Doping Effect on Optical Constant of Poly (Vinyl Chloride)

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Abstract:
Thick films of poly(vinyl chloride)(PVC)& PVC doped with Zn(etx)$_2$ salt complex have been prepared by cast method with fixed thickness almost (120±5) Microns. Optical studies were carried out in the wavelengths region(200-900)nm based on absorption & transmission measurement. Optical parameters such as absorption coefficient($\alpha$) ,refraction index($n$) and extinction coefficient($K$) were observed to be effected by adding the dopant.Electrical parameters such as real($\varepsilon$)& imaginary($\dot{\varepsilon}$) part of dielectric constant were also calculated part of dielectric constant were also calculated from the optical parameters using Maxwell equation.

Key words: Polymer Properties, Optical Constant,Poly(vinyl chloride).

Introduction:
The optical properties of amorphous semiconductors have been the subject of many recent papers. The study of the optical constants of materials is interesting for many reasons. First, the use of materials in optical fibers and reflected coating requires accurate knowledge of their optical constants over wide ranges of wavelength. Second, The optical properties of all materials are related to their atomic structure, electronic band structure and electrical properties[1,2].

The addition of conductive fillers to the polymer giving a new product called as conducting polymer composite materials(CPCM)which consist of a random distribution of conducting filler throughout an insulating polymer[3],the purpose of use of fillers can be divided into two basic categories.First,to improve the properties of materials and Second, to reduce the cost of component.

Metal-polymer composites are a relative new of technological materials; their electrical characteristics are close those of metals, whereas the mechanical properties and processing methods are typical for plastics. The conditions of electric charge transfer determine the electrical conductivity level and the dielectric properties of the heterogeneous system, in which polymer forms the matrix and conductive phase is formed by the dispersed metallic filler. The properties of (CPCM) depend on several factors, including the kind of conducting filler, the spatial distribution of filler particles, the interaction between polymer and particle size and filler[4]. Poly(vinyl chloride) commonly abbreviated PVC, is the third most widely used thermoplastic polymer after polyethylene and polypropylene in terms of revenue generated, it is one of the most valuable products of the chemical industry[5].

PVC intrinsic properties make it suitable for a wide variety of applications. It is biologically and chemically resistant, making it the plastic of choice for most household sewerage pipes and other pipe applications where corrosion would limit the use metal [5].

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The aim of this work is to focus on study the effect of filler concentration on the optical parameters of PVC.

Materials and Methods:

Ethyle Xanthate Zinc complex was prepared by method described by Khaleel[6].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 optioned. The product was recrystallized from a mixture of Petroleum ether and acetone to yield white crystals of Zn(etx)$_2$. The PVC used is supplied from Petkim company(Turkey).It is rigid polymer, fine solid powder, was free from additives by re-precipitation from tetrahydrofuran (THF) solution in ethanol. The purified polymer was dried under reduced pressure at room temperature for 24 hours and then dissolved in (THF) the desired salt additive [bis(ethylxanthato)Zinc(II)]$_2$; Zn(etx)$_2$, was added and the mixture was cast into a glass sheet of dimensions (5 ×5 cm$^2$) and kept in a dry atmosphere at (40˚C) for (24) hours. The thickness of the polymer films was (120 ±5 Micron). This films are prepared as a composite with wt% percentage ranged from 1-3% of this additive.  The absorption spectrum was recorded at room temperature using Shimadzu UV-Vis. Spectrophotometer in the wave lengths (200-900)nm.

Theory:

The optical properties of an isotropic materials (absorption, reflection....) are usually described by two optical constants,(n) (the index of refraction) and (k) (index of absorption),the relation between the various optical constants (i.e. n,k,$\alpha$,...etc...) can be studied by considering the Maxwell wave equation[7].A plane polarized wave propagation along positive Z-axis with a propagation constant (n) can be represented by:-

$$F_x=F \exp [i\omega (t-nz/c)] \ldots (1)$$

Where F is the electric field of an electromagnetic wave and n is a complex defined in terms of the real components

$$n = n_r - ik \ldots (2)$$

Which related to the velocity of propagation ,v, by:-

$$v = c / v \ldots (3)$$

By substitution of expression (2) into (1) and re-arranging these relations, the following equation is obtained:-

$$F_x = F \exp (-\omega k z / c) \exp (i\omega (t -nz /c)) \ldots (4)$$

By using the medium, the wave will undergo attenuation as exp (-$\omega k z /c$).in optical instruments the measured intensity of light is proportional to $F^2$. Thus in the medium this wave can be expressed as exp(-$2\omega k z /c$) or exp(-$az$),where $\alpha$ is called the absorption coefficient[8], which is related to k, the extinction coefficient by:-

$$\alpha = 2.303 \frac{A}{d} \ldots (5)$$

where $A$=absorbance.

d=thickness.

And we can also related to K ,The extinction coefficient by[9]:-

$$\alpha = \frac{\pi \kappa}{\lambda} \ldots (6)$$

where $\lambda$ = wave length.

The reflection of the air-film interface at normal incidence is given by[10]:-

$$R = \frac{(n-1)^2 + k^2}{(n-1)^2 + K^2} \ldots (7)$$

Where n=refractive index.

R=reflectance.

The dielectric constant $\varepsilon$, can be considered to be real and defined as:-

$$\varepsilon = n^2 - k^2 \ldots (8)$$

one can also defined the dielectric constant to be complex:-

$$\varepsilon = 2nK \ldots (9)$$
Results and Discussion:

For a better understanding of the physical properties of this material, it is interesting to study some optical constants used to describe the optical properties.

The optical absorbance as function of wavelength of the incident light for and PVC with various constant ration 1-3% is shown in Figure(1). This Figure indicate the fact that adding various amount of Zn(etx)$_2$ to pure PVC does not change the chemical structure of the materials but new physical mixture has been formed. A good support for this indication is that the peak positions have not been shifted and the intensity of this peak has been increased as a result of addition.

Fig.(1)Optical absorbance for Pure PVC and PVC with various Zn(etx)$_2$ Concentration.

Fig. (2) shows the absorption coefficient ($\alpha$) as a function of photon energy. It was seen that ($\alpha$) is increased as a result of salt content.

The variation of (k) for PVC with various filler content as a function of photon energy is shown in figure (3), which give an indication that extinction coefficient (k) increased with increasing salt content, this behavior can be attributed to the increasing of the packing density as result of salt content [11]. this result agreement to what have been found by other workers [12,13].
Table (1) illustrates the values of \((n, k, \varepsilon \text{ and } \dot{\varepsilon})\) at \(\lambda=600\) for pure and doped PVC with \(\text{Zn(etx)}_2\) with different concentration.

<table>
<thead>
<tr>
<th>Concentration</th>
<th>Doping</th>
<th>(n)</th>
<th>(k)</th>
<th>(\varepsilon)</th>
<th>(\dot{\varepsilon})</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVC pure</td>
<td></td>
<td>1.165</td>
<td>1.58x10^-6</td>
<td>1.35</td>
<td>3.69x10^-6</td>
</tr>
<tr>
<td>Zn1%</td>
<td></td>
<td>1.575</td>
<td>1.78x10^-6</td>
<td>1.48</td>
<td>3.93x10^-6</td>
</tr>
<tr>
<td>Zn2%</td>
<td></td>
<td>1.639</td>
<td>1.87x10^-6</td>
<td>2.48</td>
<td>6.12x10^-6</td>
</tr>
<tr>
<td>Zn3%</td>
<td></td>
<td>1.965</td>
<td>2.05x10^-6</td>
<td>2.67</td>
<td>6.49x10^-6</td>
</tr>
</tbody>
</table>

Table (1) shows the \((k)\) exhibits slightly increase changes with increasing \(\text{Zn(etx)}_2\) concentrations ,indeed\((k)\) changes from \(1.58x10^{-6}\) to \(2.05x10^{-6}\) when \(\text{Zn(etx)}_2\) concentration increases from \((0-3)\)wt.%. The real part \((\varepsilon)\) and imaginary part \((\dot{\varepsilon})\) of dielectric constant calculated from the optical parameters \((n \text{ and } k)\) using Maxwell equations\((8,9)\).

The variation of \(\varepsilon\) as a function of \(h\gamma\) is shown in figure (6). This oscillatory behavior can be attributed to some combined relaxation processes which usually occurred in heterogenous system \([16]\).

Fig.(4) Reflective index \((n)\) for PVC Composite as a function of photon energy

The variation of the reflectance for pure PVC and polymer composite (PVC with \(\text{Zn(etx)}_2\)) of various filler concentration as a function of photon energy \((h\gamma)\) are in shown figure (5).this figure showed that the intensity of the peak increased as a result of filler addition\([15]\).

Fig.(5) Reflectance (R) for PVC Composite as a function of photon energy.

For pure and doped PVC with different concentration of \(\text{Zn(etx)}_2\). Figure (7) show the variation of imaginary part \(\dot{\varepsilon}\) of dielectric constant versus \(h\gamma\).from this figure, we can remarkable the increasing in \(\dot{\varepsilon}\) with...
increasing dopant concentration, this result related to Zn (etx)_2 salt complex[17].

![Graph](image)

\[
\text{Imaginary part of dielectric constant(}\varepsilon\text{) as a function of photon energy.}
\]

**Fig.(7)** Variation in imaginary part of dielectric constant(\(\varepsilon\)) as a function of photon energy.

**Conclusion:**
Poly(vinyle chlode)polymer modification with Zn(etx)2 with different concentration have been successfully which were used for measurements of optical constant. The main conclusion could be drawn from this work are:

1- The optical results showed that there were no chemical changes in the composite structures.
2- The refractive index in the optical region has been found to be increases with the increasing filler content and wave length of incident light, which was attributed to the higher packing of this composites.
3- Increasing of extinction coefficient values(k), the reflectance(r) and the real and imaginary part( \(\varepsilon,\bar{\varepsilon}\) ),always related to increase the zn(etx) salt complex concentration in the pvc polymer.

**Reference:**

تأثير التطعيم على الثوابت البصرية لثولي (كلوريد الفانيل) البولي (كlorid الفانيل)

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الخلاصة:

تم تحضير أفلام من PVC و PVC المطعوم بمعدق ثنائي (أثنين زانفيتو) زنك Zn(II):Zn(II)Zn(II):Zn(II)Zn(II)Zn(II)Zn(II)Zn(II)Zn(II). تم دراسة الخواص البصرية في المنطقة (200-900) نانومتر من الطيف باعتماد قياسات الامتصاصية والانتشارية تم حساب الثوابت البصرية مثل معامل الامتصاص (α) ومعامل الإنتشار (β) ومعامل التحمل (K) ووحظ أنها تتأثر بإضافة المعدق.ثوابت الكهربية ثوابت العزل الحقيقي (ε) وثوابت العزل الخيالي (ε) حسبت بالاعتماد على الثوابت البصرية باستخدام معادلة ماكسيول.