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Study of structural and optical properties of New Films Derived PVC-2-[5-phenyl-1,3,4-thiadiazol-2-ylimino-methyl]-benzoic acid.

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ABSTRACT

Grafted polymer with Schiff base, PVC-2-[5-phenyl-1,3,4-thiadiazol-2-ylimino-methyl]-benzoic acid was prepared in THF solvent. The synthesized Schiff base was characterized by FTIR Spectroscopy, electronic spectroscopy, Elemental analysis, ¹H-NMR spectroscopy and mass spectroscopy. Effect grafting structure on optical absorption of poly(vinyl chloride) was studied using ultraviolet-visible (UV-VIS) spectroscopy. The modified films PVC-L-M^{II}, with two transition metal complexes, Co^{II} and Cu^{II} have been prepared. A number of techniques, such as FT-IR, microscope and AFM spectroscopy are used to characterize the physical properties of these films. The direct band gap in pristine and modified PVC have been determined. The two modified films have a red shift in optical properties in the ultraviolet region. The PVC-L-Co^{II} was the lower value of the optical band gap, 2.94 eV.

Keywords: Schiff base, Optical absorption; FT-IR spectroscopy; Optical band gap.

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INTRODUCTION

In recent years, conductive polymers are receiving increasing attention due to their potential usage in the areas of optics, electronics and solar energy technologies [1]. It is already an established fact that interaction of radiation with polymers leads to chain scission, chain aggregation, formation of double bonds and molecular emission. As a consequence of this, the physico-chemical properties like optical, electrical, mechanical, chemical and track properties of the polymer are modified [2]. The effectiveness of these changes produced depends upon the structure of the polymer and the experimental conditions of irradiation like energy and fluence. The study of these changes may enhance their applications in different fields [3].

Polymers have attracted great interest in the fields of integrated optics and optical interconnects. The potential applicability of organic and polymeric materials to integrated optics is large owing to both their microscopic and bulk properties [4]. One of the most important polymers is PVC, which is used in different applications. Poly(vinyl chloride), better known by its abbreviation PVC, is one of the most versatile plastics [5]. It is the second largest manufactured resin by volume worldwide. PVC is second only to polyethylene among the five kinds of general plastic materials, which was widely used in industries including architecture, electronic, chemical engineering, packaging, transportation [6].

Schiff base compounds derived from aromatic (amines or aldehydes) have a wide range of use in many fields like inorganic analytical chemistry and biological [7]. There is a great interest in the importance of compounds containing nitrogen and sulphur donor organic compounds by coordination with metal ions to form complexes [8]. Varying synthesis of 1,3,4-thiadiazole complexes have been activities because the presence of the nitrogen and sulphur [9]. Various composite materials have been recently synthesized by starting from different polymers and a wide variety of dopants like metals, oxides, inorganic salts, and other particles. Synthesis of polymer-bound chelating ligands and the selective chelation of specific metal ions is a field of active research [10]. PVC polymer can be modified by introduction of aromatic and heterocyclic moieties through halogen displacement reaction. The facial chlorine displacement from PVC indicated the possibility of easy anchoring of ligands to PVC matrix and the subsequent synthesis of immobilized transition metal complexes [11]. This article discloses the investigation of the effect of transition elements on the electrical properties of the novel materials.

EXPERIMENTAL

Instrumentation

The reagent used from sigma company. Elemental microanalysis was carried out using Elemental Analyzer Model 5500 Carlo-Erba Instruments-Italy. The UV-Visible spectra were measured in ethanol using Shimadzu UV-Vis. 160 A-Ultra-Violet Spectrophotometer in the range 200-1100 nm. The FTIR spectra in the range 4000-400 cm^{-1} were recorded as KBr disc on Shimadzu 8300 Spectrophotometer. Gall encamp M.F.B600.010 F melting point apparatus were used to measure the melting point of all the prepared compounds.

Synthesis of [2-amino-5-(phenyl-1,3,4-thiadiazole)] (A)

A mixture of benzoic acid (0.1mol, 12.2g), thiosemicarbazide (0.1mol, 9.1g) and (40ml) of POCl_3 was heated gently for 3 hrs. After cooling (250 ml) of water was added then refluxed for 4 hrs. The mixture was cooled filtered and the filtrate neutralized with KOH conc. and recrystallized in solvent ethanol [12].

Synthesis 2-[(5-phenyl-1,3,4-thiadiazol-2-ylimino)-methyl]-benzoic acid (L)

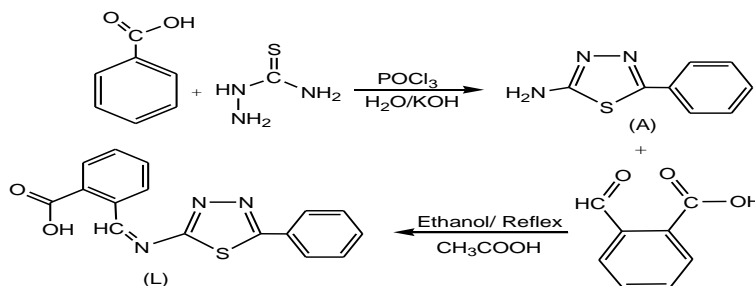
Method 1. A mixture of equimolar amounts (0.05mol) of appropriate [carboxybenzaldehyde] and the [2-amino-5-(phenyl-1,3,4-thiadiazole)], in absolute ethanol (25ml) with three drops of glacial acetic acid was refluxed 4 hrs. The reaction mixture was then allowed to cool at room temperature, and the precipitate was filtered, dried, and recrystallized from mixture (methanol and ethanol) (1:1) to give yellow powder, scheme 1.

Method 2. A mixture of equimolar amounts (0.05mol) of appropriate [Carboxybenzaldehyde] and the (2-amino-5-phenyl-1,3,4-thiadiazole), were ground with a mortar, mixed, dried and subjected to microwave

irradiation 240W for (15) minutes, after completion the reaction mixture was cooled to room temperature the solid obtained was recrystallized twice from mixture (methanol and ethanol) (1:1) to give yellow powder, yield, elemental analysis is show in table 1.

Table 1. The Some physical properties of the prepared compounds/ Found (calcd)

Comp. Formula	Yield	C	H	N	S	O
(A) C ₈ H ₇ N ₃ S	70%	54.25 (54.22)	3.93 (3.98)	23.71 (23.71)	18.11 (18.09)	---
(L) C ₁₄ H ₁₀ N ₄ O ₂	73%	61.78 (62.12)	3.69 (3.58)	13.46 (13.58)	10.70 (10.37)	10.46 (10.34)



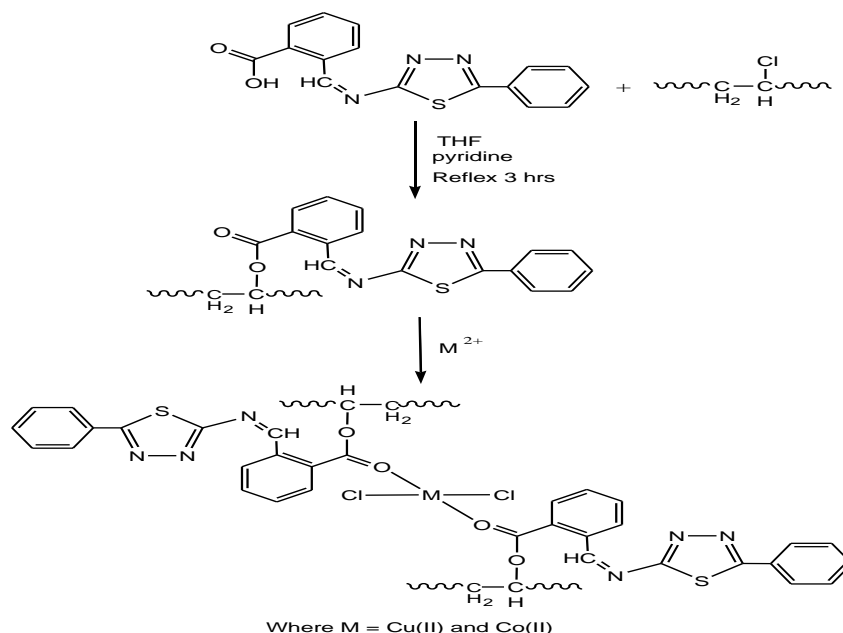
Scheme 1. Reactions for synthesis ligand (L)

Synthesis of L-grafted PVC

A mixture of 1gm of PVC dissolved in 20ml THF and 1gm from 2-[(5-phenyl-1,3,4-thiadiazol-2-ylimino)-methyl]benzoic acid and 5 drops of pyridine was refluxed for 3 hours in THF solvent. The precipitated modified polymer is separated the solvent evaporator process [11].

Synthesis of polymer metal chelates

The Cu^{II} and Co^{II} polymeric metal chelates have been prepared using PVC-L and the procedure is as follows: 0.3 gm of synthesized modified polymer (PVC-L) and 0.05 gm of metal salt solution were dissolved in 5 mL of tetra hydro furan (THF) and reflux 3 hrs in order to form the complex [PVC-L-M^{II}] [13], scheme 2.



Scheme 2. Reaction for synthesis PVC-L-M^{II}

Purification of Poly(vinyl Chloride)

Commercial Poly(vinyl chloride) (PVC) supplied from (Pet Kim company, Turkey) was freed from additives by re-precipitation from tetrahydrofuran (THF) solution in ethanol. The purified polymer was dried under reduced pressure at room temperature for 24 hrs.

Films preparation

A certain concentration of PVC and PVC-L-M(II) solution (5 gm/100 mL) in THF was used to prepare polymer films with a thickness of 40 μm (measured by a micrometer type 2610 A, Germany). The films were prepared by evaporation technique at room temperature for 24 hours. To remove the possible residual THF solvent, film samples were further dried at room temperature for three hours under reduced pressure. Linear optical absorption spectrum of the films was recorded using computerized Shimadzu UV-VIS 160A-Ultraviolet spectrophotometer full-scale in the wavelength range of 200-900 nm. The light sources are halogen lamp and socket-deuterium lamp. The detector is Si-photodiode and all measurements were performed at room temperature. UV-VIS absorption was made for prepared samples before and after conjunction [14].

RESULT AND DISCUSSION

Characterization of compound (A)

The reaction of thiosemicarbazide Hydrochloride with benzoic acid in presence of POCl_3 afforded 2-amino-5-phenyl-1,3,4-thiadiazole [12]. The structural assignment of the product was based on its data in table 2. The FT-IR spectrum of compound (A) exhibited significant two band in the range (3402-3213) cm^{-1} which could be attributed to asymmetric and symmetric stretching vibrations of NH_2 group. Besides this, band at about (1475-1423) cm^{-1} due to cyclic (S-C=N) stretching. Bands at (1518) cm^{-1} and (1484) cm^{-1} are due to the (N-H) bending and (C-N) stretching vibrations respectively [15,16].

Characterization of ligand (L)

The FT-IR spectrum of ligand shows the disappearance bands due to stretching of amino thadiazole ($-\text{NH}_2$) in compound (A). Ligand Schiff base compound (L) exhibited the following bands, stretching band near the region 1419-1478, 3155, 1611, 1777, 1207 and 1277 cm^{-1} due to (=N-N=C-) cyclic group, (OH) Stretching, stretching of azomethine group, carbonyl group and the last two bands due to thadiazole ring respectively, see table 2. $^1\text{H-NMR}$ spectrum of ligand shows the following characteristic chemical shift, (δ 8.010) ppm (s, H, OH, carboxyl group), (δ 6.973-7.807) ppm (m, 8 H, Ar), the signal at (δ 7.991) ppm (s, 1H, azomethine group), (δ 1.574) ppm (organic solvent). The positive ion mass spectral analysis of (L) observe at m/z 310.2 (M+1), confirms the theoretical molecular weight i.e. 309.34, see figures 1 and 2.

Table 2. FT-IR, Electronic spectra of the prepared ligand

Compound	M.P. $^{\circ}\text{C}$	Color	Absorption Bands(nm)	Assignment	FT-IR (cm^{-1})	Assignment
Comp. (A)	244	White-yellow	215	$\pi \rightarrow \pi^*$	3402-3213	NH_2
					1475-1423	S-C=N
			285	$n \rightarrow \pi^*$	1518	N-H
					1484	C-N
Comp. (L)	285	White-yellow	225	$\pi \rightarrow \pi^*$	1419-1478	N-N=C cyclic
					3155	OH stretching
			395	$n \rightarrow \pi^*$	1611	Azomethine group
					1207, 1277	Thadiazole ring

Sample 7_03-06-2012

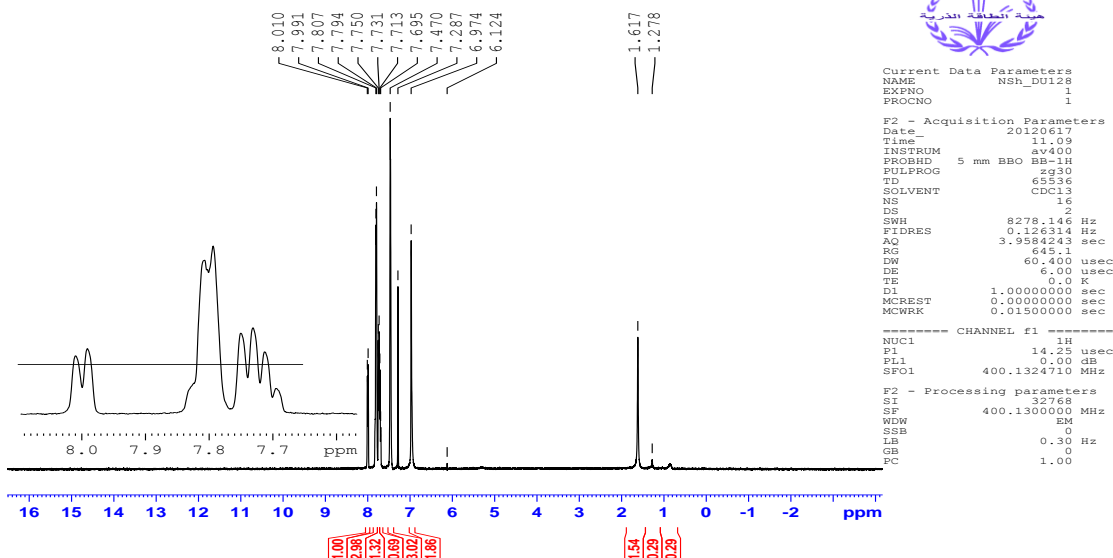


Figure 1. ¹H spectrum of ligand (L)

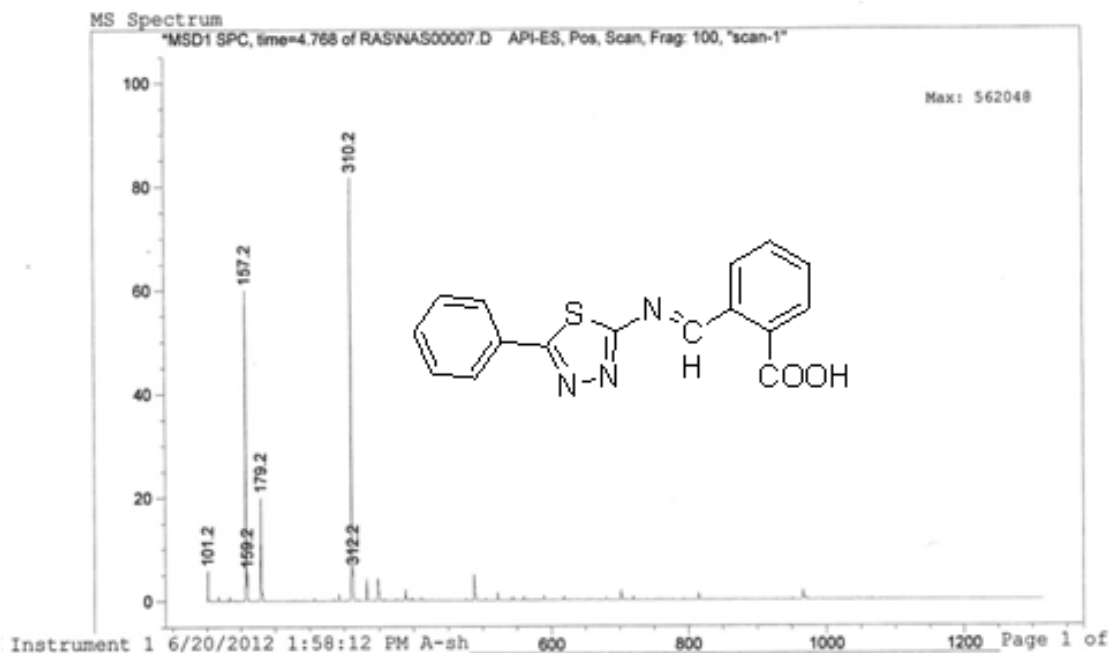


Figure 2. Mass spectrum of ligand (L)

Characterization of L-grafted PVC and its complexes

Significantly different from the FTIR spectrum of pure PVC, the FTIR spectrum of L-grafted PVC showed the disappearance of O-H band and shifted band at 1755 cm⁻¹ with the characteristic peaks of the L at 3155 and 1777 cm⁻¹. a strong band at ν(615) cm⁻¹ was observed which could be attributed to ν(C-Cl) band which is differ from PVC without modification ν(609). we could conclude that the ligand was grafted onto the PVC chains successfully.

The reaction between L-grafted PVC with Cu^{II} and Co^{II} gave different types of complexes. In the L-PVC, the band at 1755 cm⁻¹ and 1611 cm⁻¹ were assigned to the stretching of C=O and C=N shifted to a lower frequency region. This shift is probably due to the complexation of the metal to the ligand through oxygen of the carbonyl group. Stretching of metal-oxygen and metal-Cl bands of the complexes appeared in low frequency (452, 462) cm⁻¹ and (258, 267) respectively [17].

Microscope and AFM images analysis

Surface topographies of polymer films were examined by using lab. microscope and optical microscope images of all polymers at 400× magnification are given in figure 3. Atomic force microscope is an excellent tool to measure the roughness factor, pore size and also two and three dimensional topographic images of the sample. In the present study, AFM technique has been used to view the two and three dimensional images of the prepared sample over the scanned area 5.0 μm x 5.0 μm. The PVC-L-Cu^{II} and PVC-L-Co^{II} samples were subjected to atomic force microscopic studies and its topographic and three-dimensional images are shown in figure 4 and 5.

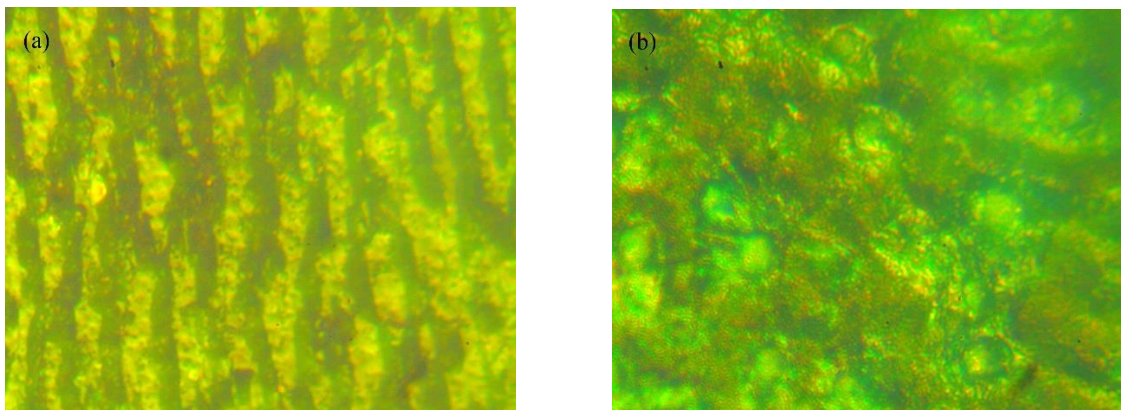


Figure 3. Optical microscope images of polymer films at 400× magnification. (a) PVC-L-Cu^{II}, (b) PVC-L-Co^{II}

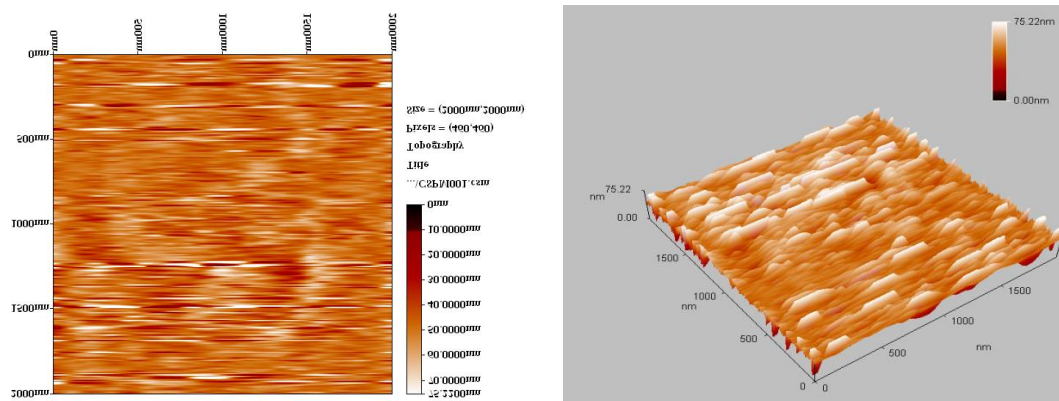


Figure 4. 2D and 3D of AFM images of PVC-L-Cu^{II}

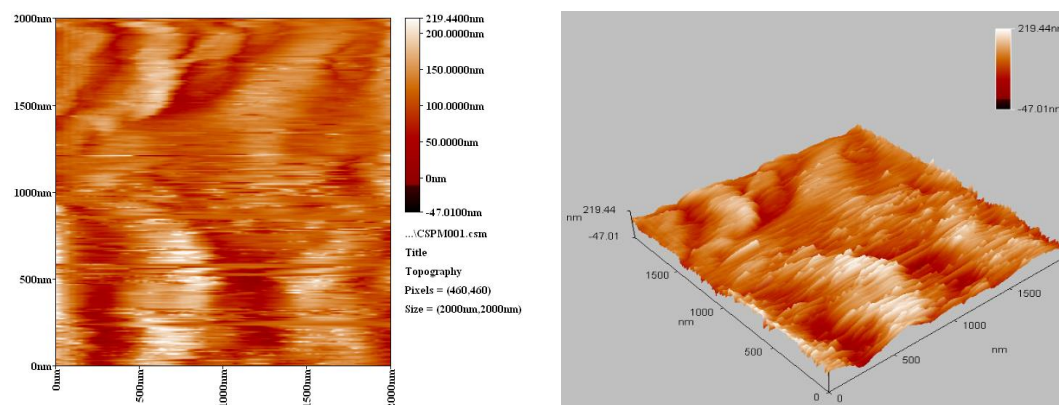


Figure 5. 2D and 3D of AFM images of PVC-L-Co^{II}

Optical band-gap

The band gap energy can be calculated using Tauc model, in direct band transition case [23]:

$$(\alpha h\nu)^2 = A_0 (h\nu - E_g)$$

Where A_0 is a constant, $h\nu$ is the photon energy and E_g is the optical band gap energy, α is optical absorption coefficient deduced from the absorption data.

The optical energy band gap calculated from Tauc's plot (Figs.6-8) varies from 5.21 eV to 2.94 eV, according to the metal type. The decrease in the band gap is attributed to the type of metal complexes. The results of optical study reported in this paper is in good agreement with the observations of other researchers. The results are shown in table 2.

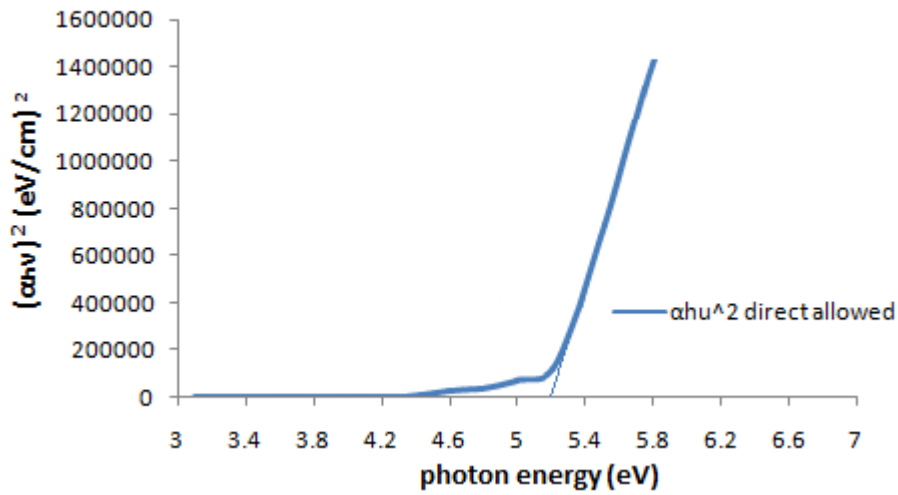


Figure 6. Allowed direct transition $(\alpha h\nu)^2$ vs energy for pure PVC

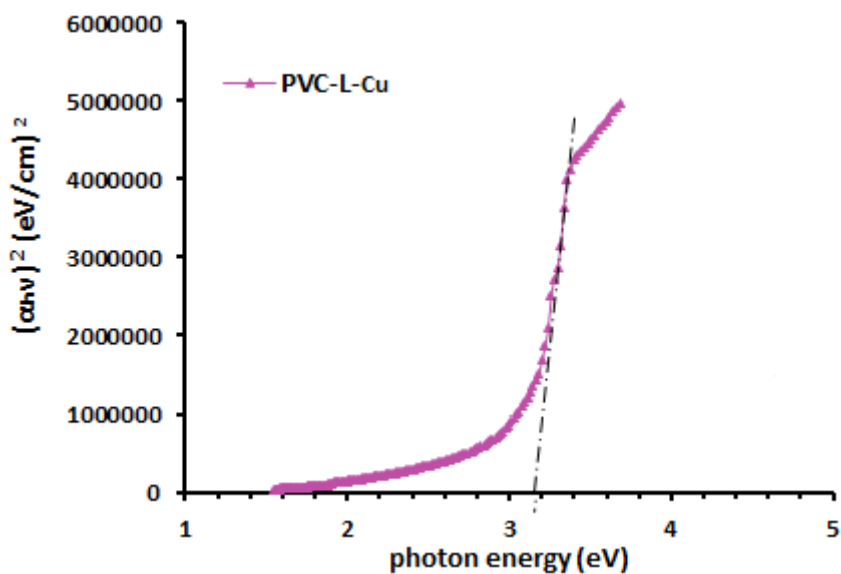


Figure 7. Allowed direct transition $(\alpha h\nu)^2$ vs energy for PVC-L-Cu^{II}

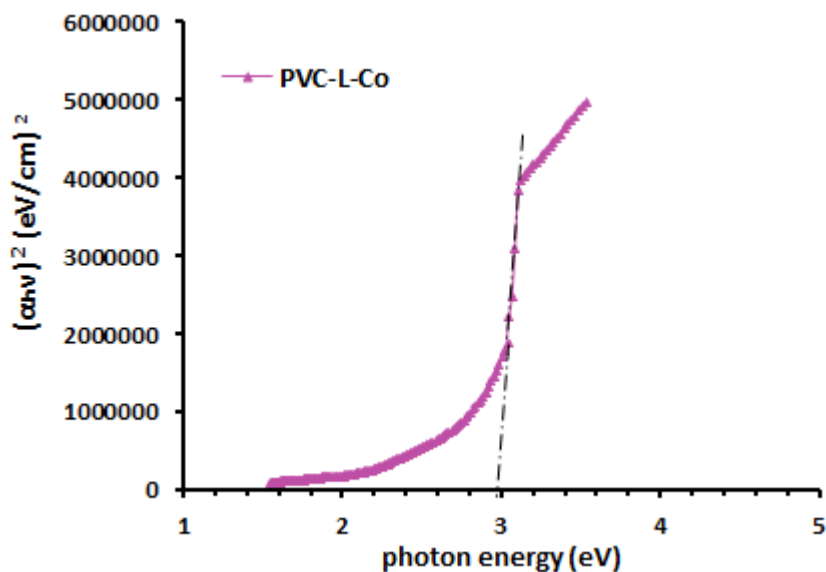


Figure 8. Allowed direct transition $(\alpha h\nu)^2$ vs energy for PVC-L-Co^{II}

The effect of the metal complexes addition on the values of activation energies is investigated and the result are shown in table 3. In addition, the shift in the energy gap could be attributed to the formation of polarons and bipolarons. The evidence of polar on formation is made that the reaction in band to band transitions due to the shifting the band density of state toward the energy gap. This observation is not like doping of conventional semiconductor when the band to band absorption strength dose not affected by the formation of dopant state in the energy gap.

Table 3. Indicate the energy band gap according to the direct allowed transition

Sample	Eg(eV)
PVC	5.21
PVC-L-Cu ^{II}	3.17
PVC-L-Co ^{II}	2.94

The results presented in figures 6-8 indicate the existence of two bipolaron bands in the energy gap. The first one represents the transition from valance band to bonding bipolaron band. The second band represents the transition from valance band to anti- bonding bipolaron band. Conductivity measurement of PVC with additive can obtain by adopting the data of energy gap [11-18], (see table 3 and figures 6-8). The conductivity measurement for PVC in the presence of additive increase in the following order:

$$PVC-L-Co^{II} > PVC-L-Cu^{II} > PVC$$

CONCLUSION

The study on the effect of PVC modification with 2-[5-phenyl-1,3,4-thiadiazol-2-ylimino-methyl]-benzoic acid complexes, the repeating units on its optical properties has shown that the energy gap of modified polymers decreases in comparison with that of pure.

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