A study on optical absorption and constants of doped poly(ethylene oxide)

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1. Introduction

Polymer composites and polymer electrolytes are the most widely used materials in the past few decades. Understanding their properties is extremely important not only for scientific knowledge but also for modern and advanced technological applications. Most polymeric materials are poor conductors of electricity because of the unavailability of large number of free electrons or ions to participate in the conduction process, so a great attention has been focused on enhancing their electrical conduction and improving their properties. In order to promote optical, thermal, and electrical properties to polymeric systems, many different materials have been developed as conducting polymers electrolytes and polymer composites [1–6].

One important aspect of these characteristics is the transition from insulating to conductive behavior by adding some conducting or electrolytic substances. Many studies have shown that the physical behavior of polymer/electrolytes depends on the filler type or structure and the method of composite preparation. Understanding the chemical and physical nature of the composites structure helps greatly to evaluate and interpret the conduction mechanism taking place in the composites bulk. Space charge limited current can be suggested to explain the charge transfer in polymers in addition to ionic conduction dominated by the amorphous phase in the polymer matrix [7–10].

Solid polymer electrolytes (SPE) are promising materials for electrochemical device applications. Nowadays they are successfully used in high energy density rechargeable batteries, full cells integrated optical devices, and electrochromic displays [5,6]. Sodium iodide is a white, crystalline salt with good properties and high luminescence efficiency. It is used in radiation detection, treatment of iodine deficiency, nuclear medicine, and in many other applications, such as X-ray detectors with high spectroscopic quality.

The physical characterization of solid films of polymer electrolyte can be carried out using a variety of analytical techniques such as impedance, X-ray diffraction, and UV-spectroscopy. Polymer electrolytes with low NaI concentration were prepared for the purpose of percolation detection or anomalous behavior in the electrical conductivity as we have recently reported in PEO/I2 polymer electrolyte with very low I2 content less than 0.5 wt% [14]. In the present study, thin films of PEO doped with sodium iodide were prepared with different concentrations: 0%, 1%, 2%, 4%, 6%, 8%, 10%, and 15% by weight. Optical and dielectric constants of those films will be determined under different UV-radiation wavelengths and sodium iodide concentrations.

2. Experimental work

2.1. Composites films preparation

Poly(ethylene oxide) with average molecular weight of 300,000 g/mol was used to prepare electrolyte films by casting...
from solution. Poly(ethylene oxide) powder and solid sodium iodine were mixed together and dissolved in methanol as a suitable solvent. The solution was then stirred continuously by a rotary magnet at room temperature for a few hours. The stirring process lasted until the mixture reached a homogeneous viscous molten state. The mixture was immediately cast to thin films on a glass plate, and the methanol was allowed to evaporate completely at room temperature and under atmospheric pressure for a few days. The composite films were dried in an oven at 40 °C for 2 days. The films obtained have thicknesses of about 70 μm and sodium iodide concentrations of 0%, 1%, 2%, 4%, 6%, 8%, 10%, and 15% by weight.

2.2. Optical measurements

One of the most direct and simplest methods for probing the band structure of materials is studying their absorption spectra. In the absorption process, a photon of known energy excites an electron from a lower energy state to a higher one. By analyzing the radiation spectra, we can understand the transition mechanism. The fundamental absorption manifests itself by a rapid rise in absorption, known as the absorption edge. This can be used to determine the optical energy gap and the type of transition [13,15]. Absorption is expressed in terms of the coefficient \(\alpha\), which is defined as the relative decrease rate in light intensity. Using a UV-spectrophotometer, the optical absorbance of valence band, electrons will be transferred from the valence band to conduction band. At high absorption coefficient levels, if the required energy is almost equal to the difference of photon absorbed is higher than or equal to the forbidden energy gap. If the required energy is almost equal to the difference between the lowest level of conduction band and the highest level of valence band, electrons will be transferred from the valence band to conduction band. At high absorption coefficient levels, where \(\alpha(\omega) > 10^4 \text{ cm}^{-1}\), the absorption coefficient \(\alpha\) for non-crystalline materials can be related to the energy of incident photon energy (\(h\nu\)) according to the formula:

\[
\alpha(\omega) = B(h\nu - E_{opt})^r
\]

where \(B\) is a constant, \(E_{opt}\) is the optical energy gap, and the exponent \(r\) is an index determined by the type of electronic transition causing the optical absorption and can take values 1/2, 3/2 for direct and 2, 3 for indirect transitions [15–17].

Figs. 1 and 2 illustrate the absorption and reflectance spectra of PEO/NaI composites with NaI content of 1, 2, 4, 6, 8, 10, and 15 wt%. It is clearly shown that absorption decreases rapidly with increasing wavelength up to 400 nm. Fig. 3 shows graphs of the product of absorption coefficient (\(\alpha\)) and photon energy (\(h\nu\)) versus photon energy (\(h\nu\)) at room temperature. The drawn straight lines obtained with \(r = 1/2\) indicate that the electron transition is direct in \(k\)-space. Extrapolation of the linear portion of these curves gives the value of optical energy gap (\(E_{opt}\)).

3. Results and discussion

The absorption coefficient \(\alpha(\omega)\) was obtained from the absorbance \(A\). After correction for reflection, \(\alpha(\omega)\) can be calculated using the Beer Lambert’s formula [12,13]

\[
I = I_0 \exp(-\alpha x)
\]

Hence

\[
\alpha(\omega) = \frac{2.303}{x} \log \left(\frac{I_0}{I}\right) = \frac{2.303}{x} A(\omega)
\]

where \(x\) is the sample thickness; \(I_0\) and \(I\) are the incident and transmitted intensities, respectively [12–15]. The refractive index can be obtained from

\[
n = \left( \frac{4R}{(R-1)^2 - k^2} \right)^{1/2} \frac{R+1}{R-1}
\]

where \(k\) is the extinction coefficient, which is related to the absorption coefficient and wavelength by

\[
k = \frac{2\lambda}{4\pi}
\]

The dielectric constant \((\varepsilon)\) and dielectric loss \((\varepsilon')\) are calculated from the relations [13]:

\[
\varepsilon' = n^2 - k^2, \quad \varepsilon'' = 2nk
\]

Solids absorb an amount of the incident light of intensity \(I_0\), and consequently optical transitions start when the energy of photon absorbed is higher than or equal to the forbidden energy gap. If the required energy is almost equal to the difference between the lowest level of conduction band and the highest level of valence band, electrons will be transferred from the valence band to conduction band. At high absorption coefficient levels, where \(\alpha(\omega) > 10^4 \text{ cm}^{-1}\), the absorption coefficient \(\alpha\) for non-crystalline materials can be related to the energy of incident photon energy (\(h\nu\)) according to the formula:

\[
\alpha(\omega) = B(h\nu - E_{opt})^r
\]

where \(B\) is a constant, \(E_{opt}\) is the optical energy gap, and the exponent \(r\) is an index determined by the type of electronic transition causing the optical absorption and can take values 1/2, 3/2 for direct and 2, 3 for indirect transitions [15–17].

Figs. 1 and 2 illustrate the absorption and reflectance spectra of PEO composites with NaI content of 1, 2, 4, 6, 8, 10, and 15 wt%.
Table 1 includes determined values of \(E_{\text{opt}}\), which decrease with increasing NaI content from 2.6 eV for pure PEO to 2.36 eV for 15 wt% composite. At lower absorption coefficient level, in the range of \(1–10^4 \text{cm}^{-1}\), \(\alpha(\omega)\) is described by the Urbach formula [16]

\[
\alpha(\omega) = \alpha_0 \exp(h\omega/\Delta E)
\]  

(7)

where \(\alpha_0\) is a constant and \(\Delta E\) is the energy gap tail interpreted as the width of the tails of localized states in the forbidden band gap [13,18]. Fig. 4 presents the Urbach plots for the composite films. The extrapolated (\(\Delta E\)) values listed in Table 1 were determined from the slope reciprocal of the linear part of each curve and Eq. (7) as

\[
\ln(\alpha) = h/\Delta E + \ln(\alpha_0)
\]

(8)

The exponential dependence of \(\alpha(\omega)\) on photon energy \((h\omega)\) indicates that the absorption processes taking place in the studied films obey the Urbach rule. These energy tails become smaller as
the concentration of NaI salt particles in the PEO matrix was reported.
Fig. 6. Dielectric constant ($\varepsilon'$) versus wavelength.

Fig. 7. Dielectric loss ($\varepsilon''$) versus wavelength.

Fig. 8. Dependence of refractive index on NaI concentrations.
in many researches [7,10,11]. Liu et al. [19] fitted a modeling relation between the dielectric constant and filler content based on the effective-medium theory (EMT), which relates the inter-phase between particles, polymer matrix, and composite morphology. The EMT model is expressed in the form of Rao equation [5,8] as

\[
\varepsilon = \varepsilon_1 \left[ 1 + \frac{\varepsilon_2 - \varepsilon_1}{\varepsilon_1 + n(1-\varepsilon_2)(\varepsilon_2 - \varepsilon_1)} \right]
\]  

(9)

where \(\varepsilon, \varepsilon_1,\) and \(\varepsilon_2\) are the dielectric constant of composite, PEO matrix, and discrete fillers, respectively, \(\nu_1\) and \(\nu_2\) are the volume fraction of continuous matrix and discrete fillers, and \(n\) is a factor related to the morphology of filled particles. Fig. 9 shows the fit of the EMT model of Eq. (9) to our PEO/NaI composites prepared via the casting method. The model fit predicts properly the increase of the dielectric constant \(\varepsilon_0\) of PEO/NaI composites with increasing filler concentrations, especially at lower NaI filler concentrations.

The refractive index, \(n\), of the PEO/NaI thin films is found to decrease with increase in the wavelength of incident photon, and tends to be constant at high wavelengths as shown in Fig. 5.
The dispersion of refractive index below the inter-band absorption edge according to the Wemple–DiDomenico single oscillator model [20–23] is given as

\[ n^2 = 1 + \frac{E_0E_d}{E_0^2 - (h\nu)^2} \]  

where \( E_0 \) is the average excitation energy for electronic transitions, \( E_d \) is the dispersion energy, which is a measure of the strength of inter-band optical transitions, \( h \) is Planck’s constant, \( \nu \) is the frequency, and \( h\nu \) is the photon energy. \( E_0 \) and \( E_d \) values were calculated from the slope and intercept \( (E_0/E_d) \) on the vertical axis of plot of \( 1/(n^2 - 1) \) versus \( (h\nu)^2 \) (Fig. 10). The values of \( E_0 \) and \( E_d \) for the PEO/Nal composites are given in Table 2. Although \( E_d \) values increase with increasing Nal concentration, \( E_0 \) values tend to decrease.

4. Conclusion

In this work, polymer electrolyte thin films of PEO/Nal have been prepared by the casting method. The films contain Nal electrolyte component as a filler at different concentrations of 0%, 1%, 2%, 4%, 6%, 8%, 10%, and 15% by weight. Optical quantities such as absorption coefficient, optical energy gap, energy tails, refractive index, and dielectric constants were determined from analysis of the absorbance and reflectance of UV-radiation spectra. From the optical results obtained it was found that the electron transition is direct in \( k \)-space and the optical energy gap decreases with increasing sodium iodide concentration. The observed dielectric constant and the refractive index increase with Nal content. The fit of the EMT model on the variation of the dielectric constant with the electrolyte content is, in general, acceptable.

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References