

Physical Characterization and Performance of Iron Polymer Composites

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ABSTRACT: The physical properties of poly(ethylene oxide) (PEO) composites containing natural iron oxides with different concentrations 2, 4, 6, 8, 10, 15, and 20% by weight were studied. Powder of iron oxides of 63- μm particle size was casted with PEO polymer. Absorption UV spectra were collected in the wavelength range 300–800 nm by using a spectrophotometer. The optical energy gap and energy tail widths of localized states of the prepared composites were determined from Urbach formula. The electrical properties were studied using AC impedance measurements performed at different temperatures and in

frequency range 100 kHz to 1 MHz. Impedance, dielectric constant, dielectric loss, and AC-conductivity showed frequency and temperature dependence. The thermal conductivity of the composites was studied as a function of iron oxides concentration and in temperature range 20–50°C. It was found that the thermal conductivity of the composites increases with filler concentration and temperature. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: 2078–2084, 2012

Key words: iron oxides; poly(ethylene oxide); absorption; dielectric constant; AC-conductivity

INTRODUCTION

A variety of materials science and engineering issues include criteria that may be employed in the materials selection process for advanced technologies. In recent years, considerable research has been devoted to modify the mechanical, thermal, electrical, and optical properties of polymer composites to meet specific technical and industrial applications. The optical properties of polymers have attracted much attention in view of their applications in optical devices with remarkable absorption, reflection, interference, and polarization properties. The characteristics of polymers can be suitably modified by the addition of some fillers and dopants depending on their reactivity with the host matrix.^{1–3} The common techniques applied in the plastic transforming industry are extrusion and compression molding. Particulate fillers such as iron, alumina, oilshale, carbon black, silica, clays, and metallic flakes or fibers can be added to polymeric systems to improve their properties and performance. Some physical changes are observed as the melt viscosity, chain stiffness, and mechanical and electrical behavior due to physi-

cal interaction between the fillers and the matrix molecules.

The importance of the particulate composite materials also involves a wide range of technical applications. Such materials could be applied as packages of optoelectronic devices, which require high-light transmittance at visible wavelength range to communicate between the inside and outside of the devices. The property characterization of polymer composites is extremely important not only for scientific knowledge but also for modern and advanced technological applications.^{4–6}

Characterization of the optical properties of iron composites is influenced by the produced morphology. Actually, one important progress in the optical properties of the particulate composites is to achieve higher light transmittance and less scattering by structure tailoring and changing the filler concentration.^{5,6}

Much attention is currently focused on obtaining new structural components to be used in electrical conduction, thermal insulation, and electromagnetic shielding. In some areas of technological demands, the size and geometrical effects play an important role in characterization of the physical properties of solid state materials. Hence, the electrical conduction is obviously an important property in choosing the appropriate polymeric system or composite for a specific electronic application. A deeper understanding of the dielectric properties usually governed by several processes including AC (varying time current) and DC (direct current) conditions, dipolar

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relaxation, interfacial polarization, and side group motion.² Heat conduction in polymers is mediated mainly by the elastic waves (phonons) only as the result of the lattice vibrations. The temperature dependence of the thermal conductivity of polymers depends mainly on the polymer structure. Thermal properties of a polymer composite can be affected by the type and geometry of the filler particles.

This study covers some optical, electrical, and thermal properties of poly(ethylene oxide) (PEO) polymer filled with natural iron/oxides. It mainly deals with the effect of iron concentration on the optical constants, AC electrical conductivity, and dielectric properties of the prepared composites at room temperature. The thermal conductivity and thermal resistivity will be estimated as a function of Warda iron oxides content and temperature by using a modified thermal conductivity setup.⁷

EXPERIMENTAL WORK

Iron oxides deposit

The natural iron deposit was obtained from Warda cave located in the north of Jordan Rift. According to a recent study⁸ of geochemical characterization of Warda, iron deposit were crushed and dried at 110°C. After that the product was sieved to -100 mesh to get a fine grained, homogeneous, and representative powder sample suitable to be used as dispersed filler in polymeric matrices. It is known that X-ray diffraction peaks are related to the composition and structure of a solid. An X-ray diffraction study carried out by Saffarini et al.⁸ identified some minerals existing in selected iron oxides samples. Analysis of the diffraction peaks showed that the deposit samples contain few iron minerals as: hematite, goethite, and magnetite in addition to quartz and calcite. Hematite mineral in all selected deposit samples is the major component. Goethite and calcite are minor minerals, and magnetite and quartz are trace minerals. The composition and structure identification are normally essential to characterize the physical behavior and performance of the studied polymer composites. The estimation of metal iron is about 45% where (95% iron oxides and 5% quartz are trace elements) by weight in the deposit.

Composites preparation

The materials investigated in this study are PEO composites containing Warda iron deposit with concentrations 2, 4, 6, 8, 10, 15, and 20% by weight, and neat PEO polymer. PEO resin with average molecular weight of 300,000 was provided as particles powder by BHD Company—USA with purity of 99%. It was used to prepare composite films by casting

from solution made of PEO and iron. PEO powder was dissolved in methanol as a suitable solvent, and then iron oxides powder of 63- μm grain size was added. The solution was then stirred continuously by a rotary magnet at room temperature for about 4 days until the mixture appear in a homogeneous viscous molten appearance. The mixture was immediately casted to thin films on a glass mould (plate) and the methanol was allowed to evaporate completely at room temperature by waiting for 2 days under atmospheric pressure. All the films were dried in oven at 40°C for 2 days.⁹ The produced PEO/iron films were of 0.3-mm thickness.

Optical measurements

The most direct and perhaps the simplest method for probing the band structure of materials is to measure the absorption spectrum UV–visible relation. The optical absorbance (A) of the composite films was taken in the wavelength (λ) range 300–800 nm using Cary-model photospectrometer. The absorption coefficient $\alpha(\lambda)$ was then calculated from the absorbance (A) spectra using the relations^{10,11}:

$$I = I_0 \exp[-\alpha x] \quad (1)$$

Hence,

$$\alpha(\lambda) = (2.303/x) \log(I/I_0) = (2.303/x)A(\omega) \quad (2)$$

where I and I_0 are the incident and transmitted intensities, respectively, ω is the angular frequency, and x is the sample thickness ($x = 0.3$ mm).

Impedance measurements

To observe the effects of concentration, frequency, and temperature on the electrical behavior of the iron oxides/PEO composites, impedance measurements were carried out using (HP) 4192A impedance analyzer. For electrical measurements, disk-like shape specimens of 1 cm in diameter were cut from the prepared sheets. The test specimen is placed firmly between two copper electrodes connected through cables to the impedance analyzer. The sample holder and test specimen were inserted inside an oven chamber. The measurements have been performed in a frequency range 100 kHz to 1 MHz and temperature range 20–50°C. Accurate temperature readings were taken in a steady state condition by a thermocouple in addition to those of the oven dial. No possible measurements were taken at higher temperatures, since PEO polymer melts at about 55°C.

The real component ϵ' and the imaginary component ϵ'' of the complex dielectric constant ϵ^* are related to the impedance Z and phase angle (ϕ) as¹²:

$$\varepsilon' = Z_i/2\pi fC_0Z^2 \quad (3)$$

and

$$\varepsilon'' = Z_r/2\pi fC_0Z^2 \quad (4)$$

where f is the frequency of the applied field; $C_0 = \varepsilon_0 A/d$, the electrode capacitance; d , the specimen thickness; ε_0 , the permittivity of free space; A , the area of the specimen; Z_i and Z_r , the imaginary and real components of the complex impedance Z expressed in terms of the phase angle ϕ as: $Z = Z_r - iZ_i$, $Z_i = Z \sin \phi$, and $Z_r = Z \cos \phi$, respectively.

The AC electrical conductivity (σ_{AC}) was calculated from the relation:

$$\sigma_{AC} = 2\pi f \varepsilon_0 \varepsilon'' \quad (5)$$

and the thermal activation energy E_a from the Arrhenius type equation:

$$\sigma_{AC} = \sigma_0 \exp(-E_a/k_B T) \quad (6)$$

where σ_0 is a material constant, T is the temperature in Kelvin, and k_B is the Boltzmann constant.^{6,10,12,13,14}

Thermal conductivity measurements

Measurements of thermal conductivity of the prepared samples were done by sending electrical pulse to transmit across double composite specimens separated by a heating current coil, all are placed in a sample holder connected to thermocouples. Our modified setup and measuring procedure are based on that design reported by Kamal et al.^{4,15} Disk specimens of 5 cm in diameter were cut from the composites for thermal conductivity measurements. All the measuring assemblies are placed in an oven, and the applied voltage and current are taken during a time interval under temperature steady state condition.

The thermal conductivity k for pure PEO and different composites with iron oxide concentrations (2, 4, 6, 8, 10, 15, and 20 wt %) was calculated from the following equation¹⁰:

$$k = IVL/2A\Delta T \quad (\text{W/m}\cdot^\circ\text{C}) \quad (7)$$

where V and I are the applied voltage and current, L is specimen thickness, and A is specimen area. The factor 2 refers to double specimens placed in the heating specimen holder. ΔT is the difference in temperature before and after application the voltage pulse.

RESULTS AND DISCUSSION

Optical results

Solids absorbed amount of the incident light of intensity I_0 , and consequently, optical transitions start

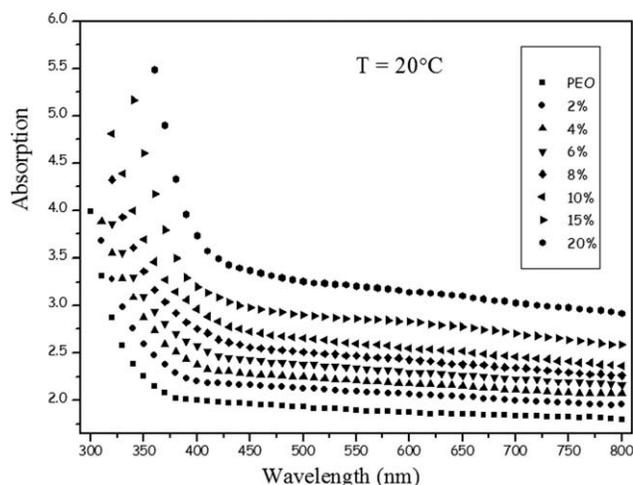


Figure 1 Absorption spectra for PEO/iron composites.

when the energy of photons absorbed is at a quantity higher than or equals 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 transfer from the valence band to conduction band. At high-absorption coefficient levels, where $\alpha(\omega) > 10^4 \text{ cm}^{-1}$, the absorption coefficient α for noncrystalline materials can be related to the energy of the incident photon ($\hbar\omega$) according to the following formula^{16,17}:

$$\alpha(\omega)\hbar\omega = B(\hbar\omega - E_{\text{opt}})^r \quad (8)$$

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 and 3/2 for direct, and 2 and 3 for indirect transitions.^{16,18} Figure 1 illustrates the absorption spectrum for the PEO/iron oxides composites of different concentrations and neat polyethylene oxide. It is clearly shown that absorption decreases rapidly with increasing the wavelength. Figure 2 shows the product of absorption coefficient (α) and photon energy ($\alpha\hbar\omega$)^{1/r} versus photon energy ($\hbar\omega$) at room temperature. The extrapolated 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 values of the optical energy gap (E_{opt}).^{16,18} Figure 2 implies that the electron transition from the valence band to the conduction band is a direct transition. Table I includes the determined values of (E_{opt}), which decrease with increasing the iron concentration.

At lower absorption level, in the range of $1\text{--}10^4 \text{ cm}^{-1}$, the absorption coefficient $\alpha(\omega)$ is described by Urbach formula¹⁷:

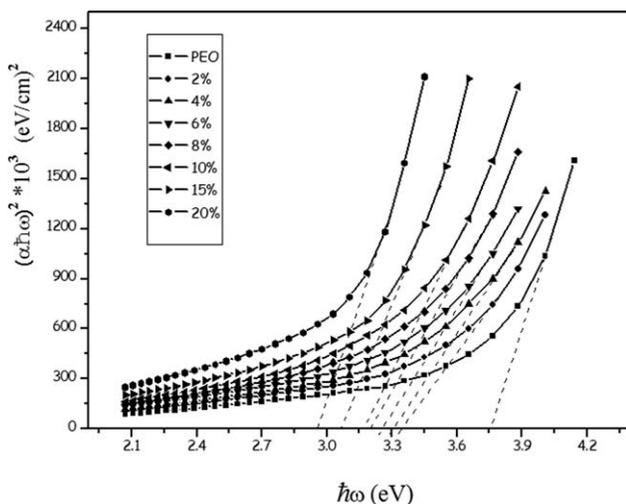


Figure 2 $(\alpha\hbar\omega)^2$ versus the photon energy for PEO/iron composite films.

$$\alpha(\omega) = \alpha_0 \exp(\hbar\omega/\Delta E) \tag{9}$$

where α_0 is a constant and ΔE is energy gap tail (or energy which is interpreted as the width of the tail of localized states in the forbidden band gap).¹⁸ Figure 3 represents the Urbach plots for the examined composites. The extrapolated ΔE values, listed in Table I, were determined from the reciprocal slope of the linear part of each curve obtained from eq. (9), which can be written as: $[\ln(\alpha) = (\hbar\omega/\Delta E) + \ln(\alpha_0)]$. The exponential dependence of $\alpha(\omega)$ on photon energy ($\hbar\omega$) indicates that the absorption processes in the studied composites obey Urbach rule.¹⁰ These energy tails become larger as the iron oxides concentration increases. In general, the energy difference between the localized states in the valence band and extended states in the conduction band represents E_{opt} and the sum ($E_{opt} + \Delta E$) represents the mobility gap.^{6,16-18} Table I includes values of the mobility gap for different composites. The increments in the tail widths can be explained by the fact that the increase in concentration could lead to creation of disorder and imperfections in the iron oxides and structure of the composites, a case which may increase localized states within the forbidden gap.

TABLE I
Optical Results for PEO Composite Films

| Composite (wt %) | E_g or E_{opt} (eV) | ΔE (eV) | $E_{opt} + \Delta E$ (eV) |
|------------------|-------------------------|-----------------|---------------------------|
| Pure PEO (0%) | 3.75 | 0.40 | 4.15 |
| 2% | 3.34 | 0.70 | 4.04 |
| 4% | 3.30 | 0.82 | 4.12 |
| 6% | 3.26 | 0.89 | 4.15 |
| 8% | 3.21 | 0.90 | 4.11 |
| 10% | 3.17 | 0.94 | 4.11 |
| 15% | 3.06 | 1.00 | 4.06 |
| 20% | 2.96 | 1.08 | 4.04 |

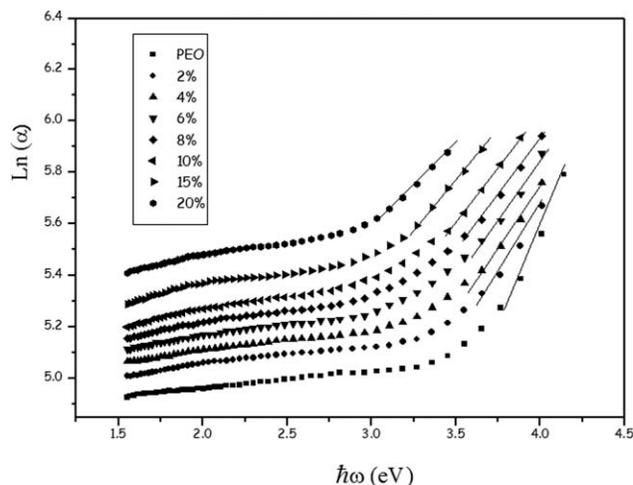


Figure 3 $\ln(\alpha)$ versus the photon energy for PEO/iron composite films.

The small values of the energy tails result from the neatness of the PEO polymer structure and scanty impurities which cause a decrease in the localized states within the forbidden band gap, and thus increasing the value of the optical energy gap.⁶

Electrical results

The thermoelectrical behavior of PEO/iron oxides composites of different iron concentrations (0, 2, 4, 6, 8, 10, 15, and 20 wt %) was examined at temperatures 20, 25, 30, 35, 40, 45, and 50°C, below the PEO glass transition temperature, and frequency range (100 kHz to 1 MHz). Figure 4 shows the variation of impedance (Z) per unit thickness as a function of frequency at room temperature for specimens of different iron oxides concentrations. The figure shows that the impedance decreases with increasing frequency. The high-impedance values at low

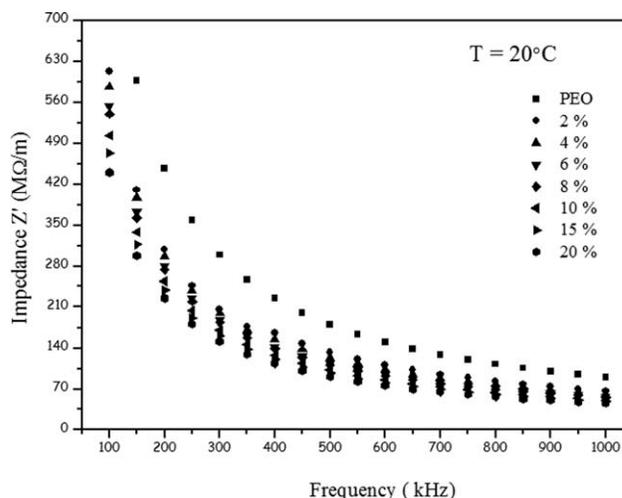


Figure 4 Variation of impedance with frequency for PEO/iron composites.

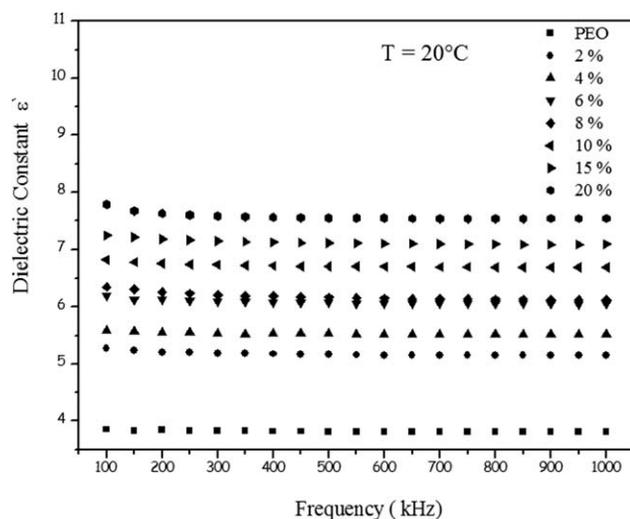


Figure 5 The dependence of dielectric constant on frequency.

frequency are due to space charge polarization, structural defects, phase boundaries in composites, and electrode polarization effects. On the other hand, the rapid decrease of impedance values at high frequencies indicates a response with alternating electric field. This behavior may be attributed to reduction of the interfacial polarization effect.¹⁹

The values of the dielectric constant ϵ' and dielectric loss ϵ'' were calculated from eqs. (3) and (4), and plotted as a function of frequency at room temperature for different composites as shown in Figures 5 and 6. Both ϵ' and ϵ'' values decrease with increasing frequency and increase with increasing the filler concentration. The high values of ϵ' at low frequency are due to space charge polarization (Wagner–Maxwell effect).^{10,16} Table II below shows the variation of ϵ' with iron oxide content at 100-kHz frequency. The dielectric constant values of the composites are

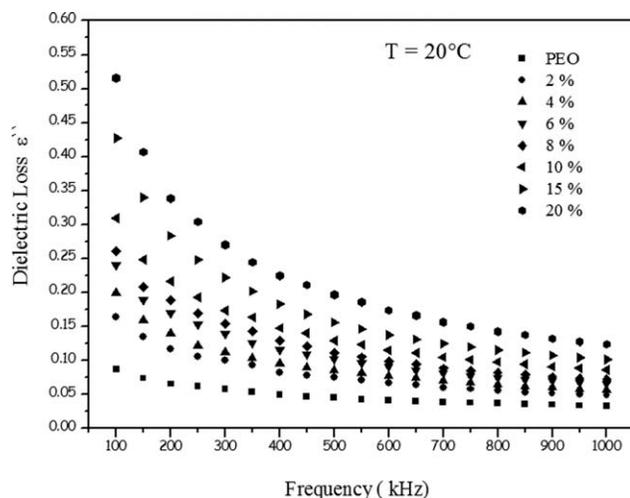


Figure 6 The variation of dielectric loss with frequency.

TABLE II
Dependence of Dielectric Constant on the Iron Oxide Content

| Iron oxide content (wt %) | Dielectric constant (ϵ') |
|---------------------------|-------------------------------------|
| 0 | 3.86 |
| 2 | 5.27 |
| 4 | 5.59 |
| 6 | 6.20 |
| 8 | 6.36 |
| 10 | 6.82 |
| 15 | 7.24 |
| 20 | 7.79 |

higher than that of the pure PEO due to metallic impurities and oxides existing in the iron deposit.⁸

Figure 7 shows the AC conductivity dependence on temperature for the 20 wt % composite at different applied field frequencies. It indicates clearly that the AC conductivity increases with increasing temperature, since charge carrier transport activated by heating and hence electrical conduction is enhanced.

The values of activation energy (E_a) for the 20 wt % composite measured at different applied frequencies (300, 500, 700, and 900 kHz) are included in Table III. E_a was calculated using Arrhenius eq. (6) from the slopes of the straight-fitted lines of $(\ln\sigma_{AC})$ versus $(1000/T)$ shown in Figure 8. It can be seen that the thermal activation energy increases with increasing the applied frequency.

Thermal conductivity results

The thermal conduction in polymer composites is produced by phonons transport (as major contributor) and from electrons and impurities existing in filled composites. Measurements of the thermal conductivity of polymeric materials are difficult since its value is relatively small and in the range (0.2–0.4

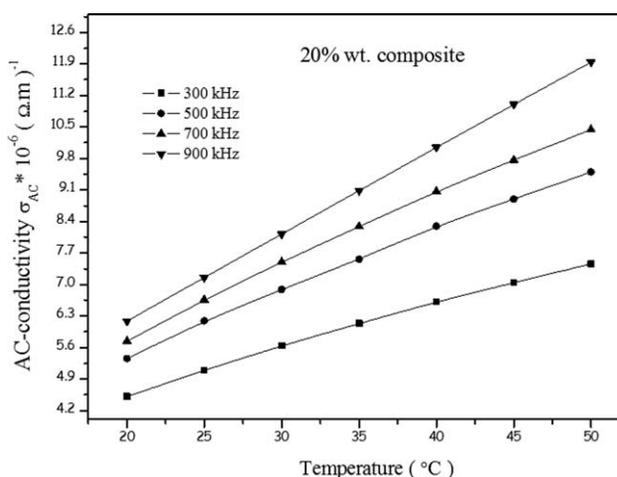


Figure 7 The AC conductivity versus temperature for 20 wt % iron/PEO composite.

TABLE III
The Activation Energy Values for 20 wt % Iron Oxides Composite

| Frequency (kHz) | Activation energy, E_a (eV) |
|-----------------|-------------------------------|
| 300 | 0.82 |
| 500 | 0.93 |
| 700 | 0.98 |
| 900 | 1.04 |

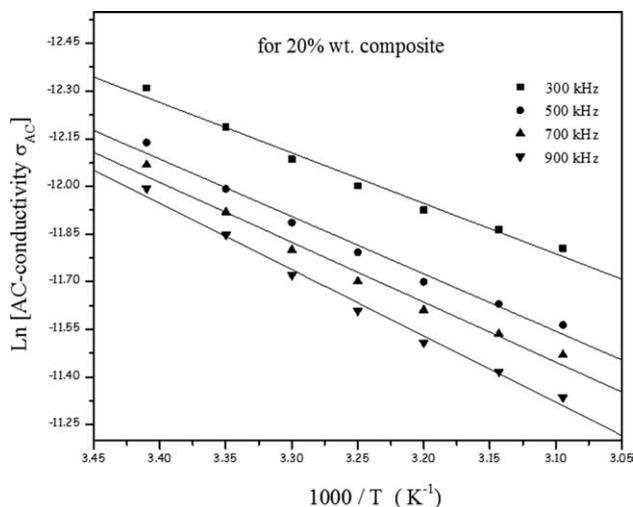


Figure 8 $\text{Ln}(\sigma_{AC})$ versus $(1000/T)$ for 20 wt % iron/PEO composite.

W/m °C). The thermal conductivity is so sensitive to the measuring conditions, physical and chemical structure of the polymer composite.

Measurements of the thermal conductivity k for the PEO/iron oxides composites yield acceptable values as a function of iron oxides concentration and temperature. Table IV shows the thermal conductivity as a function of the filler concentration at room temperature, where it increases with increasing the filler concentration.

Table V shows the variation of the thermal conductivity with temperature for the 20 wt % iron composite on heating to about 50°C. It can be seen

TABLE IV
Variation of Thermal Conductivity with Iron Oxide Concentration

| Iron oxide content (wt %) | Thermal conductivity (k) (W/m °C) |
|---------------------------|---------------------------------------|
| 0 | 0.134 |
| 2 | 0.155 |
| 4 | 0.162 |
| 6 | 0.170 |
| 8 | 0.175 |
| 10 | 0.181 |
| 15 | 0.190 |
| 20 | 0.204 |

TABLE V
Thermal Conductivity Variation with Temperature for 20 wt % Composite

| Temperature (°C) | Thermal conductivity (k) (W/m °C) |
|------------------|---------------------------------------|
| 20 | 0.204 |
| 25 | 0.215 |
| 30 | 0.226 |
| 35 | 0.236 |
| 40 | 0.246 |
| 45 | 0.255 |
| 50 | 0.263 |

that conductivity increases with temperature from a value 0.20 to 0.26 W/m °C in a small temperature rise of 5°C, which is due to thermal activation of the phonons in the composite.²⁰ In heating, phonons, electrons, and impurities are activated and thus enhance the thermal conductivity of the polymeric composites.

Fitting the variation in the thermal conductivity of the PEO composites with the filler volume fraction exhibits approximately a linear dependence (Fig. 9), which is in agreement to results reported by Agrawal et al.²¹ study on the thermal conductivity of styrene-butadiene composites.

CONCLUSION

PEO composites containing natural iron oxides with different concentrations were prepared by using the casting method. The optical, electrical, and thermal properties of PEO films filled with different iron oxides concentrations were studied.

From the measured absorption spectra, it was found that the optical energy gap of the prepared composites decreases with the natural iron oxides

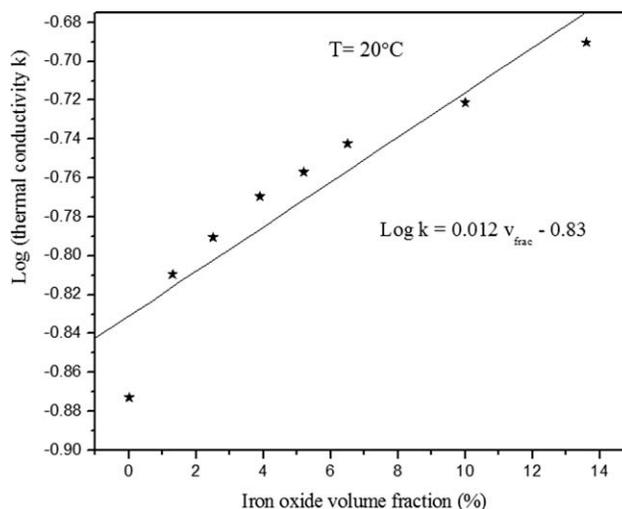


Figure 9 Agrawal model of the thermal conductivity versus composites volume fraction.

concentration increasing, and the electrons transition is direct in k -space.

Impedance spectroscopy measurements showed that the AC electrical properties of the composites depend on temperature, applied frequency, and filler content. The dielectric constant and dielectric loss decrease with increasing frequency. The dielectric constant increases as the iron oxides content increase. The AC conductivity increases with temperature increasing.

Measurements of thermal conductivity for the studied composites showed dependence on both iron oxides concentration and temperature. The observed thermal conductivity increases with the filler concentration and temperature. The approximate linear dependence of the thermal conductivity on the filler content is in agreement with the Agrawal model.

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