VOLUME 2, 2018
DOI: 10.31058/j.ac.2018.12004

Optical Properties of Modified Poly (Vinyl Chloride) by Schiff Base with Different Metals

Emad Yousif[1*], Dina S. Ahmed[1], Rahimi M. Yusop[2], Salam A. Mohammed[3]

[1] Department of Chemistry, College of Science, Al-Nahrain University, Baghdad,Iraq
[2] School of Chemical Science and Food Technology, Faculty of Science and Technology, University Kebangsaan Malaysia, elangor, Malaysia
[3] Department of Chemical and Petrochemical Engineering, College of Engineering and Architecture, University of Nizwa, Nizwa, Sultanate of Oman

Email Address

emadayousif@gmail.com (Emad Yousif), dinasaadi86@gmail.com (Dina S. Ahmed), rahimi@ukm.edu.my (Rahimi M. Yusop), salam.mohammed@unizwa.edu.om (Salam A. Mohammed)
*Correspondence: emadayousif@gmail.com

Received: 10 July 2018**; Accepted:** 20 August 2018**; Published:** 25 September 2018

Abstract:

In this study, the optical properties of modified PVC with different metals in THF have been investigated. These reactions led to formation new polymeric films (PVC-L-M) which characterized by FTIR spectrophotometry, energy gap and surface morphology. The optical data observed that the energy gap values are influenced by type of metals. The different metals led to change in energy gap values, the values of with the variation of metals have been found from 1.88 to 5.39 eV. Different metals in polymeric chain due to change in surface morphology. The results demonstrated that modified PVC and the optical band gap have been correlated with the different metals.

Keywords:

PVC Film, Optical Properties, Schiff Base, Energy Gap, Surface Morphology

1. Introduction

Modifications of poly (vinyl chloride) by radiation-induced crosslinking have been successfully used for many years on a wide industrial scale at most for wire and cable insulation [1]. Studying optical absorption specially the absorption band edge is a valid method to examine optically the induced transition instead of providing information about both the structure of band and optical energy gap in the materials. The rule of this technique is that photons with energies better than the band gap energy will be absorbed. The absorption edge in many disordered materials follows the Urbach rule [2]. It is very important to determine the band in materials specially, in the semiconductor and nanomaterial industries [3]. Band gap suggests the difference in energy between the top of valence band which filled with electrons and the bottom of conduction band devoid of electrons. The insulators band gap energy is large (>4eV), but semiconductors lower from (<3eV) [4]. With the coming of recent technologies, novel semiconductors rich in their optoelectronic properties find wide range of applications in optical, electronic and optoelectronic devices such as laser diodes (LD), light emitting diodes (LED), photo detectors (PD), integrated circuits (IC), nanotechnology, hetero structure lasers and optical modulators [5,6]. In our research, FTIR and ^{1}HNMR spectroscopy were used to characterize Schiff base. FTIR and UV–Vis spectroscopy was used to investigate the optical band gap of modified PVC. Electronic property changes in modified PVC film were monitored. The surface morphological study was investigated using microscope. The main purpose of this work is to study and calculate the optical band gaps of modified PVC.

2. Materials and Methods

2.1. Schiff Base Preparation

(2.14 g, 10.0 mmol) of biphenyl-3,3',4,4'-tetraamine and four mole equivalents of 2-hydroxybezaldehyde in anhydrous ethanol (25 mL) in the presence of (0.5 mL) glacial acetic acid, the stirred mixture was refluxed for 4 h. The deep orange solid obtained after the mixture left to cool down at room temperature then filtered, washed with ethanol and dried to give pure 1 in 84% yield. The chemical structure and elemental data were confirmed with spectral [7].

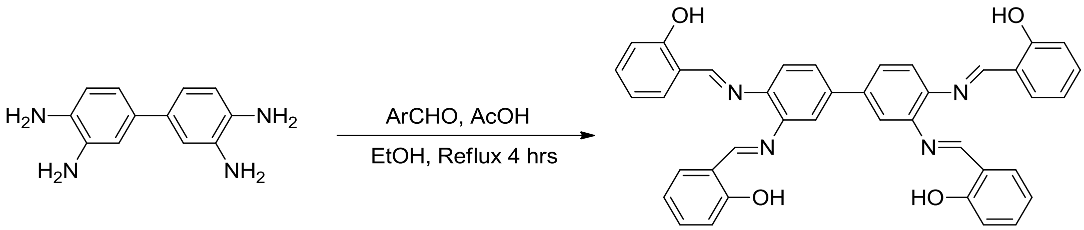

Figure 1. *Synthesis of Schiff base 1.*

2.2. Synthesis of PVC –Ligand

The modification of PVC with Schiff base 1 were performed by dissolving 0.1 g of PVC in 20 mL THF, then added 0.05 mole of Schiff base 1. Five drops of pyridine were added to the mixture. The mixture was refluxed for 4 - 6 hours. Hot mixture was cast into petri dish, the precipitated was separated as film by evaporating the solvent (THF) for 24 hours.

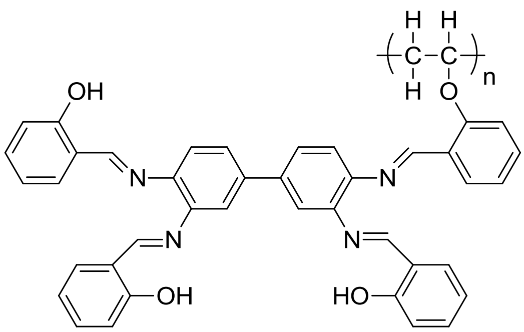

Figure 2. *Structure of PVC-L.*

2.3. Synthesis of PVC Ligand Complexes

The Cu(II), Cr(II), Ni(II) and Co(II) polymeric metal chelates have been synthesized (Figure 3), 0.3 gm of synthesized modified polymer (PVC-L) and 0.05 gm of metal salt were dissolved in 5mL of THF, The mixture were refluxed for 3 hours in order to form the complex PVC-L-M(II) by evaporation technique at room temperature for 24 h.

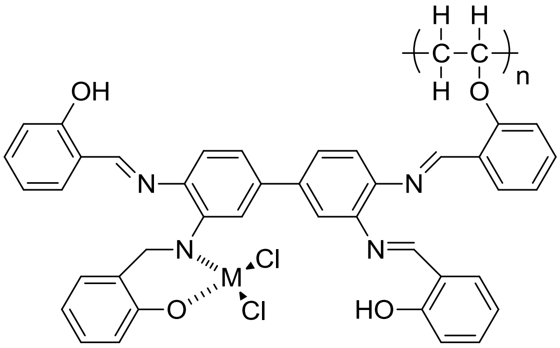

Figure 3. *Structure of PVC-L-M.*

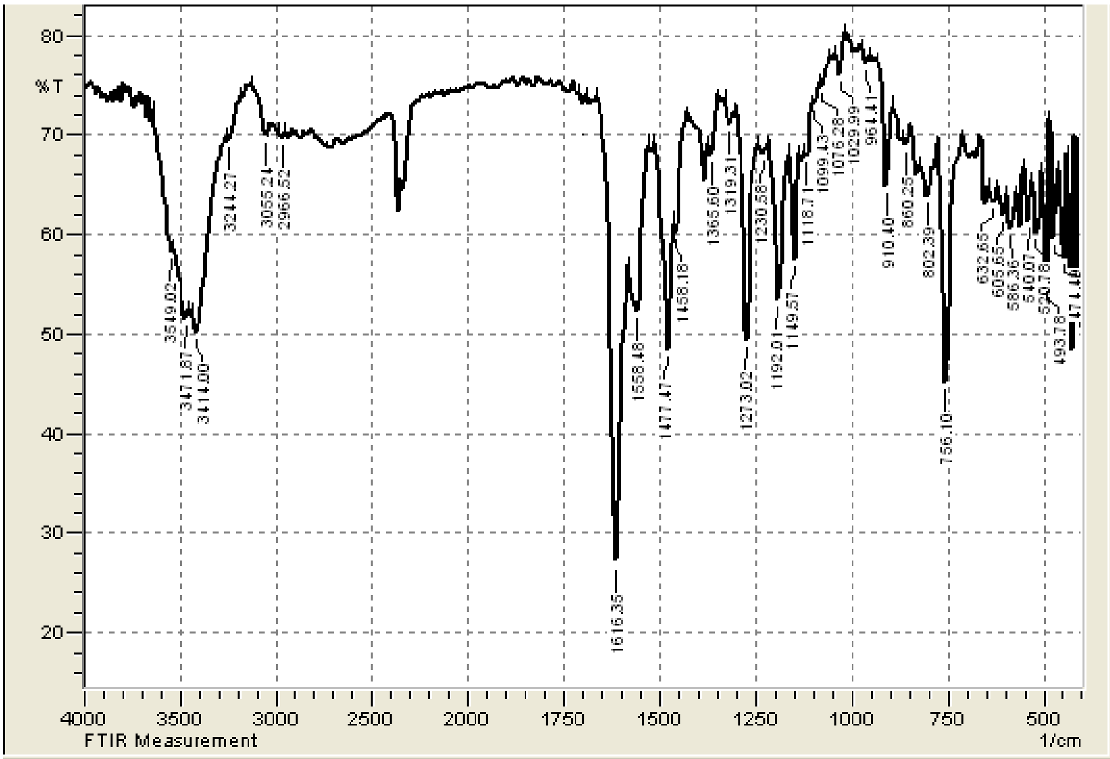

Figure 4. *FTIR spectrum of 1.*

2.4. PVC Films Preparation

0.5% concentration of PVC solution in THF was used to synthesized 40 μm thickness of PVC films, (measured by a micrometer type 2610 A, Germany). The films were prepared by poured the solution on to a glass plate, left it to dry for a day to remove any residual of THF.

3. Results and Discussion

3.1. Characterization of Schiff Base

3.1.1. FTIR Spectroscopy

FT-IR covers a wide range of chemical applications, especially for polymers and organic compounds. Used together with other analytical techniques, FT-IR can be very effective in the identification of unknown plastics and polymeric materials [18]. The FTIR spectrum of 1 show intense absorption band at 1616 cm-1 that can be due to C=N bond, also can be indicate the absence of NH2 and C=O groups absorptions which belong to ammine and aldehyde groups, respectively as show in Figure 4.

3.1.2. ^{1}H -NMR Spectroscopy

Table 1 show the nuclear magnetic resonance spectral data for 1, it can be seen singlet signals that resonate at the 9.05–8.01 ppm region attribute to the CH=N protons. They also show all the aromatic protons with the expected multiplicity and chemical shifts.

Table 1. *^{1}H -NMR spectral data of Schiff base.*

(400 MHz: DMSO-*d6*, δ, ppm, *J* in Hz)
9.17 (s, exch., 4 H, OH), 9.08 (s, 4 H, CH), 7.93 (s, 2 H, Ar), 7.71 (d, J = 8.2 Hz, 4 H, Ar), 7.64 (d, J = 8.5 Hz, 2 H, Ar), 7.44 (t, J = 8.2 Hz, 4 H, Ar), 7.25 (d, J = 8.5 Hz, 2 H, Ar), 7.00 (t, J = 8.2 Hz, 4 H, Ar), 6.99 (d, J = 8.2 Hz, 4 H, Ar)

3.2. Characterization of Modified PVC

The modification of PVC with different metals are started with nucleophilic attack of (O) atom on the carbon that carrying chlorine atom in the polymeric chain followed by displacement of chloride anion as a good leaving group. The structure of modified polymers can be confirmed by using FTIR spectroscopy, energy gap and microscope.

3.2.1. FTIR Spectroscopy

The modification of PVC with different metals can be confirmed by FTIR spectroscopy. Table 2 shows characteristic vibrations of M-N, M-O and C-Cl. Moreover, in PVC-L (modified polymer) spectrum one can see a strong band at *ν* (694) cm^{-1}. This band could be assigned to *ν* (C-Cl) band which is different from the unmodified PVC *ν* (616) cm^{-1} [8,9,10].

Table 2. *FTIR spectral data of modified PVC.*

Film	***ν* (M-N)**	***ν* (M-O)**	***ν* (C-Cl)**
PVC-L	___	544	___
PVC-L-Cu(II)	689	546	689
PVC-L-Cr(II)	670	540	670
PVC-L-Ni(II)	686	535	690
PVC-L-Co(II)	694	542	686

3.2.2. Optical Properties

The effect of metals on the values of energy gap shown in Table 3. The values of energy gap are decreased in the trend pure PVC-L, PVC-L-Ni, PVC-L-Cu, PVC-L-Cr and PVC-L-Co.

Table 3. *The energy band gap values for PVC-L and PVC-L-M at room temperature.*

Film	Eg (eV)
PVC-L	5.39
PVC-L-Ni	3.6
PVC-L-Cu	3.4
PVC-L-Cr	3.1
PVC-L-Co	1.88

There is a shift in the energy gap could be assigned to the formation of polorans in the doped films [11,14]. The polymer-metal composites may be recognized by interaction of metal with the polar group that exists in polymeric chain. The Energy gaps were measured as attitude of conductivity measurement, the conductivity measurement for PVC in the presence of additives in the following order:

PVC-L > PVC-L-Ni > PVC-L-Cu > PVC-L-Cr > PVC-L-Co

3.3.3. Surface Morphology

Polyvinylchloride (PVC) is an important commercial polymer because of its wide range of applications. It is used owing to its low cost and recoverability, excellent electrical and corrosion resistance [19,20,21]. Morphological characteristics of PVC-L-M have been studied shown in Figure 5. The thickness of polymeric thin films (40 μm) was determined using Digital Vernier Caliper 2610A micrometer (Vogel GmbH, Kevelaer, Germany).

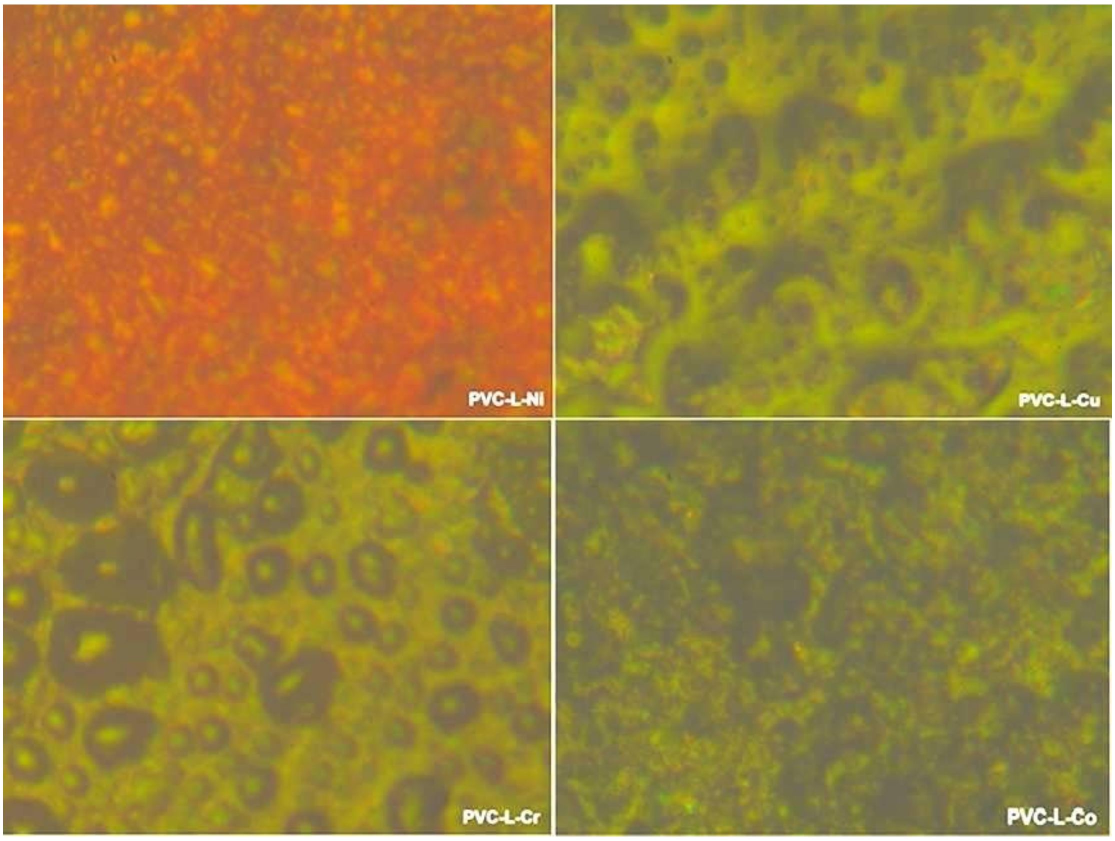

Figure 5. *Surface morphology of PVC-L-M films.*

To characterize the surface morphology of prepared films microscope was used for this purpose, the surface morphology provides notifications about roughness, defects and irregularity into the polymeric materials [15,17].

4. Conclusions

PVC bound can be synthesized by Cl displacement reaction between PVC and (L) in alkaline conditions. The structure of the modified polymers was established on the bases of its FTIR, UV-VIS spectroscopy and microscope. The optical properties of the PVC polymers modified with different metals have been investigated. These properties were determined using the Energy Gap method, the optical energy gap decreased as following order:

PVC-L > PVC-L-Ni > PVC-L-Cu > PVC-L-Cr > PVC-L-Co

The energy gap values exhibit depended on type of used metal where decreased from 5.39eV of pure PVC to 1.88 eV for Cobalt. The energy gaps were measured as a function of conductivity and found to decrease when pure PVC is chelated to the ligand.

Conflicts of Interest

The authors declare that there is no conflict of interest regarding the publication of this article.

Acknowledgments

The authors extend their appreciation to Al-Nahrain, Kebangsaan Malaysia and Nizwa universities for continued support.

References

[1] Hollain, G.D. Physical properties of irradiated polymers. *Mater. Appl.* 1980, 5, 103-108.

[2] Urbach, F. The Long-Wavelength Edge of Photographic Sensitivity and of the Electronic Absorption of Solids. *Phys. Rev*. 1953, 92, 1324.

[3] Abdullahi, S.S.; Güner, S.; Koseoglu, Y.; Musa, I.M.; Adamu, B.I.; Abdulhamid, M.I. Simple Method For The Determinatıon of Band Gap of a Nanopowdered Sample Usıng Kubelka Munk Theory. *J. of the Nigerian Association of Math. Phys.* 2016, 35, 241-246.

[4] Alidoust, N.; Toroker, M.C.; Carter, E.A. Revisiting Photoemission and Inverse Photoemission Spectra of Nickel Oxide from First Principles: Implications for Solar Energy Conversion. *J. Phys. Chem. B* 2014, 118, 7963-7971.

[5] Paskov, P.P. Refractive indices of InSb, InAs, GaSb, InAsxSb1−x, and In1−xGaxSb: Effects of free carriers. *J. Appl. Phys*. 1997, 81, 1890.

[6] Rappl, P.H.O.; Mccaan, P.J. Development of a novel epitaxial-layer segmentation method for optoelectronic device fabrication. IEEE Photon. *Technol. Lett*. 2001, 15, 374.

[7] Ahmed, D.S.; El-Hiti, G.A.; Hameed, A.S.; Yousif, E.; Ahmed, A. New Tetra-Schiff Bases as Efficient Photostabilizers for Poly (vinyl chloride). *Molecules*, 2017, 22, 1506.

[8] Ismael, M.; Hmood, A.B.; Shaalan, N.; Al-Taa'y, W.A.; Hasan, A.; Ali, M.; Al Ahmed, A.; Yousif, E. Study on Optical Properties of PVC-2,5di (2-Pyrrole hydrazone) 1,3,4-thiadiazole Complexes. *Research Journal of Pharmaceutical, Biological and Chemical Sciences*, 2016, 7, 2347.

[9] Hamad, T.K.; Yusop, R.M.; Al-Taa'y, W.A.; Abdullah, B.; Yousif, E. Laser Induced Modification of the Optical Properties of Nano-ZnO Doped PVC Films. *International Journal of Polymer Science*, 2014, 8.

[10] Bradley, D.C.; Gitlitz, M.H. Metal–Nitrogen Infrared Stretching Frequencies in Dialkylamido-transition Metal Compounds. *Nature*, 1968, 218, 353-354.

[11] Elias, S.; Susila, W.; Doyan, A.; Zainal Abidin, S.; Azmi, Z.; Zulkfli, A.; Mohd Zaki, AR.; Dahlan, K.Z.H.; Karni, T. Changes the Optical Band Gap and Apsorption Edes of Gamma – Irradiated Polymer Blends. *Journal of Applied Science*, 2005, 5, 1825-1829.

[12] Ali, A.A.; Fadhil, H.D.; Yousif, E.; Hussain, Z.; Abdul-Wahab, S. A Comprehensive Study of Conductive Polymer Matrix Composites: A Review. *Research Journal of Pharmaceutical, Biological and Chemical Sciences*, 2017, 8, 2043.

[13] Al-Taa'y, W.A.; Ameer, A.A.; Al-Dahhan, W.H.; Abddallh, M.; Yousif, E. Optical constants of poly (vinyl chloride) doped by nano ZnO. *Journal of Chemical and Pharmaceutical Research*, 2015, 7, 536-541.

[14] Yousif, E.; Abdallh, M.; Hashim, H.; Salih, N.; Salimon, J.; Abdullah, B.M.; Win, Y.F. Optical properties of pure and modified poly (vinyl chloride). *International Journal of Industrial Chemistry*, 2013, 4, 4.

[15] Júnior, G.C.; Silva, A.P.S.; Guinesi, L.S. Synthesis, characterization and electropolymerization of a new polypyrrole iron (II) Schiff-base complex. *Polyhedron*, 2004, 23, 1953-1960.

[16] Ahmed, D.S.; El-Hiti, G.A.; Yousif, E.; Hameed, A.S. Polyphosphates as Inhibitors for Poly (vinylChloride) Photodegradation. *Molecules*, 2017, 22, 1849.

[17] Ahmed, D.S.; El-Hiti, G.A.; Yousif, E.; Hameed, A.S.; Abdalla, M. New Eco-Friendly Phosphorus Organic Polymers as Gas Storage Media. *Polymers*, 2017, 9, 336.

[18] Ludwig, V.; Ludwig, Z.M.D.C.; Rodrigues, M.M.; Anjos, V.; Costa, C.B.; Dores, D.R.S. da Silva, V.R.; Soares, F. Analysis by Raman and infrared spectroscopy combined with theoretical studies on the identification of plasticizer in PVC films. *Vibrational Spectroscopy*, 2018, 98, 134-138.

[19] Martins, J.D.N.; Freire, E.; Hemadipour, H. Applications and market of PVC for piping industry. *Polímeros*, 2009, 19, 58-62.

[20] Nikam, P.N.; Deshpande, V.D. Dielectric behavior of plasticized PVC/alumina nanocomposites influenced with DC biasing field. *Mater Today Proc*, 2018, 5, 2254–2262.

[21] Alghunaim, N.S. Structural, thermal, dielectric spectroscopic and AC impedance properties of SiC nanoparticles doped PVK/PVC blend. *Results in Physics*, 2018, 9, 1136-1140.