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Effect of Carbon Black Nanoparticles on the Thermal Properties of Poly (ethylene oxide) Films

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Abstract

The present paper contains investigation of the thermal properties of thin films made of poly (ethylene oxide)(PEO)dispersed with dopants fixed amount of carbon black (0.1 wt%).

The thermal conductivity and thermal resistivity of the prepared (PEO) thin films doped with carbon black composites have been studied at different (PEO) with doped 0.1wt.% carbon black as compared to that case of the un doped (PEO)film and temperatures. It was found that the thermal conductivity increases with temperature and the thermal conductivity increases with doped 0.1wt. % carbon black content.

Keywords: PEO, carbon black, thermal conductivity, thermal resistivity.

INTRODUCTION

Many research works have been focused on increasing the observed electrical and ionic conductivities of solid polymer electrolytes(SPE) for the purpose of producing thin films to be used in promising electrical industry. Such applications of these (SPE) films include smart sensors, transistors, solid batteries, and other solid – state electrochemical devices. Among the polymers used as basic materials to manufacture polymeric electrolytes thin films are poly (ethylene oxide) and polyacrylonitrile which contribute in a significant development in batteries technology [1-5].

Poly (ethylene oxide) (PEO) is the best polymer used, because its large solvating power with ions, good process ability and outstanding mechanical properties.

Carbon black (CB), when doped in polymers, may reside at various sites, It may go substitution-ally into the polymer chains and composed charge transfer complexes (CTC), or may exist in the form of molecular aggregates between the polymer chains [6]. Carbon black (CB) is a non-crystalline form of carbon, it is conductive and largely composed of carbon atoms or aggregates of nearly spherical shape. The most important purpose of (CB) used as a filler in polymers to import thermal conductions and electrical, i.e., conductive polymer composites [7-10].

The thermal, electrical, and mechanical characterization is an essential for the industrial development of thin films of new polymers, blends, composites and advanced materials that can be used as optical devices , filters, polarizers, total reflectors, and narrow pass-band filters [11]. This paper is an extension study to previously published short communication by Zihlif et.al. [12] which contains preliminary data concern thermal properties of (PEO) films (undoped). While in the present comprehensive paper the studied (PEO) thin films are doped with carbon black nanoparticles. Also, this paper covers the thermal properties occur in doped thin films. The dependence of the thermal properties on fillers content and temperature in the range of (30^0 C-55^0 C). A number of measured quantities as thermal conductivity and thermal resistivity

Only a few studies on the effect of doping with (CB) on the conductivity of polymers are available, e.g. polyethylene, poly(vinyl fluoride), poly(vinyl alcohol), poly (vinyl chloride), poly(naphthyl acrylate). In this study the electrical conduction mechanism in doped poly(ethylene oxide) (PEO) with (CB) was investigated and the results were reported and discussed.[13]

Carbon black, when doped in polymers, may reside at various sites. It may go substitutionally into the polymer chains and compose charge transfer complexes (CTC), or may exist in the form of molecular aggregates between polymer chains [14].

Carbon black (CB) is a non- crystalline form of carbon, which can only be obtained artificially by controlled burning of hydrocarbon fuels. Carbon black works as a pigment and can also help reduce photo-oxidation [15].

Carbon black is a conductive material and is largely composed of carbon atoms or aggregates of carbon atoms, although considerable quantities of hydrogen and oxygen can also be present. Carbon black are approximately spherical but the others have complex three-dimensional shapes, which can be thought of as the partial fusing together of a number of nanometer-sized spherical primary particles [16]. (See Table 1.1 and Figure1.1). The most important CB use is as a filler in polymers to improve electrical conduction and is used in preparation of conductive polymer composites .

Table 1.1: Known properties of used CB filler.

Property	**Used CB sample**
Size	30 nm
Specific surface area	5-150 m^2/g.
Appearance	Spherical black particles

Figure 1.1: Carbon Black

EXPERIMENTAL WORK

In this study the material examined is (poly ethylene oxide)/ thin films doped with carbon black as dopant neat (PEO) thin film for contrast the noticed consequences.

Preparation of thin films

(PEO) and carbon black powders were blended together in methanol as a convenient solvent. Then for two days the mixture was mixed by using a rotary magnet to get a homogeneous mixture. On to a glass mould the mixture was directly casted to delicate films. At room temperature by waiting for two days the methanol was permitted to evaporate perfectly. All samples were dried in the oven at temperature 40ºC for two days.

The thickness of the synthesized composites was measured by a sensitive digital vernier caliper. Least count of the instrument is 0.001 mm. The thickness of all thin films were measured at six different spot places, chosen randomly, and then their average is taken. The obtained values of thicknesses are given in table 2.1

Table 2.1: Thickness values of polymer thin films

Polymer Composite Film	Thickness(µm)
Pure (poly ethylene oxide)	70
(poly ethylene oxide) + 0.1 % carbon black	120

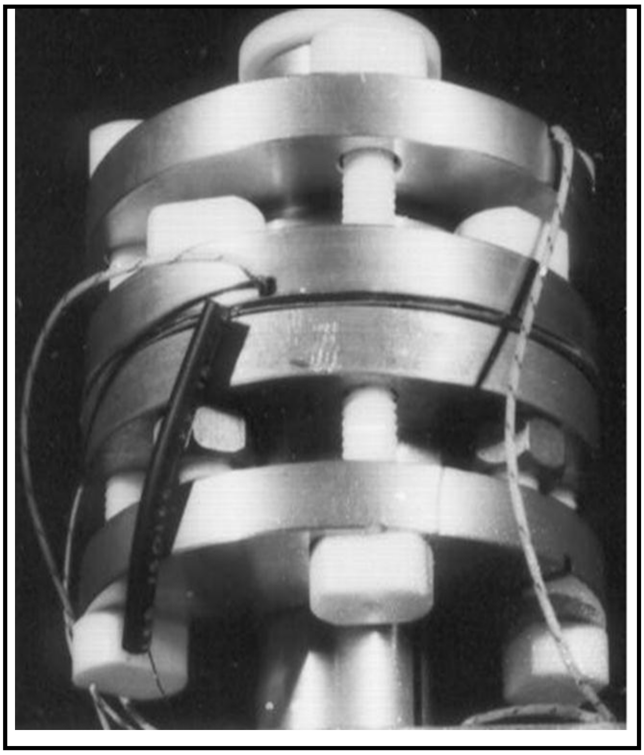
Measurements of thermal properties

The thermal conduction in solid polymer electrolytes is produced by lattice vibration waves (phonon), free electrons and impurities existing in their structure and ions transport (as major contributors). Measurements of the thermal conductivity of polymers are too difficult since there's values are relatively small and lie (in the range 0.2-0.4 W/m°C).

The thermal conductivity (k) for the prepared electrolyte thin films with different alum concentration and dopant carbon black was measured in temperature range from 30 ºC to 55 ºC. No higher temperature measurement were performed since the melting temperature for (PEO) is about 65 ºC .

The procedure of thermal conductivity measurements relies on using a setup the components of which are shown in Figure (2.1) , (2.2):Thermocouple Amplifier ,Sample holder, which contains: (Two test disk samples, heater, two sheets of Teflon used as insulators, five thermocouples, Teflon tapes. aluminum plates), oven, power supply and stop watch.

Figure 2.1: Thermocouple amplifier (AD594 instrumentation)



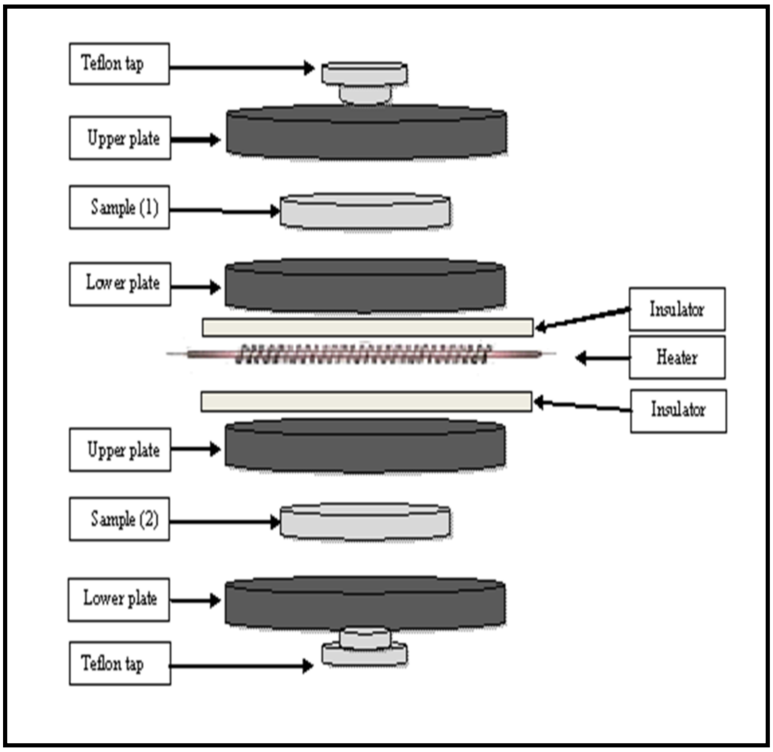


Figure 2.2: a) The sample holder. **b)** Schematic diagram of the sample holder

The procedure of thermal conductivity can be stated as follows:

1. Preparing two composite samples in form of disks held firmly in a sample holder and placed in an oven.
2. Connect the apparatus in a circuit as illustrated in figure (2.3).
3. The apparatus measures the thermal conductivity using the steady state method, where the hot and cold plates are maintained at constant temperature, measured by thermocouples fixed on the sample surfaces.
4. Giving a pulse voltage (V) for 30 seconds, just arriving to the steady state temperature, recording the current (I) value.
5. Reaching the second constant state, to indicate (*ΔT*) between the hot and the cold plates for each sample.
6. The thermal conductivity in (W/ m.º C) was calculated using the relation:

$$k = IV\frac{L}{2A\Delta T} \tag{2.1}$$

where *I* is the pulse current (Ampere), *V* is the pulse voltage (Volt), *L* is the sample thickness (m), *ΔT* is the temperature difference between T_1 and T_2 (ºC), at steady state, and *A* is the sample area (m^2). The factor 2 in the equation for using two specimens.

The average value of thermal conductivity will be:

$$k = \frac{k_1 + k_2}{2} \tag{2.2}$$

where: k_1 and k_2 are thermal conductivities of the two used specimens.

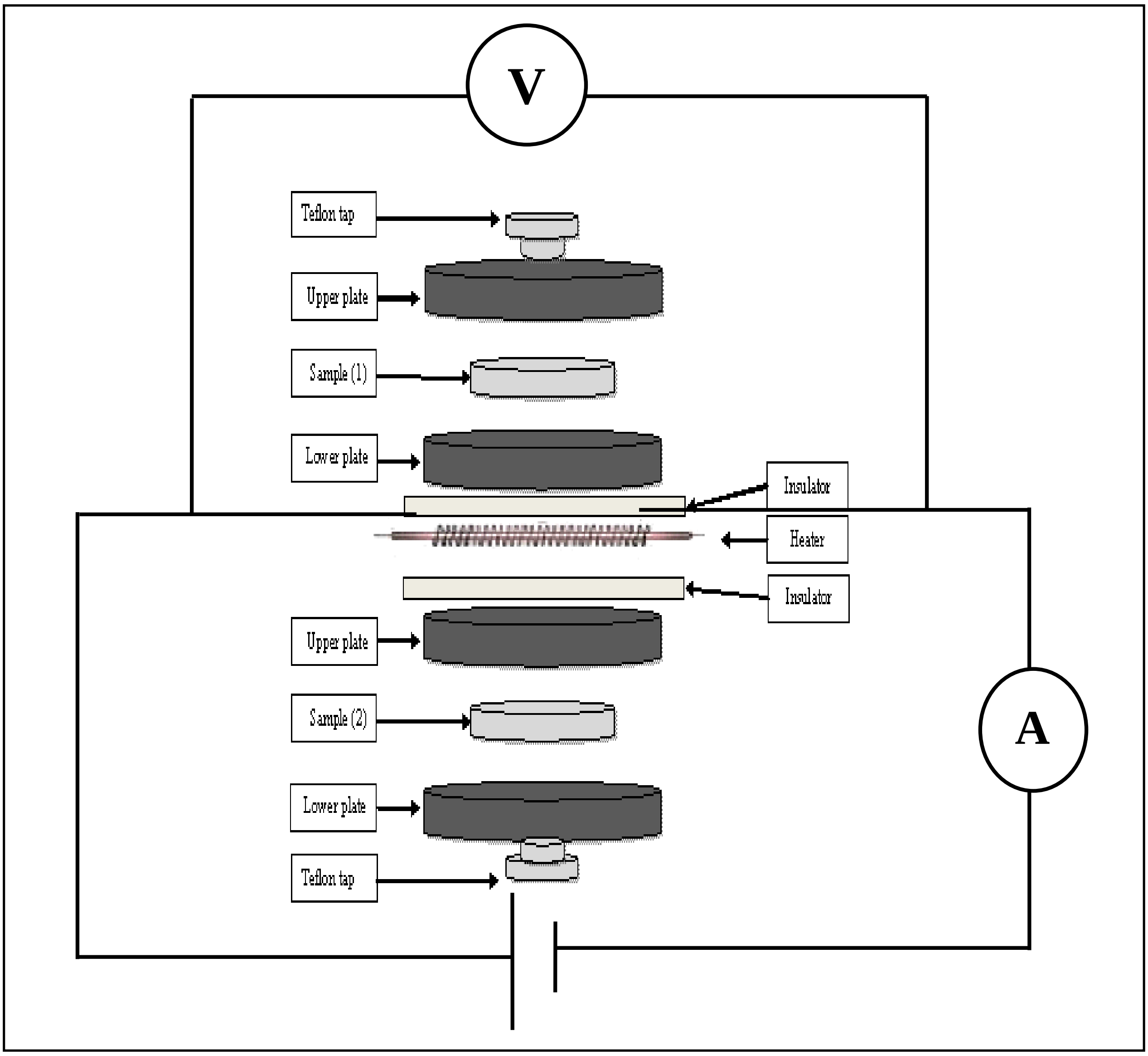


Figure 2.3: The circuit of thermal conductivity measurements

Thermal properties characterizes the response of a material to the application of heat. The temperature of a solid object and it's dimensions increase when it absorbs energy in the form of heat. The energy may be transported to cooler regions of the sample if temperature gradients exist, and ultimately, the sample melts.

Heat conduction in solids is mediated mainly by the phonons or elastic waves only as a result of the molecular vibration of the lattice, where there are no free electrons. Thermal conductivity of polymers can be described by Debye and Eiermann model [17] as:

$$k = \frac{1}{3} c_{\upsilon} \rho \upsilon \lambda \qquad (2.3)$$

where, ρ is the volume density, υ is the propagation speed of the phonons through the lattice, C_v is the heat capacity of phonons per unit volume, and λ is the mean free path between two successive collisions in such processes as: geometrical scattering and scattering by other phonons.

RESULTS AND DISCUSSION

Thermal Results

The present study cares about the studying of the thermal properties dependence on temperature in the range of (30 ^{0}C - 55 ^{0}C) for (PEO) with doped 0.1wt. % carbon black as compared to that case of the un doped (PEO) film, and determined of some physical quantities as thermal conductivity and thermal resistivity.

Figure (3.1) displays relative graphs of thermal conductivity (k) as a function of (T) for (PEO) composites. It is observed that with increasing temperature, the thermal conductivity (k) increases. In case of increasing the temperature, lattice phonons, impurities ions, and existing electrons are activated and thus the thermal conductivity increases.

Carbon black particles tend to form conductive paths and chains resulting in a fast increases in (k) and thus enhancement in (k) values [18].

Figure (3.1) and Figure (3.2) display that with doped 0.1wt.% carbon black as compared to that case of the un doped film,the thermal conductivity (k) will increase. Thus dispersing carbon black dopant in poly (ethylene oxide) matrix increases thermal conductivity of the polymer electrolyte and decreases its thermal resistance that could be helpful in thermal applications.

Thermal conductivities increase with increasing the dopants concentration, this rise could refer to compactness created by rise in concentration of dopants which increase the heat transfer among phonons diffusion [19].

Thermal conduction mechanism in (PEO) polymer matrix filled with carbon black particles is largely influenced by the formed conductive paths [20]. The thermal conductivity varies with rearrangement of carbon black particles in transport paths and their distribution in the polymer matrix [21].

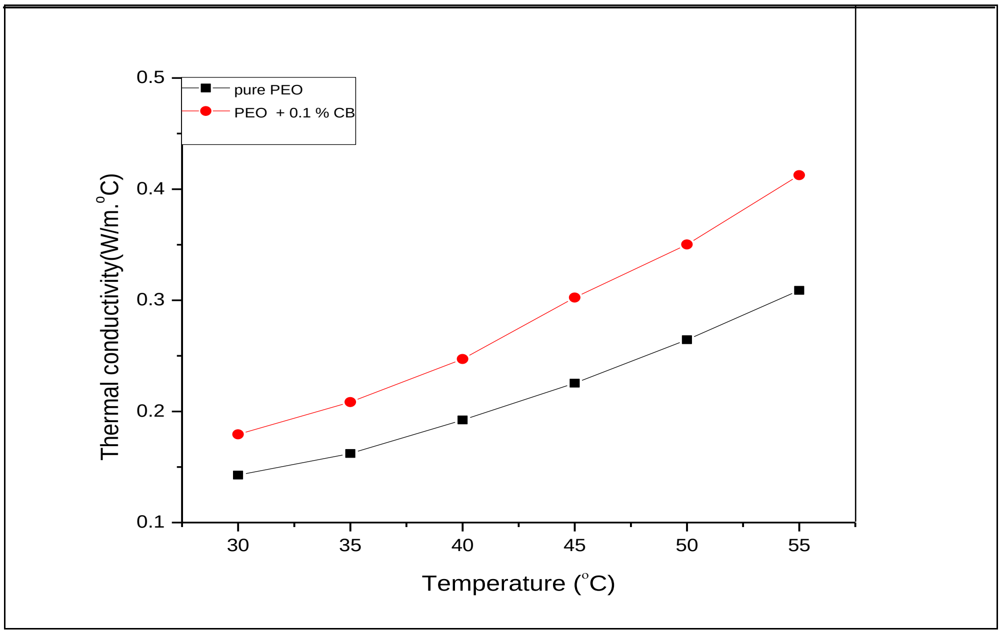


Figure 3.1: Thermal conductivity versus temperature for PEO/CB

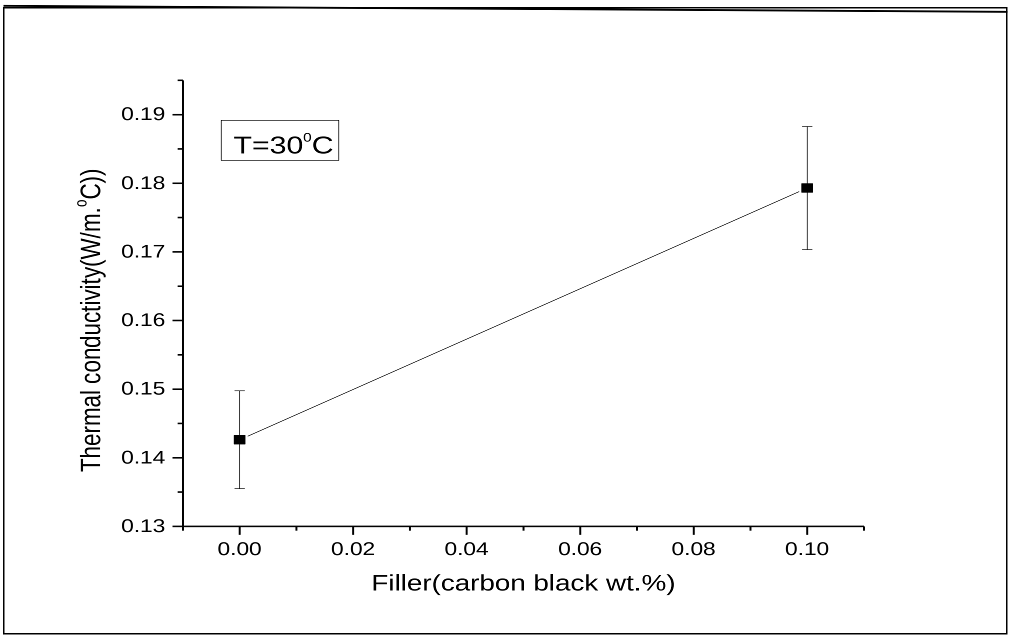


Figure 3.2: Thermal conductivity versus concentrations

Figure (3.3) displays the dependence of the thermal resistivity (r = 1/ k) on temperature.

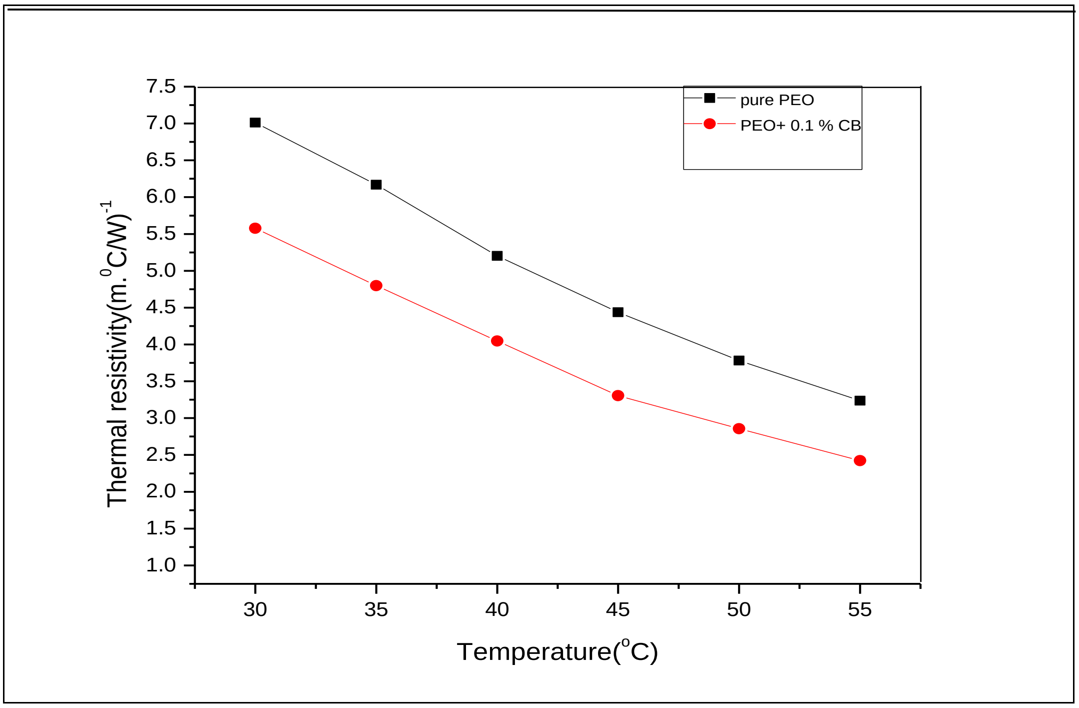


Figure 3.3: Variation of thermal resistivity (r = 1/ k) with temperature

Table (3.1) reports determined values of thermal conduction (k) and resistivity (r) for the thin films, (k) is around 0.14 (W/m. ºC) for (PEO) polymer and increases highly to about of 0.18 (W/m. ºC). Thus the carbon black dopant have large effects in enhancement of the thermal conduction of the prepared thin films.

Table (3.2) displays that a comparison between the variation of thermal and electrical conductivities of the samples with (CB) content. Both the thermal and electrical conductivity increase with increasing the dispersed (CB) phase.

Table 3 .1: Thermal resistance, thermal resistivity and thermal conductivity values

at (T= 30 ºC)

Polymer electrolyte composite	Thermal conductivity(k) (W/m.ºC)	Thermal resistivity (r) (m. ºC/W)	Thermal resistance × 10^{-4} (R) (m^2. ºC/W)
Pure PEO	0.14	7.01	4.91
PEO doped with 0.1wt.% carbon black	0.18	5.58	3.90

Table 3.2: The relation between the thermal and electrical conductivities

Polymer electrolyte composite	Thermal conductivity(k) (W/m.ºC)	Electrical conductivity(σ_{AC})$\times10^{-6}$ $(ohm.m)^{-1}$
Pure PEO	0.14	0.05
PEO doped with 0.1wt.% carbon black	0.18	0.06

CONCLUSIONS

The thermal properties of (PEO) thin films doped with carbon black were studied. By studying the results, we deduced that:

1. Thermal conductivity of the composites increases with carbon black doping.
2. Thermal conductivity of the composites increases with temperature.
3. Fitting the observed data to proposed empirical physical laws seems to be reasonable.

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