Study of Some Optical Properties of Polystyrene - Copper Nanocomposite Films

Raheem Gaayid Kadhim
Physics Department, College of Science, University of Babylon, Baghdad, Iraq
E-mail address: Sonadody30@yahoo.com

ABSTRACT

The effect of addition of nano Cu on some optical properties of polystyrene has been studied. For this purpose, many samples have been prepared by adding nano Cu to the polystyrene with different Weight percentages and different thickness. The absorption spectra have been recorded at the wavelength ranges (220-800 nm). The absorption coefficient, extinction coefficient and energy gap of the indirect allowed and forbidden transition have been determined. Results show that the absorption coefficient and extinction coefficient increase and the energy gap of the indirect allowed and forbidden transition decreases with the wt. % content of nano Cu.

Keywords: polystyrene; nano Copper; composites
1. **INTRODUCTION**

Composites can be defined as materials that consist of two or more chemically and physically different phases separated by a distinct interface [1].

The development of nanotube, platelet and particle reinforced polymer composites has grown in importance in recent years due to their attractive applications in various fields. Much interest in these materials comes from the incorporation of one, two and three-dimensional nanofillers into a polymer matrix giving high aspect ratios and/or large surface area to volume ratios [2]. In recent years, nanocomposites with practically all polymer systems have been used to improve one property or another, with varying degrees of success.

A range of factors that influence not only the morphology but also the final properties of composites have been identified, including interfacial interactions between the filler and the polymer phase (optimization of filler surface modification, kinetic and thermodynamic factors influencing intercalation and exfoliation, etc.), the nature of the polymer (polar or nonpolar, molecular weight, etc.), the nature of the filler (aspect ratio, size, geometry, cation-exchange capacity, etc.), the processing methodologies, and the amount of inorganic filler. Yet, these improved properties are the result of many different mechanisms at play, owing to the presence of inorganic fillers within the polymers consequently, an enhancement of one property does not directly translate into an enhancement of the other properties. Thus, it is important to gain insights into these different factors and considerations that are responsible for enhancing the various properties, the optimization of which may—in time—lead to nanocomposites being designed according to need [3-4].

2. **THEORETICAL PART**

2.1. **The Optical Properties**

The main purpose of studying the optical properties of the (PS-Cu) nanocomposites is to identify the effect of adding the copper nanoparticles on the optical properties of (PS-Cu). The research concerns the recording of the spectrum of absorbance for the (PS-Cu) films at the room temperature and calculating the absorption coefficient, extinction coefficient and other optical constants, as well as identifying the types of electronic transitions and calculating energy gaps.

\[
I = I_0 e^{-\alpha t}
\]

\[\alpha t = 2.303 \log \frac{I}{I_0}\]

where (t) is the thickness of the matter and (\alpha) is the absorption coefficient, it is measured by cm\(^{-1}\).

\[
\alpha = 2.303(A/t)
\]
2. 2. **Refractive Index**

It is the ratio of light speed in vacuum to its speed in a medium. This index shows how far a matter is affected by the electromagnetic waves. The refraction index consists of two parts: real and imaginary. It can be expressed by the following equation [8]:

\[
\text{n} = \frac{C}{\nu} \tag{4}
\]

where \(n\) is the refraction index, \(C\) is the light speed in vacuum and \(\nu\) is the light speed in matter.

Reflectance (R) can also be defined as the ration of the reflected ray relation at the borderline between two mediums to the incident ray. The relation between reflectivity and refractive index is shown in the following equation:

\[
R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2} \tag{5}
\]

where \(k\) is the extinction coefficient.

The absorbance (A) and transmittance (T) can also be calculated from the following equation [9]:

\[
R + A + T = 1 \tag{6}
\]

Refractive index can be expressed by the following equation [10]:

\[
n = \sqrt{\frac{4R - k^2}{(R-1)^2} - \frac{(R+1)}{(R-1)}} \tag{7}
\]

2. 3. **Extinction Coefficient**

The imaginary part of the complex refractive index \(N\) is called the extinction coefficient, as shown in the following equation [6]:

\[
N = n - ik \tag{8}
\]

where \(n\) is the real part of the refractive index. The extinction coefficient can be calculated by using the following equation [6]:

\[
k = \omega\lambda/4\pi \tag{9}
\]

where \(\lambda\) is the wavelength of incident ray.

2. 4. **Dielectric Constant**

The dielectric constant represents the ability of a matter for polarization, the matter can respond to different frequencies in a complex manner, at optical frequencies represented by light waves the electronic polarity is dominating above other remaining types of polarization [10]. The real and imaginary dielectric constant can be calculated by the following equation [11]
\[ \varepsilon = \varepsilon_1 - i\varepsilon_2 \]  
\[ \text{…………………(10)} \]

where (\(\varepsilon\)) is the complex dielectric constant, (\(\varepsilon_1, \varepsilon_2\)) are the real and imaginary parts of the dielectric constant, respectively.

The dielectric constant can be calculated by calculating the refractive index. The relation between the complex dielectric constant and the complex refractive index (\(N\)) is expressed in the following equation:

\[ \varepsilon = N^2 \]  
\[ \text{…………………………(11)} \]

From the equations (8), (9), and (10), it can be concluded that [11]:

\[ (n - ik)^2 = \varepsilon_1 - i\varepsilon_2 \]  
\[ \text{…………………(12)} \]

From the equation (11), the real and imaginary complex dielectric constant can be expressed by the following equation:

\[ \varepsilon_1 = n^2 - k^2 \]  
\[ \text{………………..(13)} \]

\[ \varepsilon_2 = 2nk \]  
\[ \text{…………………(14)} \]

3. EXPERIMENTAL WORK
3.1. Preparation of (PS-Cu) Nanocomposites

The (PS-Cu) nanocomposites are prepared by the following:

1- Nanocomposites have been prepared by melting (0.5) gm of polystyrene in (40) ml of benzene, and by using magnetic stirrer for the mixing process to obtain more homogeneous solution with temperature of 35 °C.

2- Then adding the weight percentages of additives (0%, 3%, 6%, and 9%) of (Cu) nanoparticles as shown in Table (1), and wait for 30 minutes to get mixture more homogenous, by using casting method we get the films from this mixture and casting each one of these ratios in the template (Petri dish) (it has diameter 5cm) and then left to dry mixture, then taken from the template quietly to conducting the necessary tests, by using electronic digital device to measure thickness.

**Table 1.** Weight percentages for nanocomposites.

<table>
<thead>
<tr>
<th>Wight ratio of additive %</th>
<th>PS (gm)</th>
<th>(Cu) nanoparticles (gm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.5</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>0.47</td>
<td>0.03</td>
</tr>
<tr>
<td>4</td>
<td>0.44</td>
<td>0.06</td>
</tr>
<tr>
<td>6</td>
<td>0.41</td>
<td>0.09</td>
</tr>
</tbody>
</table>
3.2. Optical Properties Measurements

The absorption spectrum of (PS-Cu) nanocomposites have been recorded in the wavelength range (220-800) nm by using the double beam spectrophotometer (Shimadzu, UV-1800 Å). The absorption spectrum have been recorded at room temperature. A computer program was employed to obtain the optical constants, absorption coefficient, extinction coefficient, refractive index and energy gaps.

3.3. Copper (Cu) nanoparticles

Was obtained as powder from (Nano shell USA) company, with size (30 nm) and high purity (99.9%). Nanomaterial (Cu ) are tested by using the apparatus (Better size 2000 laser particle size analyzer) existed in Babylon University / College of Material Engineering, Department of Electro-Chemical.

4. RESULTS AND DISCUSSION

4.1. The Absorbance (A)

![Graph showing absorbance as a function of wavelength for PS-Cu nanocomposites.](image)

Figure 1. The absorbance as function of wavelength for (PS-Cu) nanocomposites.

Figure (1) shows the absorption spectrum of (PS-Cu) nanocomposites, as a function of the wavelength of the incident light. It can be noticed from the figure that the absorbance for all films have a high values at wavelength in the neighborhood of the fundamental absorption edge (200 nm), then the absorbance decreases with increasing of wavelength.

In general, the absorbance of films has low values in the visible and near infrared region. This behavior can be explained as follows: at high wavelength the incident photons
don’t have enough energy to interact with atoms, the photon will be transmitted. When the wavelength decreases, the interaction between incident photon and material will occur, and then the absorbance will increase [12]. In other words, the incident light is absorbed by the free electrons. Consequently, by the increase of the weight percentages of copper nanoparticles, absorbance is increased. These results are in agreement with Caixia Kan et al., in 2010 [13].

4.2. Absorption Coefficient ($\alpha$)

The absorption coefficient $\alpha$ (cm$^{-1}$) it can be seen that the absorption coefficient is the smallest at high wavelength and low energy; this means that the possibility of electron transition is little because the energy of the incident photon is not sufficient to move the electron from the valence band to the conduction band ($h\nu < E_{g}$) At high energies, absorption is bigger.

This means that a great possibility for electron transitions. Consequently, the energy of incident photon is enough to move the electron from the valence band to the Conduction band. The energy of the incident photon is greater than the forbidden energy gap [4]. This shows that the absorption coefficient assists in figuring out the nature of electron transition, when the values of the absorption coefficient are low ($\alpha < 10^4$) (cm$^{-1}$) at low energies, it is expected that indirect transition of electron occurs and the electronic momentum is maintained with the assistance of the phonon, among other results is that the coefficient of absorption for the (PS-Cu) nanocomposites is less than $(10^4$ cm$^{-1}$). These results are in agreement with Caixia Kan et al., in 2010 [13].

Figure 2. The absorption coefficient $\alpha$ (cm$^{-1}$) for (PS-Cu) nanocomposites as a function of wavelength (nm).
4. 3. Optical Energy Gaps of the (allowed and forbidden) Indirect Transition

Both the allowed and forbidden indirect transition band optical energy gap. When the value of \( r = 2 \), the allowed indirect transition band optical energy gap is calculated but when the value of \( r = 3 \), the forbidden indirect transition band optical energy gap. Figure (3) show the relation between absorption edge \((\alpha h\nu)^{1/2}\) for (PS-Cu) nanocomposites as a function of photon energy, on drawing straight line from the upper part of the curve toward the \((x)\) axis at the value \((\alpha h\nu)^{1/2} = 1\) we get the optical energy gap for the allowed indirect transition. We can see that the values of optical energy gap decrease with the increasing of the weight percentages of copper nanoparticles. This attributed to the creation of site levels in the forbidden optical energy gap, the transition in this case is conducted in two stages that involve the transition of electron from the valence band to the local levels to the conduction band as a result of increasing the copper nanoparticles weight percentage. This behavior is attributed to the fact that nanocomposites are of heterogeneous type (i.e. The electronic conduction depends on added concentration), the increase of the copper nanoparticles provides electronic paths in the polymer which facilitates the crossing of electron from the valance band to the conduction band, which explains the decrease of optical energy gap with the increase of the Cu nanoparticles. These results are in agreement with Suman Mahendra et al., in 2011 [14].

![Graph of optical energy gap for (PS-Cu) nanocomposites](image)

**Figure 3.** The optical energy gap for the allowed indirect transition \((\alpha h\nu)^{1/2}\) as a function of photon energy of (PS-Cu) nanocomposites

The forbidden transition of the indirect optical energy gap is calculated in the same way, that we obtain the allowed transition of the indirect optical energy gap for the (PS-Cu) nanocomposites. Figure (4) show the forbidden transition of the indirect optical energy gap for the (PS-Cu) nanocomposites.
Figure 4. The optical energy gap for the forbidden indirect transition \((\alpha h\nu)^{1/3}\) as a function of photon energy of (PS-Cu) nanocomposites.

Table 2. The values of energy gap for the allowed and forbidden indirect transition for (PS-Cu) nanocomposites.

<table>
<thead>
<tr>
<th>Nano Cu wt%</th>
<th>(E_g) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Allowed</td>
</tr>
<tr>
<td>0</td>
<td>3.3</td>
</tr>
<tr>
<td>3</td>
<td>2.7</td>
</tr>
<tr>
<td>6</td>
<td>2.3</td>
</tr>
<tr>
<td>9</td>
<td>2</td>
</tr>
</tbody>
</table>

### 4. 4. Extinction Coefficient\((k)\)

The change of the extinction coefficient as a function of the wavelength is shown in Figure (5) for (PS-Cu) nanocomposites. It can be noted that \((k)\) has low value at low concentration, but it increases with the increasing of the concentration of (Cu) nanoparticles. This is attributed to increase absorption coefficient with the increase of weight percentages of (Cu) nanoparticles.

Absorption coefficient has a direct relation with \((k)\). Figure (2) shows that before 300 (nm) the absorbance increases with increasing of wavelength, this is because of the presence of defects inside the structure where absorb this energy and organize the selves to stabilizing...
then after 300 (nm) the absorbance decreases with increasing of wavelength. These results are in agreement with M.H. Al-Humairi, in 2013 [12].

Figure 5. The extinction coefficient as a function of wavelength for (PS-Cu) nanocomposites.

4. 5. Real and Imaginary Part of Dielectric constant

Figure 6. The Real dielectric constant ($\varepsilon_1$) as a function of wavelength for (PS-Cu) nanocomposites

The real and imaginary complex dielectric constant ($\varepsilon_1$, $\varepsilon_2$) for (PS-Cu) nanocomposites. The Figure (6) show the change of ($\varepsilon_1$) as a function of the wavelength. It can be seen that ($\varepsilon_1$)
considerably depends on \((n^2)\) due to low value of \((k^2)\) so, the real dielectric constant increased with the increase of the concentrations of (Cu) nanoparticles and it is smallest at high wavelength. Figure (7) show the change of \((\varepsilon_2)\) as a function of the wavelength.

It can be seen that \((\varepsilon_2)\) is dependent on \((k)\) values that change with the change of the absorption coefficient due to the relation between \((\alpha)\) and \((k)\).

![Figure 7](image_url)

**Figure 7.** The imaginary dielectric constant \((\varepsilon_2)\) as a function of wavelength for (PS-Cu) nanocomposites.

### 4.6. Refractive Index

![Figure 8](image_url)

**Figure 8.** The refractive index \((n)\) as a function of wavelength for (PS-Cu) nanocomposites.
Figure (8) show the change of refraction index for (PS-Cu) nanocomposites as a function of wavelength. From this figure we can be noted that the refractive index increases with increasing the weight percentages of the concentration of (Cu) nanoparticles to (PS) films. The reason of this result is, the increase of the (Cu) concentration leads to increase the density of the nanocomposites. It can be seen that the refractive index is the smallest at high wavelength. These results are in agreement with Iviaeva et al., in 2010 [15].

5. CONCLUSIONS

1- The absorption coefficient increases with increasing of the filler wt % content.
2- The forbidden energy qap decreases with increasing of the wt % filler.
3- The extinction coefficient increases with increasing of the wt % filler.

References


(Received 02 November 2015; accepted 17 November 2015)