ANNEALING EFFECT ON OPTICAL PROPERTIES OF POLY (VINYL CHLORIDE) MODIFIED BY NICKEL ETHYL XANTHATE CHELATE COMPLEX

Nadir Fadhil Habubi, Zainab Al-Ramadhan, *Rana Ismaeel Khaleel

Abstract

The present study is focused upon the optical properties of poly(vinyl chloride) thermoplastic insulator films with ethyl xanthate metal complex additive, namely: Bis(ethyl xanthato)Nickel(II):Ni(etx)\textsubscript{2}. Preparing films have a fixed thickness about (120±5 Microns). the optical data were analyzed in term of the theory concerning indirect electronic transition. The variation of the optical gap \(E_{g}^{opt}\) with metal concentration and annealing are reported. It is observed that the energy gap decreases as the metal complex content increased. The influence of PVC modified by Nickel Ethyl Xanthete Chelate complex was investigated.

Introduction

There are increasing interest in synthesis new polymeric materials because of the merger of conventional polymer properties with the electronic properties of metals and semiconductor which lead to enormous potential in both researches and commercial application[1]. Polymeric materials can be made highly conductive upon appropriate electro chemical and chemical treatment which is useful for electronic applications. this process is performed by doping with appropriate material.

The optical study gives a good information about the fundamental properties of the material under investigation[2]. Poly vinyle chloride,PVC, is a linear chain polymer, figure(1) [3], with bulky chloride side-grubs which prevent crystalline regions occurring normally.
PVC is hard and rigid material at room temperature [4]. Straight PVC is colorless rigid material. It has relatively high density and low softening point[5]. The presence of the chlorine atom causes an increase in the hardness and stiffness of the polymer is recognized PVC is also polar polymer because of C-Cl dipole. These properties make PVC polymers as a good candidate in the application. PVC has very limited solubility. The most effective solvents are those which appears to be capable of some form of interaction with the polymer. It has been suggested that PVC is a weak proton donor and effective solvents are proton acceptor. Thus the PVC polymer is soluble at room temperature in oxygen containing solvents such as ethers e.g. dioxane, tetrahydrofuran; ketones, e.g. cyclohexanone, methylisobutyl ketone and nitro compounds, e.g. nitrobenzene[7]. The importance of PVC can be extruded into pipe, conduit, or sheet while in flexible form it can be substituted for rubber in low-voltage cables and house wiring. This polymer may be regarded as the most widely used plastic material important application form high volume construction related products to simple electric wire insulation and coatings[8].

**Experimental**

**Chemical materials**

**Poly(Vinyl Chloride)**

The PVC used in this work is supplied form Petkim company (Turkey) it is rigid polymer, fine solid powder.

**Potassium Ethyle Xanthate (PEX)**

This legend was prepared by a method similar to that described by Malik, etal. [9]. 0.25 mol of Potassium hydroxide was added to 0.2mol of absolute ethanol. After stirring for three minute, unreacted Potassium hydroxide was removed by decantation. To the decantant, 0.2mol of carbon disulfide was added gradually with cooling and stirring. The yellow pasty product produced is washed with ether, filtered of and dried under reduced pressure to get yellowish crystals. (m.p. = 108 - 110 °C).

**Preparation of ethyl xanthate complexes**

These complexes were prepared by method described by Yousif [10]. To 25ml of ethanolic solution of 0.01mol, ZnCl$_2$.6H$_2$O was added, with constant stirring. After that 0.02mol of Potassium, ethyl xanthate dissolved in 25ml of water was added. This mixture was then stirred until white crystalline solid was obtained. The product was recrystallized from a mixture of Petroleum ether and acetone to yield brown crystals of Ni(etx)$_2$.

The expected chemical structure is shown below:

![Chemical Structure](image)

**Purification of Poly(vinyl Chloride) [11]**

Commercial Poly (vinyl chloride) (PVC) supplied from Petkim Company (Turkey) was free from additives by re-precipitation from tetrahydro-furan (THF) solution in ethanol. The purified polymer was dried under reduced pressure at room temperature for 24 hours.

**Polymer films and polymer ethyl xanthate metal complexes composite preparation**

The studied of Poly (Vinyl Chloride) Ethyl Xanthate Composites were prepared by the following casting method[12]: The purified PVC was dissolved in tetrahydrofuran (THF) the desired salt %wt additive[bis(ethylxanthato)Nickel (II); Ni(etx)$_2$] was added and the cast Nickel(II);Ni(etx)$_2$ was added and the mixture was cast into a glass- sheet of dimensions (5x5cm$^2$) and kept in a dry atmosphere at (40°C) for (24) hours. The thickness of the polymer films was (120 ± 5 Micron).

**The Annealing**
The samples were thermally annealed at 80ºC for six hours.

**Result and discussion**

The absorption coefficient is given by:[14]

\[ \alpha = \frac{A}{d} \quad \text{(1)} \]

where \( A \), \( d \) is the absorbance and thickness respectively, the type of electronic transition for all films was analyzed based on absorption coefficient (\( \alpha \leq 10^4 \text{ cm}^{-1} \)) for non-crystalline materials.

The absorption data were analyzed in terms of the Barden theory of phonon-assisted indirect electronic transition [13], according to this theory, the absorption coefficient (\( \alpha \)) depends on the photon energy according to this relation [14]:

\[ \alpha = \frac{A(h\nu - E_g + E_p)^2}{h\nu} \quad \text{(2)} \]

where \( A \) is a constant, and \( E_g \) is an indirect allowed band gap and \( E_p \) is a phonon absorption (+) or phonon emission (−) energy. The relation between \((h\nu)^{1/2}\) and \((h\nu)^{1/3}\) versus photon energy for the undoped PVC sample (control) is shown in figures (2a,b) for allowed and forbidden transition.

Figures (2a,b) show single absorption peaks and this is confirmed that pure PVC (control) has no electronic transition in the visible region. For doped samples, two distinct absorption peaks appear. Results are shown in figures (3a,b) that was attributed to the formation of polarons and bipolarons in the doped films [15].

The evidence of polaron formation is made that the reactions in band to band transition due to shifting in the band density of state toward the optical energy gap when the band to band absorption strength does not affected by the formation of dopant state in the energy gap [16].

The effect of the weight % metal complex addition on the values of optical gap energies 1 and 2 with phonon energies is also investigated and the result are shown in Tables (1-a) and (1-b). The results presented in figures (3a,b) indicate the existence of two bipolaron bands in the optical energy gap. The first one represents the transitions from valance band to bonding bipolaron band. The second band represented the transition from band to anti-bonding bipolaron band which are in good agreement with other workers [17,18].

Both Tables (1-a) and (1-b) shows energy band gap (\( E_g \)) allowed and forbidden respectively for all PVC films with different concentration of Ethyl Xanthate metal complex together with assisting phonon energy. These values are calculated from the linear portion and the result is shown in figure (2a,b). From these Tables (1-a) and (1-b), one can predict that \( E_g \) is always decrease with increasing concentration percentage of additive.

This fact is also obtained by other workers [19]. From tables (2-a),(2-b) and figures (4,5-a,b), it has been observed that the optical energy gap of PVC (control) is decrease after annealing compare to that before annealing but for 1% doping the \( E_g \) is increase compared with that before annealing. We note that 1% doping is enough to exist the thermally dynamic equilibrium and this make cross linking and might increase the energy gap, for 2% and 3% doping, one can show the shift in absorption edge and the decrease in \( E_g \) after annealing, the shift in the absorption edge with the heat treatment is explained by a change in the defect structure of solids. This states in the band structure is responsible for the low values of \( E_g \). The decrease in the optical gap after annealing is due to the effect of oxidation [20].

**Conclusion**

1. The ethyl xanthate metal complex is effectively modifying the optical properties (i.e. optical energy gap) of PVC films. The band gap is decrease with increase filler concentration.
2. The UV-visible absorption spectra of pure films show a characteristic absorption band, but after addition of ethyl xanthate metal complex, two distinct bands are appeared.
3. The annealing give good result to the optical properties of PVC-Ni(etx)\(_2\) composite.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( E_{g1}(\text{eV}) )</th>
<th>( E_{p1}(\text{eV}) )</th>
<th>( E_{g2}(\text{eV}) )</th>
<th>( E_{p2}(\text{eV}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVC(control)</td>
<td>-</td>
<td>-</td>
<td>4.121</td>
<td>0.201</td>
</tr>
<tr>
<td>1%</td>
<td>1.955</td>
<td>0.0565</td>
<td>3.349</td>
<td>0.115</td>
</tr>
</tbody>
</table>

Table 1-a: Indirect allowed optical energy band gaps and assisting phonons energies for PVC-Ni(etx)\(_2\) composite.
Table 1-b: Indirect forbidden optical energy band gaps and assisting phonons energies for PVC - Ni(etx)₂ composite.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Eg₁(eV)</th>
<th>Ep₁(eV)</th>
<th>Eg₂(eV)</th>
<th>Ep₂(eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVC(control)</td>
<td>-</td>
<td>-</td>
<td>4.017</td>
<td>0.129</td>
</tr>
<tr>
<td>1%</td>
<td>2.075</td>
<td>0.097</td>
<td>3.275</td>
<td>0.105</td>
</tr>
<tr>
<td>2%</td>
<td>1.905</td>
<td>0.083</td>
<td>2.985</td>
<td>0.075</td>
</tr>
<tr>
<td>3%</td>
<td>1.739</td>
<td>0.056</td>
<td>2.725</td>
<td>0.014</td>
</tr>
</tbody>
</table>

Table 2-a: Indirect allowed optical energy band gaps and assisting phonons energies for PVC - Ni(etx)₂ composite after annulling.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Eg₁(eV)</th>
<th>Ep₁(eV)</th>
<th>Eg₂(eV)</th>
<th>Ep₂(eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVC(control)</td>
<td>-</td>
<td>-</td>
<td>3.9</td>
<td>0.15</td>
</tr>
<tr>
<td>1%</td>
<td>3.4</td>
<td>0.13</td>
<td>3.85</td>
<td>0.1</td>
</tr>
<tr>
<td>2%</td>
<td>3.2</td>
<td>0.1</td>
<td>3.7</td>
<td>0.13</td>
</tr>
<tr>
<td>3%</td>
<td>2.15</td>
<td>0.05</td>
<td>2.5</td>
<td>0.1</td>
</tr>
</tbody>
</table>

Table 2-b: Indirect forbidden optical energy band gaps and assisting phonons energies for PVC - Ni(etx)₂ composite after annulling.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Eg₁(eV)</th>
<th>Ep₁(eV)</th>
<th>Eg₂(eV)</th>
<th>Ep₂(eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVC(control)</td>
<td>-</td>
<td>-</td>
<td>3.65</td>
<td>0.15</td>
</tr>
<tr>
<td>1%</td>
<td>3.3</td>
<td>0.1</td>
<td>3.6</td>
<td>0.13</td>
</tr>
<tr>
<td>2%</td>
<td>3.15</td>
<td>0.05</td>
<td>3.5</td>
<td>0.1</td>
</tr>
<tr>
<td>3%</td>
<td>2.45</td>
<td>0.05</td>
<td>2.45</td>
<td>0.05</td>
</tr>
</tbody>
</table>
Fig. 2, b:

$$(\alpha h\nu)^{1/3}$$ Vs. photon energy (forbidden indirect transition) for pure PVC.

Fig. 3, a:

$$(\alpha h\nu)^{1/2}$$ Vs. photon energy (allowed indirect transition) for 3% Ni(etx)$_2$ additive.
Fig. 4,a: 
\((\alpha h\nu)^{1/2}\) vs. photon energy (allowed indirect transition) for pure PVC after annealing.

Fig. 4,b: 
\((\alpha h\nu)^{1/3}\) vs. photon energy (forbidden indirect transition) for pure PVC after annealing.
Fig. 5.a:
Ni$^{\%}$($\alpha$hf)$^{1/2}$ Photon energy (allowed indirect transition) for 3% Ni(etx)$_2$ additive after annealing.

Fig. 5.b:
Ni$^{\%}$($\alpha$hf)$^{1/3}$ Photon energy (forbidden indirect transition) for 3% Ni(etx)$_2$ additive after annealing.

References


