Preparation of (PS-PMMA-ZnCl₂) Composites and Study their Electrical and Optical Properties

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Abstract: In this paper, Effect of Zinc chlorides on optical and electrical properties of (PS-PMMA) copolymer have been investigated. The samples of composites were prepared by using casting technique. The optical properties measured in the wavelength range from 200 nm to 800 nm. The experimental results showed that the absorbance, absorption coefficient, energy band gap, extinction coefficient, refractive index and real and imaginary parts of dielectric constants are increasing with the increase of the Zinc chloride concentration. The electrical properties measured in temperature range from 30°C to 80°C. The results showed that the D.C electrical conductivity (PS-PMMA) copolymer is increased with the increasing of the weight percentages of Zinc chloride and temperature. The activation energy of composites decreases with increase of Zinc chloride concentration.

Keywords: electrical properties, copolymer, optical properties, Zinc chloride

1. Introduction

The doped polymers may present useful applications in integrated optics or in real time holography. In order to tailor materials with improved properties within the doped polymer class, it is necessary to understand and control the electronic mechanisms involved in the optical behavior [1]. Optical polymers have attracted considerable attention in recent years because of their important industrial applications. PMMA is one of the earliest and best known polymers. PMMA was seen as a replacement for glass in a variety of applications and is currently used extensively in glazing applications. The material is one of the hardest polymers, and is rigid, glass-clear with glossy finish and good weather resistance. PMMA is naturally transparent and colorless. The transmission for visible light is very high. Polymeric composites of PMMA are known for their importance in technical applications [2]. Polystyrene (PS) is amorphous polymer with bulky side groups. General purposes PS are hard, rigid, and transparent at room temperature and glass like thermoplastic material which can be soften and distort under heat. It is soluble in aromatic hydrocarbon solvents, cyclohexane and chlorinated hydrocarbons [3].

2. Experimental Part

The homopolymer polymers (polystyrene and polymethyImethaacyrl) were dissolved in chloroform by using magnetic stirrer in mixing process to get homogeneous solution. The weight percentages of zinc chloride are (0, 2, 4 and 6) wt.% were added and mixed for 10 minute to get more homogenous solution, after which solution was transferred to clean glass Petri dish of (5.5cm) in diameter placed on plate form. The dried film was then removed easily by using tweezers clamp. The composites were evaluated spectra photometrically by using UV/160/Shimadzu spectrophotometer.

Absorptance (A) is defined as the ratio between absorbed light intensity (IA) by material and the incident intensity of light (Io)

\[ A = \frac{I_A}{I_0} \]  

Transmittance (T) is given by reference to the intensity of the rays transmitting from the film(I) to the intensity of the incident rays on it (I₀) (T=I/ I₀), and can be calculated by [4]:

\[ T = \exp[-2.303A] \]  

and Reflectance (R) can be obtained from absorption and transmission spectra in accordance with the law of conservation of energy by the relation [4]:

\[ R + T + A = 1 \]  

Absorption coefficient (α) is defined as the ability of a material to absorb the light of a given wavelength

\[ \alpha = 2.303A/t \]  

Where A: is the absorption of the material t: the sample thickness in cm.

According to the generally accepted non-direct transition model for amorphous semiconductors proposed by:

\[ \alpha h\nu = B(h\nu - E_g)^r \]  

Where B is a constant related to the properties of the valance band and conduction band, hν is the photon energy, E_g is the optical energy band gap, r=2,or3 for indirect allowed and indirect forbidden transition

The Refractive index (n), the index of refraction of a material is the ratio of the velocity of the light in vacuum to that of the specimen:

\[ R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2} \]
When the \( k \to 0 \)

\[
R = \frac{(n-1)^2}{(n+1)^2} \quad (7)
\]

\[
n = \frac{1+R^{1/2}}{1-R^{1/2}} \quad (8)
\]

The extinction coefficient \( k \) was calculated using the following equation:

\[
K = \alpha \lambda /4\pi \quad (9)
\]

Dielectric constant is defined as the response of the material toward the incident electromagnetic field. The dielectric constant of compound \( e \) is divided into two parts real \( (e_1) \) and imaginary \( (e_2) \). The real and imaginary parts of dielectric constant \( (e_1 \text{ and } e_2) \) can be calculated by using equations \([5]\):

\[
e = e_1 - ie_2 \quad (10)
\]

\[
e_1 = n^2 - k^2 \text{ (real part)} \quad (11)
\]

\[
e_2 = 2nk \text{ (imaginary part)} \quad (12)
\]

The resistivity was measured over range of temperature from \((30 \text{ to } 80)\)°C using Keithly electrometer type \((616C) \). The volume electrical conductivity \( \sigma_v \) defined by:

\[
\sigma_v = \frac{1}{\rho_v} = \frac{LV}{AI} \quad (13)
\]

Where,

- \( A \) = guard electrode effective area.
- \( V/I = R \) = volume resistance (Ohm).
- \( L = \) average thickness of sample (cm).

In this model the electrodes have circular area \( A = D^2\pi/4 \) where \( D = 0.5 \) cm.

The activation energy was calculated using equation:

\[
\sigma = \sigma_0 \exp\left(-\frac{E_a}{k_B T}\right) \quad (14)
\]

\( \sigma \) = electrical conductivity at T temperature

\( \sigma_0 \) = electrical conductivity at absolute zero of temperature

\( k_B \) = Boltzmann constant

\( E_a \) = Activation Energy

### 3. Results and Discussion

#### 3.1 The Absorbance of \((\text{PS-PMMA-ZnCl}_2)\) Composites

Figure (1) shows the spectral dependence of the absorbance of the \((\text{PS-PMMA-ZnCl}_2)\) composites with different concentrations of salt. The absorbance is very large in the UV-region; this decay becomes relatively slower in the visible and near infrared regions, this attributed to the absorbance of polymers (PS and PMMA) in the UV-region.

Also, the absorbance of composites is increased with increase the concentration of zinc chloride, this behavior due to the absorbance of salt \([6]\).

#### 3.2 The Absorption Coefficient and Energy Gap of Composite

The variation of the absorption coefficient of the composites with photon energy is shown in figure (2). From this figure, we can see that the absorption coefficient is increased with increasing of the zinc chloride concentration which may be due to the absorption by the impurities. The absorption coefficient is smaller and stable in the low photon energy because of the scattering of the photon energy \([6]\).

Figures (3 and 4) show the energy band gap of composites. From the value of the absorption coefficient, we can conclude that the composites have indirect energy band gap. The energy band gap is calculated by using Eq.\((5)\) as shown in figures\((3 \text{ and } 4)\), it is decrease with increasing the zinc chloride concentration; this attributed to decrease the distant between the conduction band and valence band with the increase zinc chloride concentration\([3]\).

#### 3.3 Refractive Index and Extinction Coefficient

Figure (6) shows the variation in the refractive index \( n \) of composites with incident photon energy. The values is increased with increasing photon energy. This indicates that the electromagnetic radiation pass through the material is slower in the VIS and UV regions however the speed is higher in the visible and near Infrared region. Also, the increase of refractive index with the increasing of concentration of the zinc chloride attributed to increase the density of composites \([7]\).

#### 3.4 Dielectric Constant

Figures (7 and 8) show the variation of the real and imaginary dielectric constant with photon energy respectively. The real and imaginary dielectric constants are increasing with the increase the zinc chloride concentration. The behavior of the real and imaginary dielectric constant related to increase the numbers of charge carries. The concentration of the additives plays an important role in both cases due to the electronic polarization. The effect is very clear in the high photon energy region \([7]\).

#### 3.5 The Effect of Zinc Chloride Concentrations on D.C Electrical Conductivity of \((\text{PS-PMMA-ZnCl}_2)\) Composite

The variation of D.C electrical conductivity of \((\text{PS-PMMA-ZnCl}_2)\) composite is shown in figure (9). This figure shows...
that the D.C electrical conductivity increases with the increase of concentration of the zinc chloride. The behavior of D.C electrical conductivity with concentration of salt attributed to increase of carries charge in composites [8].

3.6 The Variation of the D.C Electrical Conductivity of (PS-PMMA-ZnCl2) Composites with Temperature

Figure (10) shows the variation of D.C electrical conductivity of composites with temperature. We can see that the electrical conductivity of composites is increased with increase the temperature this attributed to increase the movement of polymer chains and ions of ZnCl2 with increasing the temperature [9].

3.7 Activation Energy

The activation energy was calculated by using Eq. 14 as shown in figure (11). The activation energy of D.C electrical conductivity of (PS-PMMA-ZnCl2) composites is decrease with increasing the salt concentration, this behavior due to decrease the distance between conduction band and valance band with increasing the zinc chloride concentration [10].

4. Conclusions

- The absorbance is very large in the UV, region and it is increased with increasing the concentration of zinc chloride.
- The absorption coefficient is smaller and stable in the low photon energy.
- The absorption and (k) will increase as a result of the scattering centers in the composites.
- The values of the refractive index (n) of the composites increase exponentially with increasing photon energy.
- The real and imaginary dielectric constant shows the exponential increase with increasing the incident photon energy.
- The optical constants are increased with increasing the zinc chloride concentration.
- The electrical conductivity was increased with increasing the concentration of salt and temperature
- The activation energy was decreased with increasing the weight percentages of zinc chloride.

References
