An Analysis Study of The Effect of Concentration of Carbon Black on The Electrical Conductivity of Unsaturated Polyester

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Abstract

Carbon black (BP-2000) play an important affect in improvement the electrical conductivity of unsaturated polyester. We added different weight percentage of carbon black (10, 15, 20, and 30 wt%) to polyester in order to obtain composite. Practical measurements were shown that increasing this additive material to polymer led to increase electrical conductivity from (4.7×10^{-10} $ohm^{-1}cm^{-1}$) for pure polymer to (5.1×10^{-4} $ohm^{-1}cm^{-1}$) for polymer +30wt%carbon black. Also, we concluded that the activation energy in pure polymer has two value in two temperature regions; 0.15ev in (300-360)K and 0.6ev in (360-425)K, while in composite for all weight percentage of BP, there is only one value of activation energy about(0.11-0.15) ev in (300-410)K.

Estimated theoretical equation is sigmoid function was achieved by making fitting curve for all practical data using (Table Curve 2D, version 5.01) software. This help us to estimate mathematical model for the shape behavior of (conductivity- temperature) curve, and to find any value of electrical conductivity for any weight percentage that is not taken experimentally.

Key Words:- Polyester, Carbon Black, Electrical Conductivity, Theoretical Model.

دراسة تحليلية لتأثيرتركيز أسود الكاربون على التوصيلية الكهربائية للبولي أستر غير المشبع

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الخلاصة

يلعب أسود الكاربون (BP2000) دور مهم في تحسين التوصيلية الكهربائية للبولي أستر غير المشبع. تمت إضافة نسب وزنية مختلفة من أسود الكاربون (10, 15, 20, 30%) الى البولي أسترللحصول على متراكبات. بينت القياسات العملية بأن زيادة المادة المضافة الى البوليمر تؤدي الى زيادة التوصيلية الكهربائية من (4.7×10^{-10} $ohm^{-1}cm^{-1}$) للبوليمر النقي الى(5.1×10^{-4} $ohm^{-1}cm^{-1}$) للبوليمر مع 30% كاربون. كذلك استنتجنا بأن طاقة التنشيط في البوليمر النقي لها قيمتين في منطقتي درجة الحرارة: الاولى 0.15ev عند درجة الحرارة K(300-360) والثانية 0.6ev عند درجة الحرارة K(360-425)، بينما في المتراكبات ولكل النسب الوزنية من الكاربون فان هناك قيمة واحدة لطاقة التنشيط بحدود ev (0.11-0.15) عند درجة الحرارة K(300-410).

تم استنتاج موديل نظري لتأثير تركيز الكاربون على التوصيلية الكهربائية للبولي أستر غير المشبع واستنبطنا معادلة نظرية هي دالة (Sigmoid function) وذلك بعمل منحنيات تطابق لكل النتائج العملية باستخدام برنامج (Table Curve 2D, version 5.01) . وهذا يساعدنا بامكانية التنبؤ بموديل رياضي لسلوك شكل المنحني (توصيلية كهربائية-درجة حرارة)، كذلك امكانية ايجاد اية قيمة عملية للتوصيلية الكهربائية لاية نسبة وزنية غير مأخوذة عمليا".

1- Introduction

The electrical conductivity of the polymers was improved by introducing conductive materials such as (carbon black, graphite, metallic powder, and superconductivity material) to create a composite [1]. The degree to which the physical properties are changed depends on a great extend upon many properties. The most important of these properties which enhance the electrical conductivity are the particle size and the volume fraction of the conductors in the polymers, the method of preparation and the extent of homogeneity of the composites as well as the intrinsic physical properties of the polymer [2-5].

The addition of conductive filler into polymers generally enhances the electrical properties of the latter. Conductive particle filled into polymers have been used in many applications such as electrochemical displays, sensors, catalysis and redox capacitors etc.[6, 7].

Exfoliated graphite is generally produced from various intercalation compounds subjected to a thermal shock. Commercially prepared graphite uses flaky particles of sulphuric acid- based complexes by exposure to the flame of burner[8]. Different types of carbon based additives have been added to enhance the electrical, mechanical, structural, and thermal properties of a polymer. Most commonly additives used are carbon blacks, carbon nano-tubes and carbon fiber.

Recently, Chand and Nigrawal[9] have reported the DC conductivity behavior of milled carbon fiber reinforced polymer composite. They found that DC conductivity of these composites increased on increasing the filler content. Electrical and thermal properties of carbon filled polyester have also been reported by other researches. It has been reported that sharp increase in the conductivity emerged when the filler content reached at the critical concentration [10]. Exfoliated graphite or expanded graphite with low density, and its special characteristics of absorbing heat by expansion, has its application as a fire retardant. Exfoliated graphite possesses both a surface with a remarkable homogeneity and a large surface area. Graphite being highly conducting and flaky in shape leads to very low percolation threshold this characteristic helps in the development of high energy density and powerful batteries [11, 12].

The study of physical properties of the composites such as electrical conductivity and their dependence on temperature and composition provides the first main challenge to theories of the solid state and give scientists more information on solids and their electronic applications. Therefore, this work was designed to prepare new composite polymer and to investigate their structure and electrical properties experimentally and theoretically.

2-Experimental Work

2-1 Preparation of unsaturated polyester

In around bottom flask, equipped with mechanical stirrer, the appropriate weight of additive carbon black peals 2000 with different concentration (10, 15, 20. and 30wt%) and the resin were dissolved in a few amount of methanol. The mixture was stirred for about 30 minutes until the additive dissolve completely and become homogeneous, then methanol was removed under vacuum and the mixture was cooled to room temperature.

To a beaker, the mixture, 1wt% of methyl ethyl keton peroxide (MEKP was used as an initiator catalyst. It was available as 50wt% solution in dimethylphthalate, it was supplied by (Aldrich corporation) and 0.5 wt% of cobalt octoate (Cobalt octoate was used as accelerator), were added. The mixture was stirred and degassed by centrifuging (300 cycle/min.) and then cast between two glass sheet treated with wax and PVA solution (Polyvinyl alcohol) as a releasing agents.

Great care was taken in the casting process to avoid introducing air bubbles. The cast was then cured at room temperature to 24h.. The sheets were cutted to get the final shape, using a wheel saw cutter to minimize the deformation of the specimen during the cutting process.

Carbon blacks used in this work is BP-2000 type and has particle size (15nm) and very high electrical conductivity.

2-2 Electrical Conductivity Measurements

There are different methods for determination of DC volume resistivity of insulating materials. According to ASTM recommendations [13] for measurement of electrical resistance of insulating materials, three electrodes cell or (guard ring electrode method) was used to study the effect of the filler addition and the temperature on volume resistivity of polymer composite.

The ASTM standard states that the volume resistivity ρ is calculated as follows:

$$\rho = \frac{A}{L} R \quad \text{…………….………….(1)}$$

Where R is the volume resistance, in ohm, measured as the ratio between the desired applied voltage and the current passing through the sample under test which measured by electrometer. L is the average thickness of the sample, and A is the guarded electrode effective area.

The electrodes, in this model, have circular area as given:

$$A = \frac{D_o^2}{4} \pi \quad \text{….…………………..(2)}$$

Where D_o=1.82cm, is the dimension indicated in fig.(1).

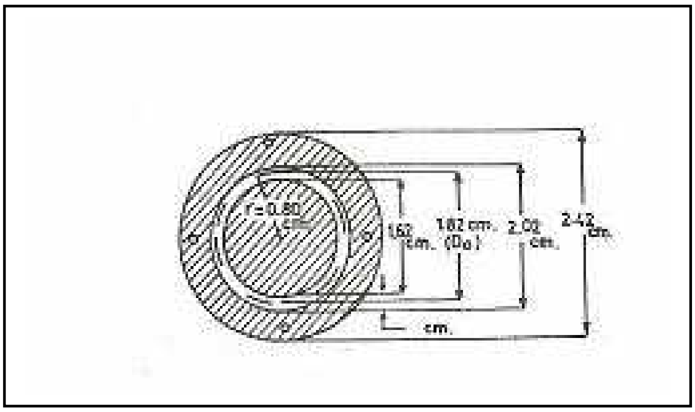


Figure (1) Schematic diagram of electrode

A suitable measuring system is used to study and measured the effect of the applied electric field on the electrical properties. The electrodes are made of copper metal, and a uniform pressure on the specimen was applied by four adjustable screws. The electrical input was provided by DC power supply (Philip Harris Limited) which provide an output voltage (0- 3000)volt, and the output current was measured by using Keithlaye 616 digital solid state electrometer, which provides direct reading current up to 10^{-15} ampere full scale.

The test sample was in the form of a disc, the samples were covered with aluminum electrodes by vacuum evaporation on both faces of the sample to minimize the contact resistance. The sample was placed between the two electrodes and the desired test voltage is selected from the voltage supply, then the current passing through the bulk of the test sample, at selected temperature, is measured by the electrometer.

The measurement of volume resistivity were preformed in the temperature range between (30- 100) ^{o}C by using temperature controlled oven (Hereaus-Electronic) which was shielded against external electromagnetic field.

2-3 Estimates Theoretical Modeling

The theoretical modeling of effect of variation of weight percentage of carbon black BP2000 on the electrical conductivity of unsaturated polyester was taken by using “Table Curve 2D, version 5.01”.

3- Results and Discussions

3-1 Practical Part

The effect of temperature on the electrical conductivity(lnσ) of polyester-Carbon Black in different concentration of carbon in polymer (10. 15, 20, and 30)wt% is illustrated in fig.(2). Increasing concentration of carbon black in polymer led to increase the electrical conductivity. Moreover, it was found that the lower concentration of carbon black in a sample, the lowest in conductivity value. The conductivity data are summarized in table (1).

The activation energy was calculated by using the following Arrhenius equation [14]

$$\sigma = Aexp(\frac{E_a}{KT})......................(3)$$

Where: Ea is the activation energy of conduction, K is Boltzmann's constant, T is temperature in K, and A is constant.

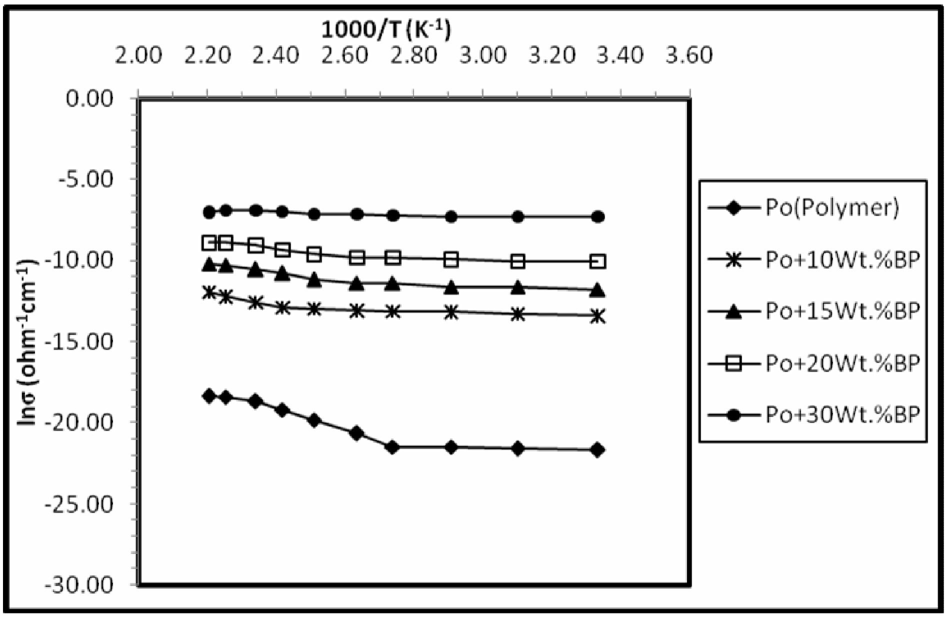


Figure (2) Temperature dependence of the electrical conductivity of unsaturated polyester with different weight percentage of Carbon Black BP-2000

Table (1) DC- Conductivity data for investigated polyester and its composites

Compound	σ^* (ohm^{-1}cm^{-1})	E_a (ev)	Temperature (K)
Pure polymer	4.7×10^{-10}	0.15	300- 360
		0.6	360- 425
Po+10wt%	2.2×10^{-6}	0.13	300- 410

Po+15wt%	3.21×10^{-5}	0.14	300- 410
Po+20wt%	4.4×10^{-5}	0.15	300- 410
Po+30wt%	5.1×10^{-4}	0.11	300- 410

For specimens of pure polymer, two stages of activation energy for electrical conduction are indicated; the first stage with low activation energy (0.15eV) and the second stage with higher activation energy (0.6eV). This suggest two different activation processes, the band conduction and the conduction by hopping[15].

At higher concentration of carbon black (30wt%), the activation energy is even smaller (0.11eV), which can be attributed to a possible increase in the number of conduction paths created in the specimens. At higher filler concentration, the temperature independence of the electrical conductivity is attributed to the tendency of CB particles to form aggregation which acts as direct pathway for the charge carriers, i.e.; the charge carriers will have no trouble travelling within the pathway that has been formed by carbon aggregations. The same conclusion has been reported in different experiments on polymer- metal composites [15].

The properties of a pellet sample by pressing is uniaxial and produces particle- particle contacts in the pressing direction and form a percolation path, because the die wall prevents the particle from spreading out and avoiding each other.

If the carbon black aggregates are randomly distributed, then reordering of the composite will destroy percolation paths and form new one. According to the distribution of the conduction filler are constant, and then the probability of the same number of percolation path is unchanged. This will cause no loss of conductivity as illustrated in our results.

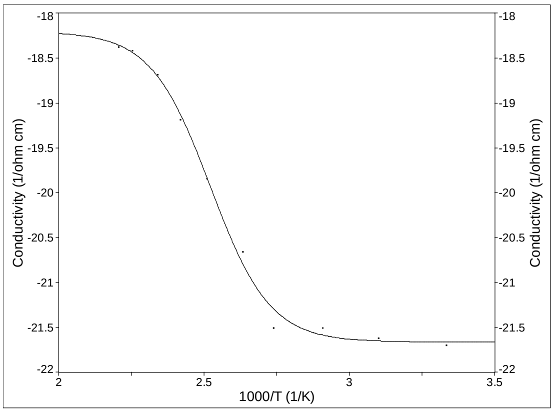
The distribution of the filler in the polyester depends upon the size of the particle. So that, few particles of large size are required to make up the same volume percent conductive filler, and smaller numbers of particles decrease the opportunity to create a percolation path after polymer chain motion was destroyed. The presence of enough particles in the matrix causes a die and reborn percolative paths to be in equilibrium. This may explain why more percolation paths in high concentration of carbon filler are destroyed by polymer chain motion rather than being created due to the large size of the particles and their smaller number [16].

3-2 Theoretical Part

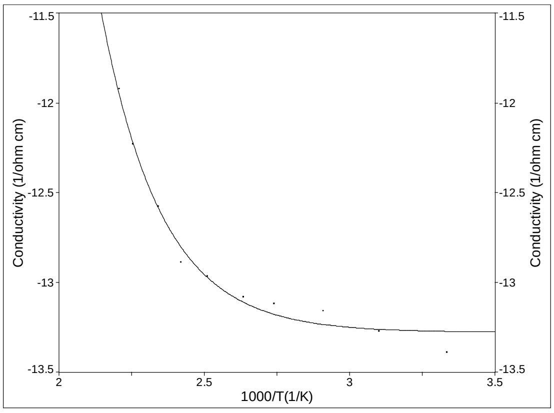
For these experimental curves, fitting curves was taken by use ((Table Curve 2D)) program as illustrated in fig.(3- a, b, c, and d) for pure polymer and with different weight percentage of carbon black BP- 2000; (10,15, and 20)wt%, respectively. The best fitting equation for these curves is sigmoid function given as follows:

$$Y = a + \frac{b}{1+\exp\left(-\frac{(x-c)}{d}\right)} \quad \text{..........................(4)}$$

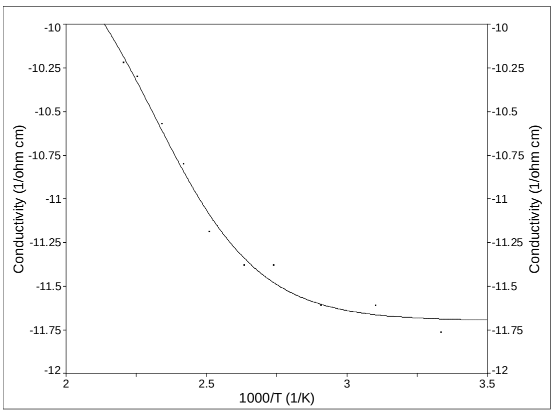
The value of these parameters (a, b, c, and d) are shown in table (2)



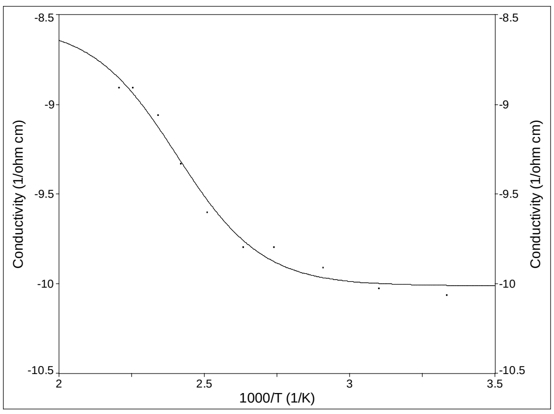
(a)



(b)



(c)



(d)

Figure(3) Fitting curves for electrical conductivity for unsaturated polyester in different percentage weight of carbon BP2000
(a) pure polymer (b) Po+10wt% (c) Po+15 wt% (d) Po+20 wt%

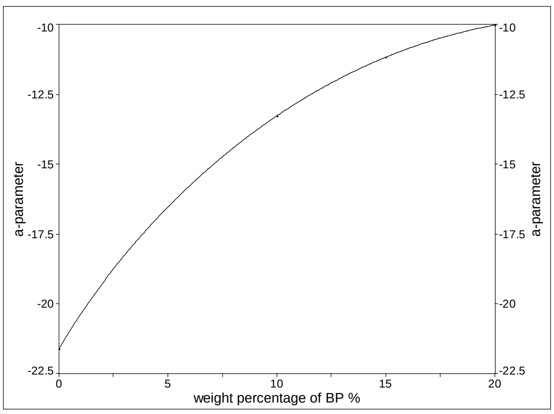
Table (2) The parameters of theoretical (sigmoid) equation

Parameter	Polymer	Po+10wt%	Po+15wt%	Po+20wt%
r^2	0.9955432	0.98431818	0.98780138	0.98497644
a	-21.663184	-13.278428	-11.697506	-10.010921
b	3.4591356	154.79661	2.3559886	1.4549996
c	2.5219478	1.2262468	2.3157671	2.4053534
d	-0.10213518	-0.20643177	-0.18647311	-0.14646805

Where r^2 represent correlation factor between experimental and fitting curve.

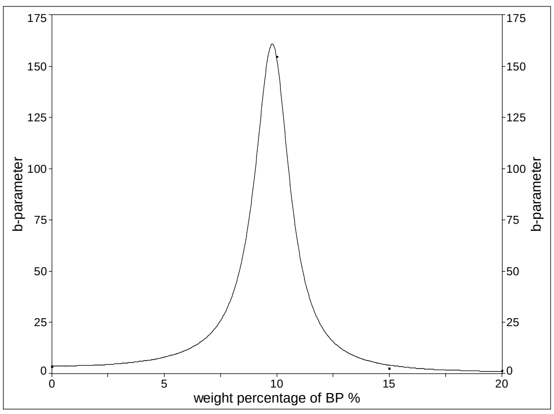
A sigmoid curve is produced by a mathematical function having an "S" shape and refers to the special case of the logistic function. Figs.(4- 7) describes the variation between each parameter of sigmoid theoretical equation with variation of weight percentage of Carbon black BP2000. Also, we take fitting curve for each curve, and the fitting equation is illustrated above the curve.

$$y = -21.613373 + 1.4455653x - 0.19350961x^{1.5}$$



Figure(4) The relation between a-parameter and weight percentage of BP%

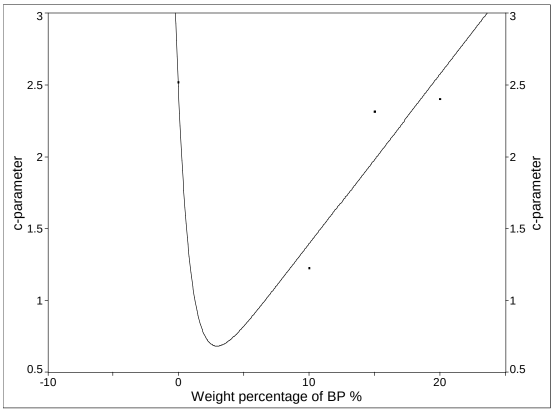
$$y^{-1} = 0.27591715 - 0.014001003x + 0.003575408x^{2.5}$$



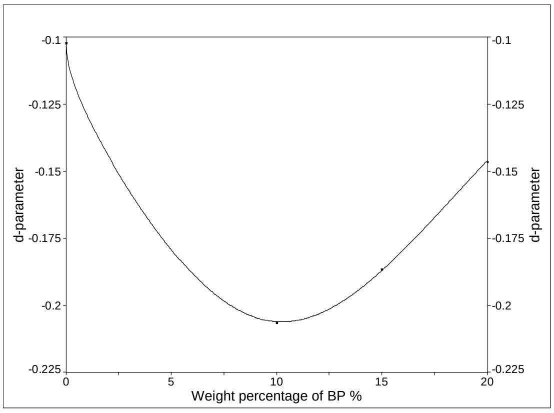
Figure(5) The relation between b-parameter and weight percentage of BP%

$$y = 0.21363959 + 0.1179189x + 2.3083007e^{-x}$$

$$y^{-1} = -9.7788317 - 0.015603376x^2 + 2.0513657x^{0.5}$$



Figure(6) The relation between c-parameter and weight percentage of BP%



Figure(7) The relation between d-parameter and weight percentage of BP%

To calculate the final parameter of sigmoid theoretical equation (eq.(4)), we choose weight percentage of BP as test; C=5wt%BP, so the estimated theoretical equation will become as follow:

$$y = 16.54905 + \frac{7.9514361}{1+e^{-\left(\frac{(x-0.8187873)}{-0.17914973}\right)}} \qquad \text{……………(5)}$$

As well as we take another test; c=25wt%, so the sigmoid theoretical equation become

$$y = -9.6629416 + \frac{0.37058447}{1+e^{-\left(\frac{(x-3.1616121)}{-0.10782702}\right)}} \qquad \text{…………(6)}$$

These estimated sigmoid theoretical equation are plotted with experimental curve as shown in fig.(8). The behavior of theoretical and practical curves is similar. This theoretical model gives us ability to obtain any electrical conductivity at any weight percentage of carbon black that isn't taken experimentally.

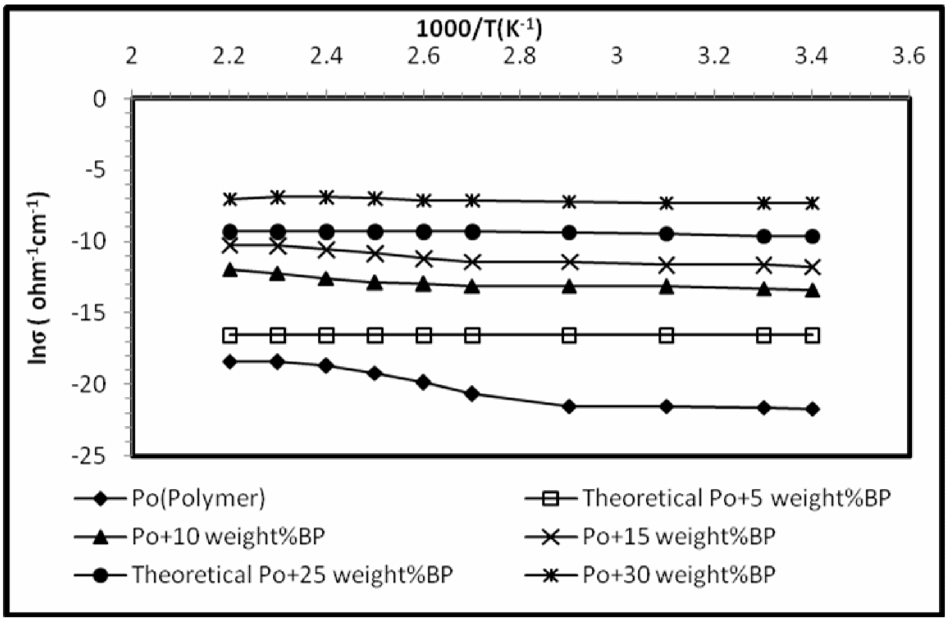


Figure (8) Theoretical and experimental Temperature dependence of the electrical conductivity of unsaturated polyester with different weight percentage of Carbon Black BP-2000

4- Conclusion

Effect of concentration of carbon black BP2000 on the electrical conductivity of unsaturated polyester was investigated. Electrical conductivity of polymer was increased with increasing concentration of weight percentage of carbon black that added to polymer. Whereas, the activation energy of pure polymer affecting by material adding to be one value.

Sigmoid function was the best fitting equation to estimate theoretical model for the effect of concentration of carbon black on the electrical conductivity of unsaturated polyester.

$$Y = a + \frac{b}{1+\exp\left(-\frac{(x-c)}{d}\right)}$$

This model describes the behavior of the shape (s-shape) for temperature dependence conductivity of polyester composite. In addition, it gives us the ability to know the value of electrical conductivity of this polymer in any concentration of carbon black that isn't taken experimentally.

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