Effect of Mixing on the Optical Parameters of Polymer Blend (PMMA:PVC:PS) Thin Films

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Abstract. The thin films have been prepared using casting method at normal weather conditions of pressure and temperature. The films treated thermally for three hours at 45 °C. The UV-VIS double beam technique used to determine absorption and reflection spectrum. The thickness of the prepared thin films is measured using a handheld gauge of coating thickness measurement. Excel and MATLAB program used to calculate and simulate parameters and figures. The optical properties of PMMA:PVC:PS mixtures have been investigated. There is a clear change in the optical parameters due to mixing ratio. The result shows the indirect energy gap values reduced from 1.58 to 1.9 electron-volts. Mix a ratio of PMMA, PVC & PS leads to enhance some of the optical parameters like optical energy gap, absorbance, extinction coefficient and optical conductivity. The four kinds of thin films have different properties: The polymer blend (50%PMMA:25%PVC:25%PS) has the smallest values of the energy gap and linear refractive index, and the highest extinction coefficient values. The polymer blend (25%PMMA:25%PVC:50%PS) has a small value of energy gap and the best optical conductivity. The polymer blend (25%PMMA:50%PVC:25%PS) has the highest Urbach energy and absorption for the short wavelength (370 to 620 nm). The polymer blend (50%PVC:50%PS) has a good reflection, linear refractive index and skin depth, but it has the lowest values of extinction coefficient and optical conductivity.

1. Introduction
Polymers have been used traditionally not for their electronic properties, but because of their attractive chemical, mechanical and electrically insulating properties. Whatever, it is possible to control electrical conductivity of polymer over the range from insulating to highly conducting state [1]. Polymer mixing is the simplest technique (and effective method) in polymer engineering for creating new solid materials with more enhanced properties [2, 3]. The determination optical constants of polymers are important for various optical applications such as in solar cells, polymer-based light-emitting diodes, light electrochemical cells and design of optical systems [4-6]. There are several methods used to determine the optical constants of polymer films like transmission spectra, external reflection spectra or internal reflection spectra [7, 8]. Because of the importance and widespread use of polymers, there are many studies to improve some of their optical and electrical properties [9, 10]. Mix polymers or addition of some salts to polymers lead to change some optical and physical properties, such as doping the Polystyrene (PS) with KPF6 salt lead to decrease electronic transition and indirect energy gap [11], doping Polyvinyl-chloride (PVC) with DCM dye decreases energy gap and change the values of optical constants [12]; and by increasing the concentration of PMMA in the blend of polymethyl-methacrylate (PMMA)/ Polyvinyl acetate (PVA), the energy gap values increased and the refractive index values reduced [13]. In this work we selected three types of polymers (PVC, PS & PMMA) for their distinctive properties and their extensive use in our daily life. Our aim of this work is to study the optical properties of these thin films. This work investigated the effect of different
blending ratio of three polymeric materials, thermoplastics (PMMA:PVC:PS) on the optical properties of the blend. Furthermore, it could be interested to the researchers and technologists who work in optical applications.

2. Procedure

2.1. Preparation
The different weights of PVC, PS & PMMA (CDH Laboratory Chemicals) have mixed together as shown in the table below. The samples weighted using sensitive balance (four digits). Every mixture dissolved separately by 15ml of Tetrahydrofuran (BDH Chemicals Limited) in a glass beaker. The orifice of the beaker was tightly closed to prevent the volatilization of the solution. Then, the solution stirred using magnetic heater stirrer for 2-3 hours. The resultant solution is cast on a glass substrate and left to dry under normal weather conditions. Then samples placed in the oven at 45 °C for 3.5 hours.

Table 1. Mixing Ratio of prepared films

| No. | PMMA (gm) | PVC (gm) | PS (gm) | Symbol |
|-----|-----------|----------|---------|--------|
| 1   | 0.50      | 0.25     | 0.25    | S1     |
| 2   | 0.25      | 0.25     | 0.50    | S2     |
| 3   | 0.25      | 0.50     | 0.25    | S3     |
| 4   | 0         | 0.50     | 0.50    | S4     |

2.2. Measurements
The thickness of the prepared thin films is measured using a handheld gauge of coating thickness measurement. Absorption and reflection spectrum of prepared films have been tested using the UV double-beam spectrophotometer (PG instrument model T80) with bandwidth 190-1100 nm. The absorption coefficient is calculated using the equation [14]:

\[ \alpha = \frac{2.303A}{d} \]

where A is the value of absorption and d is the thickness of films.

The indirect allowed and forbidden transitions happen with helpful of like-particle called phonon. The value of optical energy gap \( (E_g) \) for this transmission type is calculated using the equation [15]:

\[ \alpha E = B(E - E_g \pm E_{ph})^r \]

where B- proportional constant depend on the type of material, \( E \)- the photon energy and \( E_{ph} \)-phonon energy. The sign is (+) for phonon absorption and (-) for phonon emission, for allowed indirect transition used \( r = 2 \).

Near the optical absorption edge, the relationship between absorption coefficient (\( \alpha \)) and photon energy (\( h\nu \)) is known as Urbach empirical rule, which is given by the following equation [16,17]:

\[ \alpha = \alpha_0 \exp\left(\frac{h\nu - E_0}{E_U}\right) \]

where \( \alpha_0 \) and \( E_0 \) are the coordinates of the convergence point of the Urbach “bundle”, \( E_U \) is the Urbach energy. We can calculate Urbach energy according to equation (3) by plotting between ln(\( \alpha \)) and photon energy (\( h\nu \)), then by taking reciprocal of the slope of obtained straight lines, we can find the value of Urbach energy \( E_U \), where \( E_U = \Delta(h\nu)/\Delta\ln(\alpha) \).

The values of absorption (A) and reflectance (R) are determined by UV-Visible double beam spectrophotometer. The relation between refractive index and reflectance is given by equation [18,19]:

\[ \text{Refractive Index} = \frac{1}{1 - R} \]
\[ R = \frac{(n - 1)^2 + k^2}{(n + 1)^2 + k^2} \]  
\[ \text{When } (n - 1)^2 \gg k^2, \quad R = \frac{(n-1)^2}{(n+1)^2} \]  
The refractive index determined by the formula [20]:  
\[ n = \frac{1 + \sqrt{R}}{1 - \sqrt{R}} \]  
The extinction coefficient \( k \) is calculated by equation [21]:  
\[ k = \frac{\alpha \lambda}{4\pi} \]  
The optical conductivity is calculated by equation [22]:  
\[ \sigma = \frac{\alpha n c}{4\pi} \]

Where \( \sigma \) - optical conductivity and \( c \) - speed of light.

3. Results and discussion

Study the optical properties of polymer blend PMMA:PVC:PS thin films are important to understand the optoelectronic nature [23,24]. These properties can be explicated, in the view of the interaction between the thin films particles and the incident photons. Optical absorption study is a simple way to obtain band gap energy and explain the structure of polymeric materials [17]. Our optical investigation and discussions of ternary PMMA:PVC:PS thin films based on absorbance and reflectance measurements in the spectral range 370 - 900 nm.

In this section we will determine the absorption coefficient (\( \alpha \)), optical energy gap (\( E_g \)), Urbach energy (\( E_u \)), optical constants (\( n \) and \( k \)), skin depth (\( \delta \)) and optical conductivity (\( \sigma \)).

Absorption, transmission and reflection spectra: The absorbance and the reflectance for the wavelength range (370-900 nm) shown in Figure 1.

The figure shown the highest absorption values of the polymer blend (25%PMMA:50%PVC:25%PS) for the short range. The highest reflection of the polymer blend (50%PVC:50%PS) and the lowest reflection of the polymer blend (50%PMMA:25%PVC:25%PS). It is obvious that these spectra could be divided into two regions:

1. The high absorption region, which lies between about 370 nm \( \leq \lambda \leq 600 \text{ nm} \)
2. The high reflection and permeability region, which is the region of wavelength \( \lambda \geq 600 \text{ nm} \).

Figure 2 shows how the optical absorption coefficient of four films prepared under same conditions the absorption edge is shifted toward the lower energies as PMMA increased. In addition, the absorption coefficient increases with increasing PMMA concentration overall spectral range. The result corresponds to R.M. Ahmed "the intensity of absorption peak has increased by increasing the concentration of PMMA in the blend" [13].

![Figure 2](image.png)

The figure shows a change in electronic transitions due to mixing. The type of transition is indirect, while there are direct transitions in the range (2.5_3.25 eV) in the sample (50% PMMA: 25% PVC: 25% PS) only.

Figure (3) shows the relation between values \((\alpha E)^2\) and incident photon energy, which used to determine energy gap values for indirect-allowed transitions. The results indicate that the lowest value of the energy gap of the polymer blend (50%PMMA:25%PVC:25%PS) is 1.58 electron-volts and the highest value of the polymer blend (50%PVC:50%PS) is 1.9 electron-volts. That’s mean increase in PMMA ratio reduce the optical energy gap this is agreement with I.S. Elashmawi and N.A. Hakeem’s result “Optical absorption spectra suggested the presence of an optical gap (Eg) which decreased with increasing PMMA content” [25].
Determination of Urbach Energy: Franz Urbach was the first to observe experimentally an exponential increase of absorption coefficient with the photon energy [26]. Further research showed that the empirical regularity developed by Urbach for direct-gap and indirect-gap semiconductors and a variety of crystalline and amorphous materials [27,28]. For amorphous materials (contrary to crystals) the absorption edge is smeared more away and the temperature dependence of the absorption edge slope is less pronounced, see equation (3) [16].

The obtained values of Urbach energy were tabulated in Table 2. It is observed that the values of $E_U$ were increased from 2.27 to 3.45 meV; where highest value of composite (25% PMMA: 50% PVC: 25% PS), so this result hasn’t agree with R. M. Ahmed [13].

The skin depth of PMMA thin films: There are some important parameters which related to the photons absorption of thin films, e.g. skin effect or skin thickness. Skin depth ($\delta$) depends also on the energy of incident photons and the conductivity of thin films, so one can correlate skin effect and the
optical properties in any material [27]. The relation between skin depth (or skin effect) and absorption coefficient ($\alpha$) is [28]:

$$\delta = \frac{1}{\alpha} \quad (9)$$

Figure 5. Dependence skin depth upon wavelength for polymer blends PMMA: PVC: PS

The skin depth ($\delta$) values were calculated for the samples using equation (8). The variation in $\delta$ with the wavelength is shown in figure 5. According to figure 5, the value of $\delta$ increased as the wavelength increased in the visible region. In another side decreased from 2000 nm to 1000 nm by increasing PMMA ratio. From figures (1&5) the skin depth is reflectance related, other than predicted by the researchers W.A. Al-Taa'y et al [31].

Extinction coefficient and refractive index: The relation between extinction coefficient and wavelength as shown in figure (5) shows that the lowest values of extinction coefficient for the polymer blend (50%PVC:50%PS). The highest values of extinction coefficient for the polymer blend (50%PMMA:25%PVC:25%PS). From the result its clear increase polymer PMMA ratio in the composite lead to increase values of extinction coefficient ($k$).

Figure 6. Extinction coefficient as a function of wavelength
The refractive index is an important property for polymeric materials, especially for materials that used in the fabrication of optical devices, like modulation and filters. To determination, the refractive index can be used equation (5).

From figure 4 we observe a change in the refractive index. The highest refractive index values of the polymer blend (50%PVC:50%PS) and its values immediately increase with increasing wavelength. The high refractive index values due to two reasons: thermal annealing and blending of materials [32-34 ].

Optical conductivity: Laboratory results indicate that increasing the ratio of PS in the polymer blend leads to higher values of the optical conductivity. In another side, the optical conductivity decreases with increasing incident photon energy, see figure 8. The best optical conductivity was for the polymer blend (25%PMMA:25%PVC:50%PS) among the prepared thin films.

![Figure 7. Refractive index as a function of wavelength](image1)

![Figure 8. Optical conductivity as a function of photon energy](image2)
Table 2. The indirect optical energy gap, Urbach energy, skin depth, refractive index and optical conductivity of non-crystalline thin films of PMMA:PVC:PS

| Symbol | Matrix of PMMA:PVC:PS | Optical energy gap Eg (eV) | Urbach Energy EU (meV) | Skin depth δ (cm) | Refractive index in average (n) | Optical conductivity \( \times 10^{14} \) |
|--------|------------------------|---------------------------|------------------------|-------------------|-------------------------------|----------------------------------|
| S1     | 50%PMMA:25%PVC:25%PS   | 1.58                      | 2.27                   | 1200              | 2                             | 3.88                             |
| S2     | 25%PMMA:25%PVC:50%PS   | 1.62                      | 2.50                   | 1350              | 2.1                           | 4.6                              |
| S3     | 25%PMMA:50%PVC:25%PS   | 1.75                      | 3.45                   | 1650              | 2.35                          | 2.99                             |
| S4     | 50%PVC:50%PS           | 1.9                       | 2.47                   | 2250              | 4.15                          | 4.35                             |

4. Conclusions
Three kinds of popular polymers are mixed with different ratios. Change a ratio of one of them lead to enhance some of the optical properties. The polymer blend (50%PVC:50%PS) has a good reflection and linear refractive index. Increase the ratio of PMMA to 50% in the blend leads to enhance the energy gap and extinction coefficient, and increase the ratio of PS to 50% leads to improve the energy gap and optical conductivity while increase the ratio of PVC leads to 50% leads to improve the absorbance in the range wavelength (370 to 620 nm).

5. References

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