [b,*], H. Abo Mostafa [c]

[a] *Electron Microscopes and Thin Film Department, National Research Centre, Dokki, P.O. Box 12622, Postal Code: 11787, Cairo, Egypt*
[b] *Inorganic Chemistry Department, National Research Centre, Dokki, P.O. Box 12622, Postal Code: 11787, Cairo, Egypt*
[c] *Physics Department, Faculty of Science, Menoufia University, Egypt*
[d] *Physical Science Department, Rabigh-college of science and art, King Abdulaziz university, P.O. BOX 344, Rabigh 21911, Saudi Arabia*

Received 20 November 2011; accepted 27 April 2012
Available online 7 May 2012

KEYWORDS
PVA/PPY composite;
$CoCl_2{\cdot}6H_2O$;
XRD;
IR;
TEM;
Optical properties

Abstract Polyvinyl alcohol-polypyrrole (PVA/PPY) composite polymer films were prepared by chemical polymerization. Cobalt chloride $CoCl_2{\cdot}6H_2O$ was used at different concentrations as doping (x = 0.2–1.0 g). The produced films were characterized by X-ray diffraction (XRD), Infrared spectroscopy (IR) and transmission electron microscopy (TEM). The optical properties of all produced films were studied, where the optical absorption of the prepared films decreases with increasing the x value of $CoCl_2{\cdot}6H_2O$ in both VIS (500–700 nm) and UV (200–400 nm) regions. The calculated energy gaps (E_{g1} and E_{g2}) were found to decrease as the $CoCl_2{\cdot}6H_2O$ concentration increases. While Eg_3 tended to be constant as $CoCl_2{\cdot}6H_2O$ content increases.

© 2012 Production and hosting by Elsevier B.V. on behalf of King Saud University. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/3.0/).

---

[*] Corresponding author. Tel.: +20 10 6506612; fax: +20 23 3335968.
E-mail address: dollyriri@yahoo.com (S.M. Mousa).

Peer review under responsibility of King Saud University.

Production and hosting by Elsevier

http://dx.doi.org/10.1016/j.arabjc.2012.04.037

1878-5352 © 2012 Production and hosting by Elsevier B.V. on behalf of King Saud University.
This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/3.0/).

Contents

1. Introduction S1787
2. Experimental. S1787
2.1. Preparation S1787
2.2. Characterization S1787
3. Results and discussion S1788
4. Conclusion S1791
References. S1791

1. Introduction

In the recent years, the field of conjugated polymers has attracted the attention of many scientists due to the interesting electrical and optical properties of these compounds (Deronzier and Moutet, 1989). There has been increasing interest in soluble conducting polymers because of their potential applications, such as soluble ion-exchangers, energy-storage materials, corrosion-resistant coatings and catalysts (Eisazadeh et al., 1993; Eisazadeh et al., 1994; Armes and Aldiss, 1999).

Nowadays, conducting polymers also known as conductive plastics are being developed for many uses such as compact capacitors, ant statistic coating, electromagnetic shielding and smart windows which capable to vary the amount of light to pass (Benget and Krutmeijer, 2000). Polypyrrole, (PPY) is one of these new generations of polymeric materials. It has been the main focus due to the advantages such as environmentally stable, ease to synthesis and relatively high conductivity as compared to the other derivatives (Hamzah et al., 2004; Hamzah et al., 2003; Benseddik et al., 1995). However, limitation such as insolubility and poor mechanical strength are barriers for mass production. Improvement of these properties can be achieved either by forming copolymers of pyrrole or by forming PPY composites or blends with commercially available polymers or inorganic materials which offer better mechanical and optical properties, stability and process ability (Paoli et al., 1984; Lindsey and Street, 1984), so polypyrrole combines with an insulating polymer has superior mechanical properties (Niwa and Tamamura, 1984; Otero and Sansinena, 1996). The polymer composites can be prepared either by electrochemical or chemical polymerization. In this work, the polyvinyl alcohol was used as insulating polymer and combined with PPY by using chemical polymerization to improve the properties of PPY. Inorganic additives such as transition metal salts have considerable effect on the optical and electrical properties of PVA polymer (Khaled and Basha, 1989; Baha et al., 1988; Barakat et al., 1989; Noguchi et al., 1998). In the present study PVA is incorporated that acts as host material in the conducting composite polymer containing composite polymer containing PPY. The concentration of the doping namely hydrous cobalt chloride was varied in order to investigate the influence of doping compositions on structure, optical and electrical properties of the composite polymer.

2. Experimental

2.1. Preparation

Three grams of polyvinyl alcohol (PVA) with MW = 7000, was dissolved completely in 100 ml distilled water under constant stirring. The mixture heated at 90 °C for 1 h and was let to cool down to room temperature. From the cooled mixture, 30 ml were mixed with 1.0 g of pyrrole (PY) monomer already dissolved in 15 ml of distilled water. The mixture was further stirred for 5 min. Finally, 0.2 g cobalt chloride ($CoCl_2{\cdot}6H_2O$) were used as a doping in the composite mixture and stirred further for 10 min. Different amounts of Cobalt salt (x = 0.4, 0.6, 0.8 and 1.0 g) were added as stated above, so different samples were prepared. Thick films were made by casting method, where the mixture for each sample was poured in a glass Petri dish and let to dry at room temperature for 120 h, after this time, the films were ready to cut into suitable pieces for characterization.

2.2. Characterization

X-ray diffraction patterns (XRD) were recorded by using Brukur D8 advanced diffractometer (Germany) with copper (Kα) radiation, where the instrument allows Bragg's low and works at (40 kV and 40 mA) with 0.02°/0.4 s. Infrared measurements (IR) were recorded by JASCO–FT/CR-3000E infrared spectrometer from 4000 to 550 cm^{-1} (ATR-FTIR was used in this work due to high thickness and opacity of the prepared samples). The morphology and the particle size of the prepared samples were examined by transmission electron microscopy (TEM) JEOL JEM-1230 operating at 120 kV. The tools used for optical measurements of the caste films at normal light incidence in the wavelength range from 300 to 900 nm.

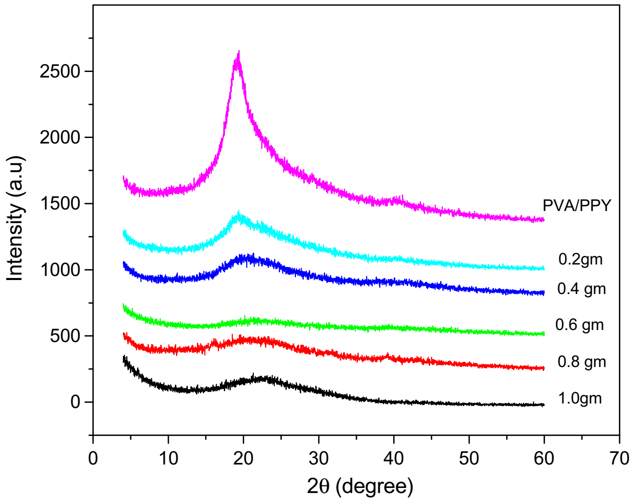

Figure 1 XRD patterns of PVA/PPY composite and that doped with filler (0.2, 0.4, 0.6, 0.8 and 1.0 g of $CoCl_2$ $6H_2O$).

3. Results and discussion

Fig. 1 shows the XRD patterns of pure PVA/PPY and that doped with $CoCl_2{\cdot}6H_2O$ salt range from 0.0, 0.2, 0.4, 0.6, 0.8 and 1.0 g. The XRD pattern of PVA/PPY composite film reveals an intense peak at scattering angle ($18 < 2\theta < 20$) corresponding to a spacing of 4.57 (PVA) indicating semi-crystalline nature, (El-Tantawy et al., 2004; Hung et al., 2005; Bhargav et al., 2007). The semi-crystalline nature of PVA results from the strong intermolecular interaction of PVA chains through intermolecular hydrogen bonding. The intensity of the diffraction peak of PVA is determined by the number of PVA chains packed together. It was noticed that there is no any characteristic peak observed for PPY, because the PPY films have been reported to be highly disordered and non-crystalline (Kassim et al., 1994). After complexation with fillers, the patterns of the composite films show amorphous structure where, the intensity of PVA diffraction peak gradually decreased with further increasing of cobalt due to the interactions between PVA/PPY and the mixed fillers leads to a decrease in the intermolecular interaction between PVA/PPY chains and thus the crystalline degree (Yu et al., 2003).

Fig. 2 exhibits the IR spectra of PVA–PPY composites films and that doped with $CoCl_2{\cdot}6H_2O$ filler. For all spectra, strong bands were occurred at 3800–3200 cm^{-1} which arises from O–H and N–H stretching frequency of PVA and PPY (Ege, 1989). Several bands were observed at 2940–2820 cm^{-1} due to CH_2 group vibration (Sweeting, 1968). The absorption at 1630 cm^{-1} was assigned to the C═C ring stretching of pyrrol (Sun et al., 1996). The characteristic absorption bands of PVA which are 1763, 1420, 1128, 917 and 820 cm^{-1} were observed for all spectra with some shifts due to the

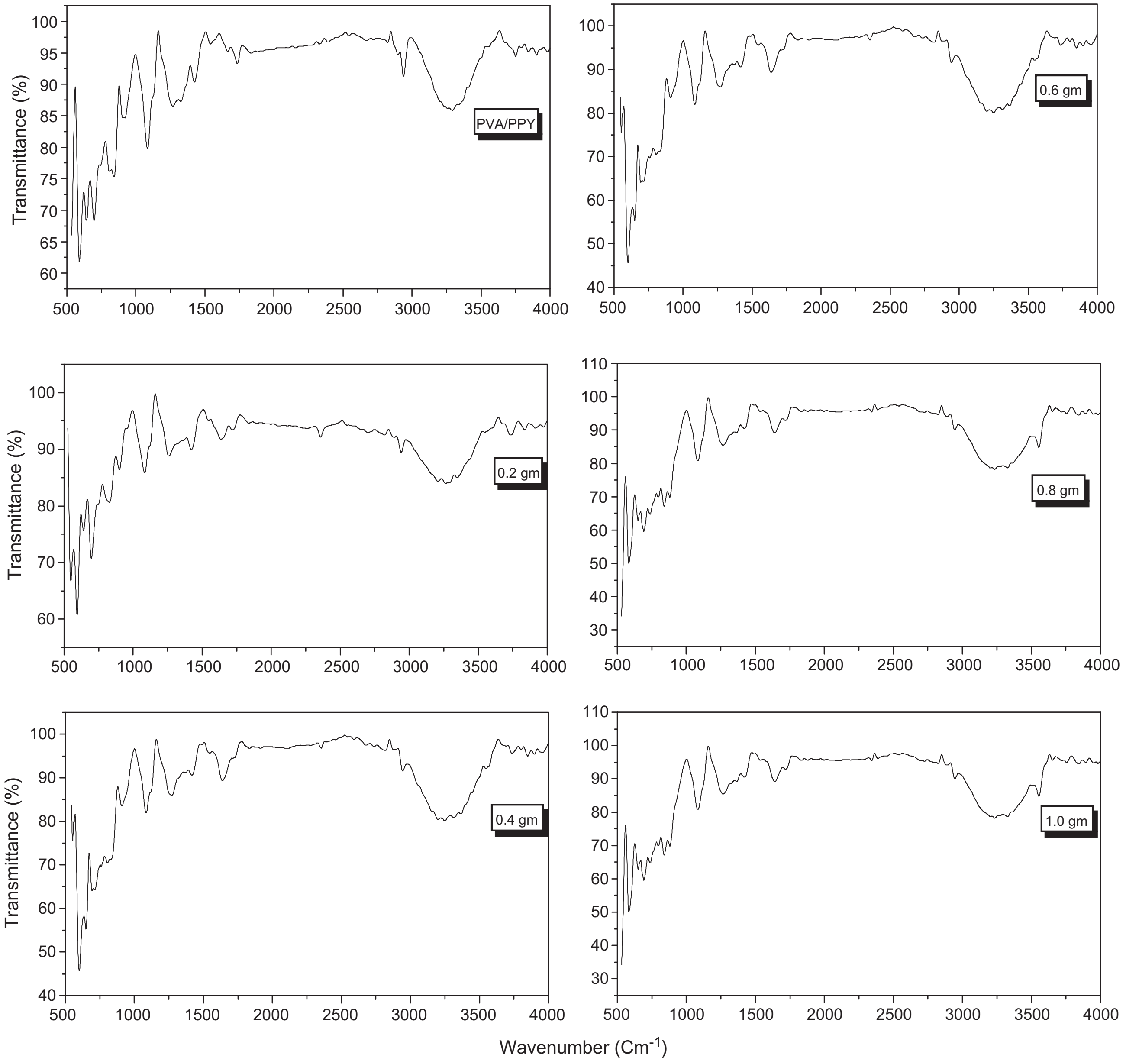

Figure 2 FTIR spectra of PVA/PPY composite and that doped with filler (0.2, 0.4, 0.6, 0.8 and 1.0 g of $CoCl_2\ 6H_2O$).

formation of PVA–PPY composite and doping with Co^{+3}. These bands are assigned to C═O, C–H band of CH_2 group, (CH–OH), C–O and CH rocking of PVA respectively (Rajendan et al., 2003). The absorption band at 917 $cm^{-1}$was found to be characteristic of syndiotatctic structure of the prepared film (Rajendran et al., 2004) and can be also for C–H (out of plane deformation) (Eisazadeh, 2007). The appearance of band at 1560 cm^{-1} is indicative of the formation of small conjugated polyene sequence which is presumably responsible for the color of doping with PVA–PPY (Chakraborty et al., 1999). The absorption band at 640 cm^{-1} indicates the presence of hydroxyl group (Sweeting, 1968). At 690 cm^{-1}, an absorption band was observed may be due to C–C or C–H vibration for PPY, while the absorption bands occurred at 1084 and 1260 cm^{-1} were attributed to C–O and C–H of PVA respectively (Tawansi et al., 1998). Further, the vibration peaks found in the range 1000–600 and 2300 cm^{-1} can be attributed to (C–Cl) and (M–O) where M═Co^{+3} which indicated that the doping was complexes with polymer matrix (El-Zahhar et al., 2003).

Fig. 3 represents the TEM images of PVA/PPY composite and that treated with cobalt fillers. For pure PVA/PPY, it can be seen that, the morphology of the composite reveals an agglomeration in nano-spherical particle like shaped in the range from 50 to 60 nm. By complexation with filler ratios $x = 0.2$, 0.4 and 0.6 g (Fig. 3b, d), the particle size decreased to 4 nm this due to that the addition of the fillers restrict the growth of the polymerization process of PVA/PPY composite. Further increase of the filler ($x = 0.8$ and 1.0 g), the nanoparticles tend to form High agglomeration.

The UV–VIS spectra of the sample under investigation were recorded, the spectra of pure PVA/PPY and that doped with

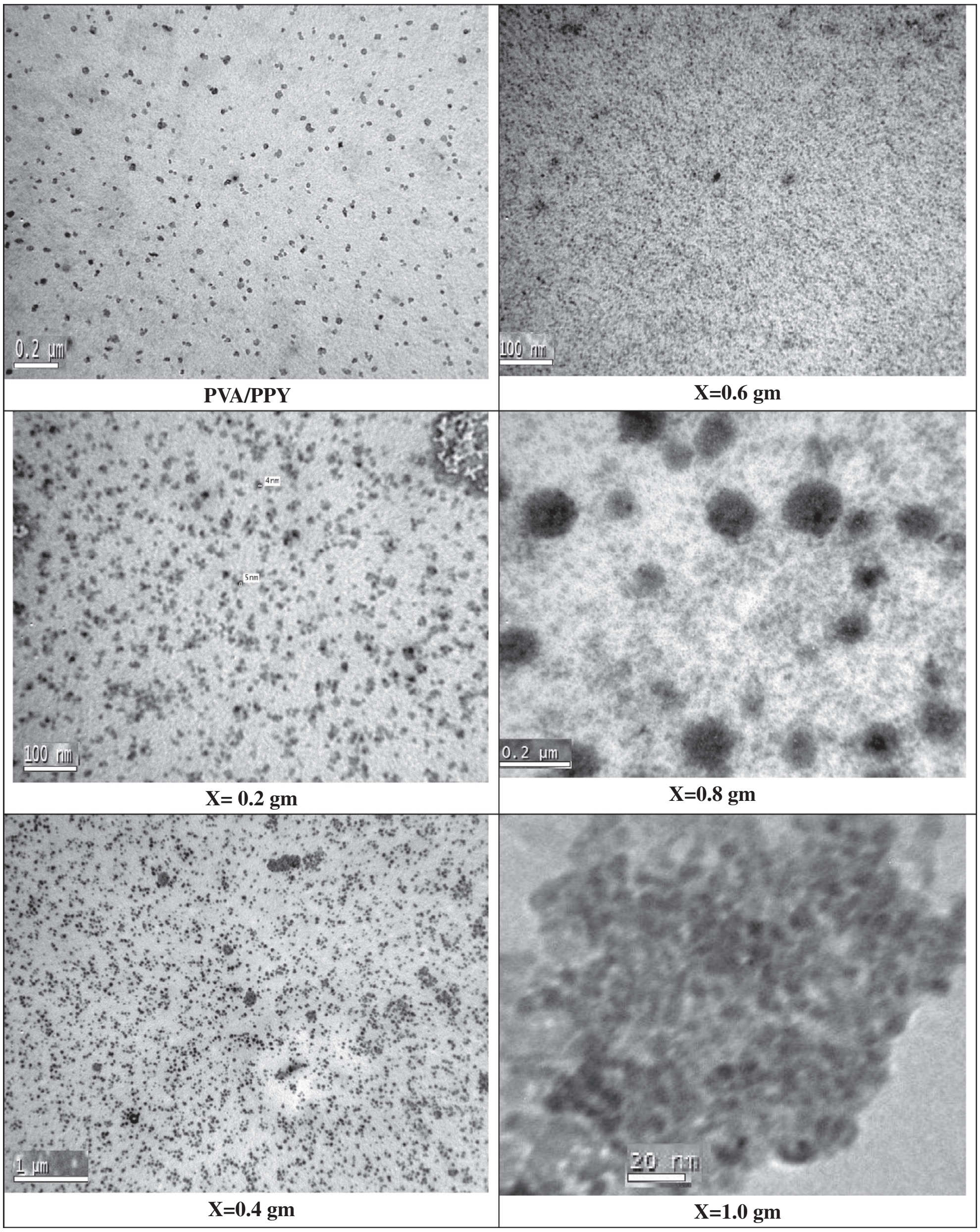

Figure 3 TEM photographs of PVA/PPy and that doped with filler 0.0, 0.2, 0.4, 0.6, 0.8 and 1.0 g $CoCl_2$ $6H_2O$).

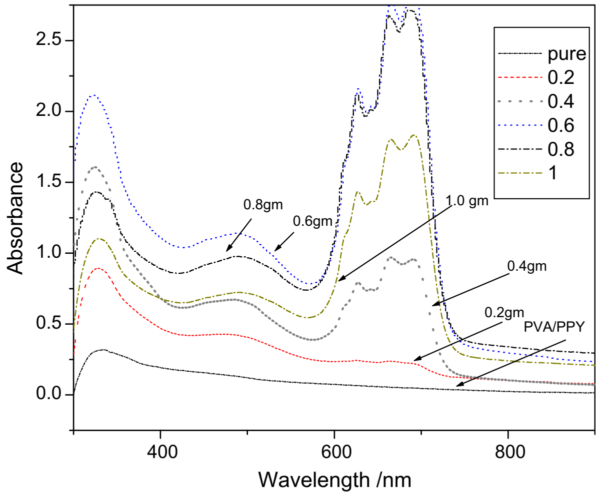

Figure 4 The absorption spectra in the UV–VIS region for films of PVA/PPY and that doped with (0.2, 0.4, 0.6, 0.8 and 1.0 g of $CoCl_2$ $6H_2O$).

different cobalt chloride salt concentrations (x = 0.2, 0.4, 0.6, 0.8 and 1.0 g) is shown in Fig. 4. The optical absorption of the prepared films decreases with increasing the x value of $CoCl_2{\cdot}6H_2O$ in both VIS (500–700 nm) and UV (200–400 nm) regions, where the PVA has one spectral bands at 340 nm (Abdelazeez and Abdelrazek, 2006). The intensity of the bands increases with increasing the $CoCl_2{\cdot}6H_2O$ contents providing an evidence for the incorporation of Co^{2+} into PVA/PPY matrix where as their positions are slightly shifted to higher wave length (red shift). Two absorption bands observed near 500 and 625 nm are characteristic to the presence of octahedral structure around the Co(II) ion. The presence of Co^{2+} ions entirely as six coordinated. The asymmetry of these bands can be attributed to the Jahn–Teller effect. This distortion is found to decrease gradually with increasing the $CoCl_2{\cdot}6H_2O$ content which may indicate a tendency to local ordering in the amorphous polymer structure by cobalt chloride addition (El-Shahawy, 1993). This local ordering may be played by the role of intra- and inter-molecular interactions between the polymer chains. Thus, the octahedron is expected to become more symmetric due to the contraction effect brought about by such interactions. Another band observed at 666 nm indicates the presence of Co(II) in a tetrahedral coordination. The presence of Co(II) in mixed coordination has been reported in Nassar and Abbas (1981) and Gray et al. (1984).

The absorption coefficient α can be determined as a function of frequency using the formula

$$\alpha(v) = \frac{A}{d} \times 2.303 \tag{1}$$

where A is the absorbance at frequency ω and d is the thickness of the sample.The optical band gap for an indirect transition can be determined by using the relation (Davis and Mott, 1970)

$$E_g = hv - (\alpha hv/\beta)^{1/2} \tag{2}$$

where β is a constant.

The energy gap is calculated in the range near the absorption edge (300–800 nm) as indicated in Table 1 and Figs. 5 and 6 illustrates the plots between $(\alpha hv)^{1/2}$ and hv for pure

Table 1 The values of energy gaps E_{g1}, E_{g2} and E_{g3} for pure PVA/PPY and that doped with $CoCl_2{\cdot}6H_2O$.

$CoCl_2{\cdot}6H_2O$ doping (g)	E_{g1} (ev)	E_{g2} (ev)	E_{g3} (ev)
0	2.68	–	–
0.2	2.52	2.27	1.60
0.4	2.42	2.15	1.69
0.6	2	1.93	1.68
0.8	2.1	1.94	1.68
1.0	2.03	1.98	1.68

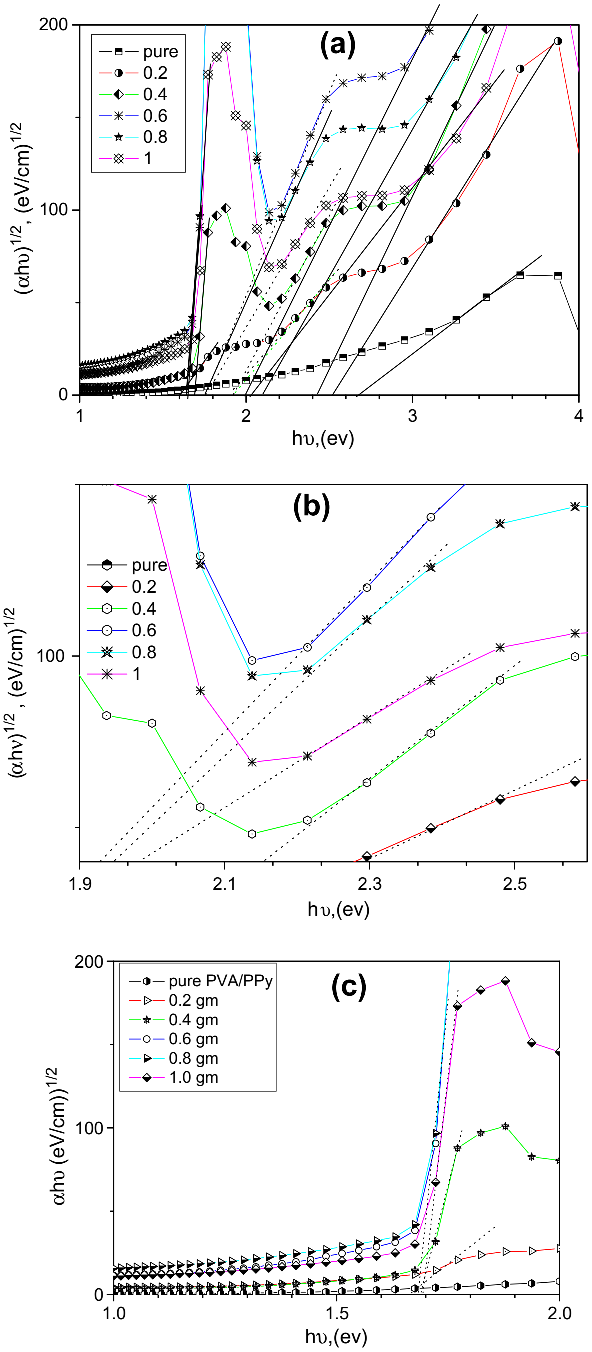

Figure 5 The plots of $(\alpha hv)^{1/2}$ versus hv for films of pure PVA/PPY and that doped with different $CoCl_2{\cdot}6H_2O$; (a)E_{g1}, (b) E_{g2} and (c) E_{g3}.

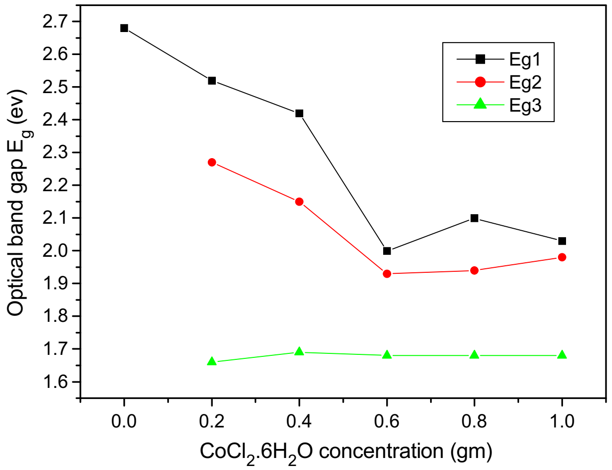

Figure 6 The dependence of optical band gap on doping concentration.

PVA/PPY and that treated with $CoCl_2{\cdot}6H_2O$ near the absorption edge produce a linear fit over a wider range of $h\nu$. This linearity indicates the existence of indirect allowed transitions. The extrapolation of linear dependence to the abscissa yields the corresponding forbidden band width E_g. It is observed from the figure that a linear dependence for pure PVA/PPY in one region representing one optical absorption edge as mentioned before in the previous work (Zidan et al., 2003), while PVA/PPY doped with $CoCl_2{\cdot}6H_2O$ give two regions representing three optical absorption edges. These absorption edges are characterized by higher optical energy gap, E_{g1} and two lower energy gaps E_{g2} and E_{g3}, the three energy gaps are attributed to the optical transitions from the valence sub-bands to the conduction band minimum (El-Sayed and Sakr, 2003). It is clear that E_{g1} and E_{g2} decreases as the $CoCl_2{\cdot}6H_2O$ increases to 0.6 g then saturated while E_{g3} nearly unchanged with increasing $CoCl_2{\cdot}6H_2O$ content as shown in Fig. 6. The variation of the calculated values of both higher and lower optical energy gaps may reflect the role of the doping in modifying the electronic structure of the PVA/PPY matrix due to appearance of various Polaroid and defect levels. The density of localized states was found to be proportional to the concentration of these defects and consequently, to $CoCl_2{\cdot}6H_2O$ content. Increasing $CoCl_2{\cdot}6H_2O$ content may cause the localized states of different color centers to overlap and extend in the mobility gap (Murri et al., 1992). This overlap may give us an evidence for decreasing energy gap when $CoCl_2{\cdot}6H_2O$ content is increased in the polymeric matrix. The higher optical energy gap, E_{g1} seems to be related to the PVA/PPY matrix and its width changes due to the induced energy states from the symmetrical field of cobalt ions. It is argued that the lower absorption edge E_{g2} and E_{g3} evidences the presence of another type of induced states depending on the doping level of $CoCl_2{\cdot}6H_2O$.

4. Conclusion

The X-ray analysis showed an amorphous structure of the produced films after complexation of PVA/PPY with $CoCl_2{\cdot}6H_2O$ as filler. The IR spectra showed vibration peaks in the range 1000–600 cm^{-1} and at 2300 cm^{-1} which indicated that the doping was complexed with polymer matrix. The TEM images showed that the particle size decreased by complexation with filler at (x = 0.0–0.6) where excess addition of filler restricted the growth of polymerization process of PVA/PPY and high agglomeration was observed for the rest samples (x = 0.8 and 1.0 g) with high content of filler due to the formation of very fine nanoparticles. The UV–VIS spectra provide evidence for the formation of metal–polymer complex. Also, the optical properties showed that the pure PVA/PPY has one optical absorption edge, while PVA/PPY doped with $CoCl_2{\cdot}6H_2O$ have three optical absorption edges.

References

Abdelazeez, M., Abdelrazek, E.M., 2006. Physica B.

Armes, S.P., Aldiss, M., 1999. J. Chem. Soc., Chem. Commun., 88.

Baha, A.F., Amin, M., Darwish, K., Abdel-Samad, H., 1988. J. Polymer 5, 115.

Barakat, N., El-Hennawi, H.A., El-Ocker, M., Shraf, F., 1989. J. Phys. D: Appl. Phys. 22, 786.

Benget, N., Krutmeijer, E., 2000. The Nobel Prize in Chemistry. Conductive Polym., 1–15.

Benseddik, E., Makhlouki, M., Bernede, J.C., Lfrant, S., Pron, A., 1995. XPS studies of environmental stability of polypyrrol-poly(vinyl alcohol) composites. Synth. Metals 72, 237–242.

Bhargav, P.B., Mohan, V.M., Sharma, A.K., Narasimha Rao, V.V.R., 2007. Int. J. Polym. Mater. 56, 579.

Chakraborty, M., Mukherjee, D.C., Mandal, B.M., 1999. Synth. Metals 98, 193.

Davis, E.A., Mott, N.F., 1970. Philos. Mag. 22, 903.

Deronzier, A., Moutet, J.C., 1989. Acc. Chem. Res. 22, 249.

Ege, S.N., 1989. Organic Chemistry. The University of Michigan, Ann Arbor, pp. 361.

Eisazadeh, Hossein., 2007. World J. Chem. 2 (2), 67–74.

Eisazadeh, H., Spinks, G., Wallace, G., 1993. G Mater. Forum 17, 241.

Eisazadeh, H., Spinks, G., Wallace, G.G., 1994. Polymer 35, 3801.

El-Sayed, E.A., Sakr, G.B., 2003. Phys. Stat. Sol. (A). 198, 188.

El-Shahawy, M.A., 1993. Polym. Bull. 31, 199.

El-Tantawy, F., Abdelkader, K.M., Kane Ko, F., Sung, Y.k., 2004. Eur. Polym. J. 40, 415.

A.A. El-Zahhar, M. Ismail, H.A. El-Naggar, 2003. In: Seventh ARAB International Conference on Polymer Science & Technology, Cairo, Hurghada, Egypt, 5–9.

Gray, P., Klein, L.C., 1984. J. Non-Cryst. Solids 68, 75.

Hamzah, H.M., Saion, E.N., Kassim, A., Ekramul, M., 2003. 73–76.

Hamzah, H.M., Saion, E., Yahya, N., Kassim, 2004. Ac conductivity measurements of PVA–PPY conducting polymer composites 248–261.

Hung, S.J., Lee, H.K., kang, W.H., 2005. J. Korean. Ceram. Soc. 42, 77.

Kassim, A., Davis, F.J., Mitchel, G.R., 1994. Synth. Met. 62, 41.

Khaled, M.A., Basha, M.A.E., 1989. Ind. J. Phys. 63A, 399.

Lindsey, S.E., Street, G.B., 1984. Conductive composites from poly(vinyl alcohol) and polypyrrole. Synth. Metal. 10 (1), 67–69.

Murri, R., Schiavulli, L., Pinto, N., Ligonzo, T., 1992. J. Non-Cryst. Solids 139, 60.

Nassar, A.M., Abbas, A.F., 1981. Ind. J. Pure Appl. Phys. 17, 417.

Niwa, O., Tamamura, T., 1984. J. Chem. Soc., Chem. Commun. 470, 817–818.

Noguchi, H., Jodai, H., Yamaura, K., Matsuzawa, S., 1998. Polym. Int. 47, 428.

Otero, T.F., Sansinena, J.M., 1996. J. Electroanal. Chem. 412 (109–11), 6.

Paoli, M.A.D., Waltman, R.J., Diaz, A.F., Bargon, J., 1984. Conductive composites from poly (vinyl chloride) and polypyrrole. J. Chem. Soc., Chem. Commun. 15, 1015–1016.

Rajendan, S., Sivakumar, M., Subadevi, R., 2003. J. Power Source 12, 225.

Rajendran, S., Sivakumar, M., Subadevi, R., 2004. Mater. Lett. 58, 641.

Sun, Z., Sun, Y., Yang, Q., Wang, X., Zheng, Z., 1996. Surf. Coat Technol. 79, 108.

Sweeting, O.J., 1968. The Science and Technology of Polymer Films. Interscience Publishers, Newyork.

Tawansi, A., Oraby, H., Zidan, H.M., Dorgham, M.E., 1998. Physica B., 126–254.

Yu, Y.H., Lin, C.Y., Yeh, J.M., Lin, W.H., 2003. Polymer 44, 2553.

Zidan, H.M., Tawansi, A., Abu-Elnader, M., 2003. Physica B. 339, 78.