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Electrothermal and Optical Properties of Hybrid Polymer Composites

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The Electrothermal and optical properties of hybrid polymer composites made of poly (ethylene oxide) (PEO) matrix filled with different zinc oxide (ZnO) concentrations (0, 2, 4, 6 and 12 wt %), and strengthened with iodine (0.1 wt %) have been investigated. The electrical properties have been studied using the impedance technique as a function of ZnO concentrations, applied frequency ranges from 10 KHz to 3 MHz, and temperature in range (25-55 °C). The AC electrical properties showed frequency, temperature, and zinc oxide dependence. It was found that with increasing the ZnO concentration and with decreasing the applied frequency the dielectric loss and dielectric constant will be increased. The determined activation energy decreases with increasing the ZnO content and iodine charge complexes. The thermal conductivity has been studied, and it was found that the thermal conductivity increases with both ZnO concentration and temperature. The optical properties have been examined as a function of ZnO concentration, and applied UV-wavelength ranges from 300 to 800 nm. The determined optical dispersion parameters, such as the optical energy and refractive index are discussed.

Keywords: Polymer, ZnO, Iodine, Impedance, Electrical, Thermal, Activation energy, Optical constants.

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1. INTRODUCTION

The electrical, thermal, and optical properties of polymeric composites have been of great interests from both fundamental and practical purpose. The conductive polymer composites can be controlled by selecting the types of filling components and concentrations for improving characteristics to suit a certain technical and commercial applications [1-3]. Among these fillers is the zinc oxide (ZnO) which has prominent physical properties, Due to these properties , it has high potential applications in optical and thermo-electronic industries [4-7].

Iodine that acts as oxidized agent produces a free positive charges on the polymer chains which are suggested to form charge transfer complexes in the polymer matrix, which in turn facilitate the electrical energy transport in the composite bulk [8]. Poly (ethylene oxide) (PEO) is a semicrystalline homopolymer with general formula (-H2C-O-CH2-)n and melting temperature of about 65 °C. and it has a wide range of applications [9].

In this research, the optoelectrical and thermal properties of hybrid PEO composites have been investigated as a function of filler concentrations, applied field frequency in the range from 10 to 3 MHz and temperature range from 30 °C to 55 °C, i.e., less than the melting temperature of PEO polymer. We study the effects of ZnO and Iodine dopants on the optical properties of PEO prepared composites as a function of zinc oxide concentration by using UV-spectrophotometer in the spectral wavelength range from 300 nm to 800 nm.

2. EXPERIMENTAL WORK

2.1 Thin Films Composite Preparation

Poly (ethylene oxide) powder (average molecular weight is 300,000 g/mol) was dissolved in methanol as a suitable solvent. Zinc oxide ZnO (molecular weight: 81.38), and 0.1 wt.% iodine were added to the solution. Then at room temperature and for one day, dissolved system was continuously stirred by a rotary magnet until the mixture reached a homogeneous viscous molten state and rapidly was casted on a glass plate as thin films. The methanol will be evaporating completely under atmospheric pressure and at room temperature for two days. The composite films are fully dried using an oven at 40 °C for one day. The films obtained contain different ZnO concentrations (0, 2, 4, 6 and 12 wt.%) by weight. This procedure provided thin films of 70 μm thickness measured by a sensitive digital caliper at 5 different places chosen randomly. The observed morphology of the produced thin films has a transparent and homogeneous feature with good dopants distribution.

2.2 AC-Electrical Measurements

Measurements of Ac-electrical properties were carried out by the Hewlett Packard (HP) 4192A impedance analyzer. The test samples were carefully placed between copper electrodes in the sample holder. These electrodes were connected to the impedance analyzer by cables. Impedance measurements were taken in a frequency range from 300 kHz to 3 MHz and over a range of temperature (30-55 ºC). The reason for taking this range is not reach the temperature of 60 ºC where the PEO polymer begins

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to melt. In order to study the temperature effect on the Ac-electrical properties, the sample holder was placed inside an oven chamber. Temperature readings can be taken accurately through a thermocouple in addition to the Temperature readings from the oven dial.

2.3 Thermal Conductivity Measurements

Measuring the thermal conductivity (*k*) of polymers is very difficult since their values (*k*) is too small in the range of (0.21-0.4 W/m·K) [10]. Thermal conductivity measurements were carried out using the heat pulse method, which is based on the transmission of electrical pulse through double test samples separated by a current coil placed inside the sample holder connected to thermocouples for temperature measurements.

The cell assembly which is insulated to reduce the heat loss is placed in an oven. Temperature readings were taken every half hour to reach the steady state of thermal equilibrium. The quasi-steady-state temperature difference (ΔT) was found to be identical for the thermocouple pairs on one side, and to those on the other side. This means that the heats flux have symmetry on both sides.

2.4 Optical Measurements

The determined physical quantities in the present paper were calculated from equations and models reported in numerous research reports [11]. The optical absorption spectra of all prepared composites thin films were measured at room temperature, by using UV-VIS (a Cary) spectrophotometer with wavelength range from 300 nm to 800 nm.

3. RESULTS AND DISCUSSION

3.1 AC-Electrical Result

Figure (1) shows the variation of the AC-impedance per unit thickness as a function of frequency at room temperature for the prepared PEO composites. In general, this figure shows that the impedance decreases with increasing frequency. At low frequency, impedance had high values, that mean more resistive behavior, due to electrode polarization and space charge effects occur in composites bulk [12]. The dielectric constant (real part of the permittivity) is a measure of the amount of energy stored in the dielectric due to applied electric field, and the dielectric loss (imaginary part) is measure of an amount of energy dissipated in the dielectric due to applied electric field [13].

Figure (2) shows the variation of the dielectric constant with ZnO concentration measured at different frequencies. The dielectric constant decrease with increasing the applied frequency, while it increases from about 3 for pure PEO to a value 9, with increasing the ZnO content up to 12 wt. % measured at frequency 200 kHz. The decrease in dielectric permittivity with increasing frequency may be associated to the inability of the polymeric dipoles to spin rapidly resulting in a lag between the oscillating dipole frequency and that of the applied field [14]. The enhancement in dielectric constant value with ZnO concentration is mainly due to electronic contribution. The dielectric loss decreased with increasing the frequency and due to high periodic reversal of the field at the specimen/electrodes interface. Both the dielectric loss and dielectric constant decrease with increasing frequency indicating a normal dispersion behavior of dielectric composites having mobile charge carriers [15].

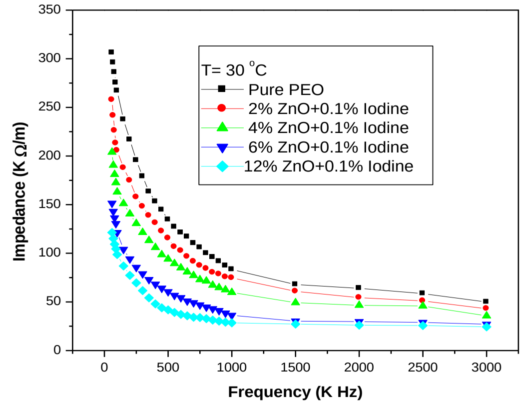

Fig. 1 – Impedance versus frequency for PEO/ZnO composites

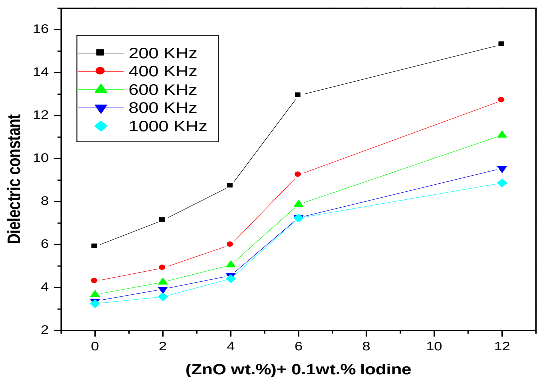

Fig. 2 – Variation of dielectric constant with ZnO concentrations

Figure (3) shows the variation of AC electrical conductivity with ZnO filler concentration. The increase in AC conductivity was observed as a function of filler content at different applied frequencies which means that PEO composites become less resistive with increasing the conducting filler content. The AC conductivity is increases with increasing the ZnO concentration. This increase in Ac conductivity may relate to space charge polarization, electron mobility, and iodine charge complexes [16].

The values of activation energy were calculated from the slopes of the best straight lines fit obtained by plotting the natural logarithm of the ac-conductivity versus the reciprocal temperature for each PEO thin films at the applied frequencies. Figure (4) shows that the activation value decreases with increasing the ZnO concentration in a thermally activated process, which is consistent with the observed increase in the Ac conductivity shown in Figure 3, that means the prepared PEO films become more conductive. The observed decrease in the activation energy values with increasing the ZnO content can be dominated by electrons hoping to the localized states [17].

3.2 Thermal Results

The thermal conductivity for the prepared PEO composites was measured in temperature range from 25 °C to 55 °C. Figure (5) shows the thermal conductivity for PEO composites, it can be seen that the thermal conductivity increases slightly with increasing temperature. Thermal conductivity in general will have observed enhancement, mainly due to the heat transferred by photons, electrons and impurities during the thermal process. Part of the thermal enhancement may be due to compactness provided by increasing the dopant concentration which increases the heat transfer through phonons diffusion [18].

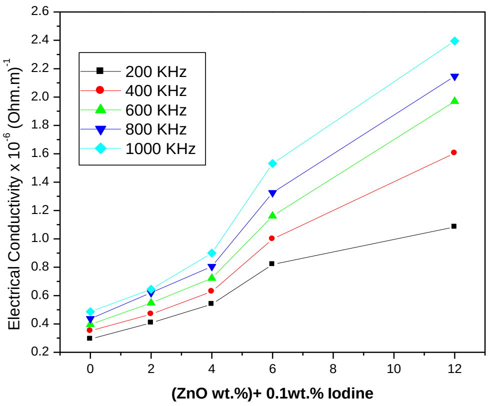

Fig. 3 – Variation of AC conductivity with ZnO concentrations

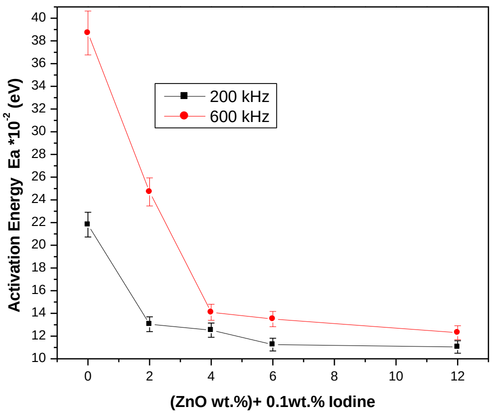

Fig. 4 – Variation of E_a with ZnO content

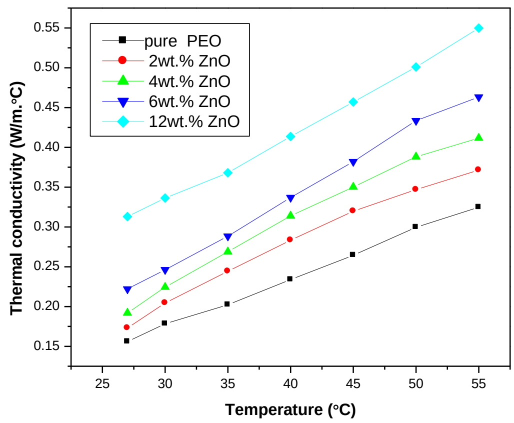

Fig. 5 – Variation of thermal conductivity with temperature for PEO/ZnO composite

Table (1) includes the observed values of the measured thermal conductivity (k) for the composites, k is about 0.156 (W/m·°C) for PEO polymer and increases to about of 0.313 (W/m·°C) for 12 wt.% ZnO concentration. Thus the dopants ZnO and iodine fillers have large effect in enhancement the thermal conduction of the prepared thin films [19].

Table 1 – Results correlation between the electrical and thermal conductivities

PEO thin films	Thermal conductivity (k) (W/m·°C)	Electrical conductivity × 10^{-6} (Ohm·m)$^{-1}$
Pure PEO	0.156	0.434
2 wt.% ZnO/0.1 wt.% iodine	0.173	0.585
4 wt.% ZnO/0.1 wt.% iodine	0.192	0.789
6 wt.% ZnO/0.1 wt.% iodine	0.222	1.26
12 wt.% ZnO/0.1 wt.% iodine	0.313	2.26

Table (1) also shows a comparison between the electrical and thermal conductivities behavior of the prepared thin films as a function of ZnO content. Both the electrical conductivity and thermal conductivity increase with increasing the dispersed ZnO phase in the PEO matrix.

Lorenz number is a thermo-electrical parameter characterizing the effect of temperature on both the thermal and electrical conductivities of a solid that links the electrical conductivity and the thermal conductivity (k). Figure 6 shows the variations of Lorenz number with fillers concentration, it can be seen that the Lorenz number increases with increasing ZnO concentration. The increase of the Lorenz number refers to the difference in the rates of increasing of ac electrical and thermal conductivities with the filler content.

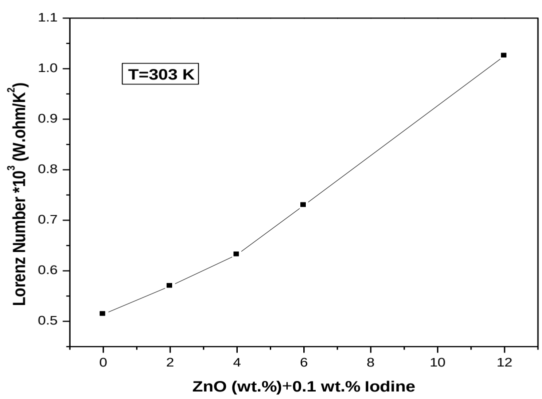

Fig. 6 – Variation of Lorenz number with ZnO concentration

3.3 Optical Results

Figure 7 shows the UV-visible absorption spectra of PEO composites at room temperature. It can be noted that the optical absorption is increasing in composites when the concentration of the ZnO increases, and decreases rapidly with increasing the incident photon wavelength. Absorption coefficient ($\alpha\omega$) for non-crystalline composites can be indentified with to the incident photon energy ($\hbar\omega$) according to Tauc relation [20]. The optical energy gaps were calculated by plotted Tauc plot between $(\alpha\hbar\omega)^2$ and $(\hbar\omega)$ as shown in figure 8. Extrapolation of the linear part of these curves gives the optical energy gap. The values of optical band gap are shown in Figure 9. From the graph, it is seen that the optical energy gap decreases with increasing the ZnO concentration complexes by (0.1 wt.%) iodine.

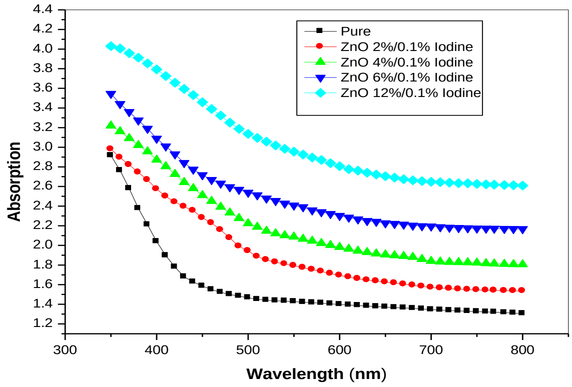

Fig. 7 – The absorption spectra for the PEO/ZnO/0.1 wt.% iodine thin films

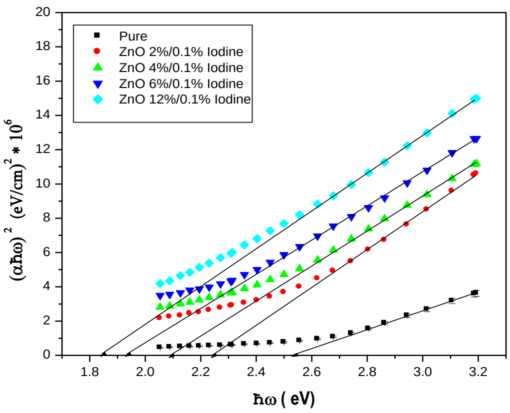

Fig. 8 – Plots of $(\alpha\hbar\omega)^2$ vs. $\hbar\omega$ for the PEO/ZnO/0.1 wt.% iodine thin films

Optical band gap determines the threshold for the photons absorption [21]. The decrease in the value of the optical energy gap indicates enhancement in the semiconducting level of the PEO thin films with increasing the ZnO concentration and formation the iodine charge complexes. As shown in table (2).

The refractive index obtained from the refraction value and the extinction coefficient related to the absorption coefficient and the wavelength [22]. It seen that the extinction coefficient increases with increasing the wavelength.

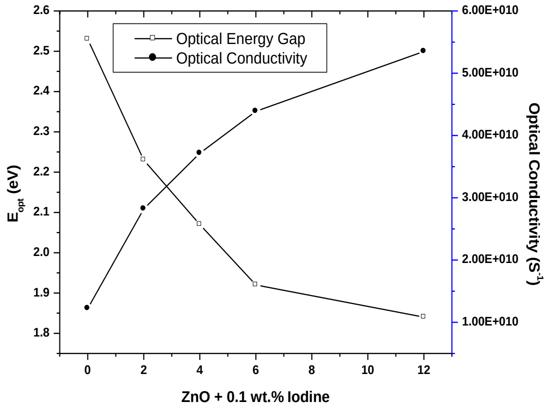

Fig. 9 – A correlation between the observed optical energy gap and conductivity as a filler concentration for the PEO/ZnO/0.1 wt.% iodine thin films.

Table 2 – Optical values of PEO/ZnO thin films doped with Iodine

PEO thin films	Optical band gap (eV)
Pure PEO	2.53
2 wt.% ZnO/0.1 wt.% iodine	2.23
4 wt.% ZnO/0.1 wt.% iodine	2.07
6 wt.% ZnO/0.1 wt.% iodine	1.92
12 wt.% ZnO/0.1 wt.% iodine	1.84

Figure 10 shows the variation of the refractive index for PEO thin films with wavelength for different ZnO concentrations. It is seen that the refractive index decreases with increasing the applied wavelength and ranges from 2.7 to 4.2 for pure PEO and 12 wt.% respectively at wavelength 350 nm.

The optical conductivity [23] is one of the tools for investigating the electronic states in composites. If an external electric field applied on the system then, the currents are induced and a redistribution of charges occurs. For minimum enough fields, the induced currents and the induced polarization are proportional to the inducing field. It is found that the optical conductivity increases with decreasing the ZnO concentration [10, 24].

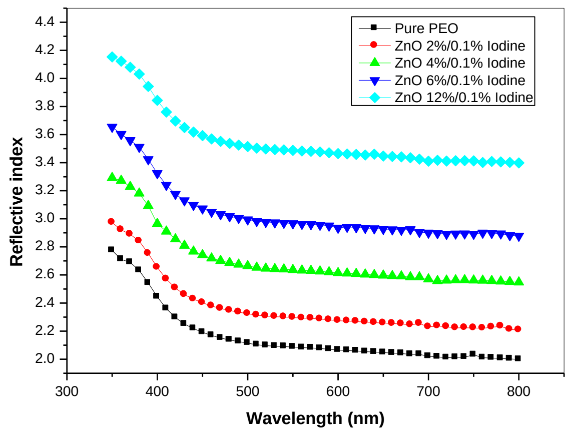

Fig. 10 – The variation of refractive index (n) for PEO/ZnO/0.1 wt.% iodine thin films with the UV-wavelength.

4. CONCLUSIONS

The electrothermal and optical behavior of the thin films made of the PEO matrix doped with ZnO and iodine was studied as a function of the filler concentrations, applied frequency and temperature. From the results obtained, some conclusions can be drawn. The complex impedance decreases with applied frequency and the concentration of ZnO. The dielectric constant of the films decreases with increasing frequency and increases with increasing filler concentrations, Also, it was seen that increasing ZnO content and temperature in the presence of the iodine dopant enhances the thermal conductivity of the thin films. The observed enhancement in the electrical conductivity by heating can be explained by hopping and tunneling events of the free electrons in the ZnO dopants. The enhancement of thermal conductivity was attributed to the heat transmitted by the phonons and hoping electrons during the thermal processes. The present system of PEO/ZnO thin films was characterized in terms of determined optical properties. The optical energy gap and other basic constants depends clearly on ZnO concentration. It was found that for the pure PEO sample the optical energy gap is higher than that for PEO/ZnO doped films, and it decreases with increasing in the ZnO content.

The dielectric constants and refractive index showed dispersion as a function of frequency. Also, it was found that the dielectric constants and the refractive index increased with increasing the ZnO concentration. The determined optical conductivity was found to increase with the ZnO content. The presented correlation between the observed optical energy gap and optical conductivity at different ZnO concentration exhibits better electrical conduction level.

REFERENCES

1. S.C. Tjong, G.D. Liang, *Mater. Chem. Phys.* **100**, 1 (2006).
2. J. Lee, D. Bhattacharyya, A.J. Easteal, J.B. Metson, *Curr. Appl. Phys.* **8**, 42 (2008).
3. A.G. Hadi, N. Mohammed, S. Kareem, Hashim, *J. Babylon University/Pure and Applied Sciences* **22** No 2, 885 (2014).
4. M. Shuxiang, W. Dezhen, Q. Shengli, W. Zhanpeng, *J. Nanomaterials* **2011**, ID 950832 (2011).
5. A.K. Radzimska, T. Jesionowski, *Rev. Mater.* **7**, 2833 (2014).
6. S. Wacharawichanant, N. Hongbunyoung, P. Churdchoo, T. Sookjai, *Sci. J. UBU* **1** No 2, 21 (2010).
7. J. Zheng, R. Ozisik, R.W. Siegel, *Polymer* **46**, 10873 (2005).
8. A. Abu-Jamous, A.M. Zihlif, *Physica B* **405**, 2762 (2010).
9. K. Dahmouche, M. Atik,N.C. Mello, T.J. Bonagamba, H. Panepucci, M. Aegerter, P. Judeinstein, *Mater. Res. Soc. Symp. Proc.* **435**, 363 (1996).
10. D. Tabor, *Gases*, *Liquids and Solids* and *Other States of Matter* (Cambridge University Press: 1991).
11. Z.M. Elimat, *Radiat. Eff. Defect. S.* **169**, 686 (2014).
12. Z.M. Elimat, *J. Compos. Mater.* **49**, 3 (2015).
13. S.A. Lanje, S.J. Sharma, R.S. Ningthoujam, J.-S. Ahn, R.B. Pode, *Adv. Powder Technol.* **24**, 331 (2013).
14. A.A. Hussein, A.A. Sultan, T.A. Saki, *J. Kerbala University (Scientific)* **10** No 3, 348 (2012).
15. A.A. El-Bellihi, W.A. Bayoumy, E.M. Masoud, M.A. Mousa, *Bull. Korean Chem. Soc.* **33** No 9, 2949 (2012).
16. N. Chand, D. Jain, *Bull. Mater. Sci.* **27**, 227 (2004).
17. L.A. Ramajo, M.M. Reboredo, M.S. Castro, *J. Mater. Sci.* **42**, 3685 (2007).
18. Z.M. Elimat, F.S. Al-Aqrabawi, T. Abu Hazeem, Y. Ramadin, A.M. Zihlif, *Int. J. Thermophys.* **34**, 2009 (2013).
19. A. Dasgupta, R.K. Agarwal, *J. Compos. Mater.* **26**, 2736 (1992).
20. J. Tauc, *Amorphous and Liquid Semiconductors* (Plenum: NewYork: 1974).
21. J. Kayathri, N. Rani Meiyammai, S. Rani, K.P. Bhuvana, K. Palanivelu, S.K. Nayak, *J. Mater.* **7**, ID 473217 (2013).
22. M.D. Giulio, G. Miccci, R. Rella, P. Siciliano, A. Tepore, *phys. status solidi a* **136** No 2, K101 (1993).
23. E.I. Ugwu, A.S. Olayinka, F.I. Olabode, *J. Eng. Appl. Sci.* **4** No 2, 126 (2009).
24. H.P. Myers, *Introductory Solid State Physics* (London: Taylor and Francis: 1990).