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Electrical And Thermal Properties Of Epoxy Resin Filled With Carbon Black

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Abstract

Thermal and electrical conductivity of an insulating polymer can be achieved by dispersing conducting particles (e.g., metal, carbon black) in the polymer. The resulting materials are referred to as conducting polymer composites. Electrical and thermal properties of epoxy-carbon black composites were studied in this work. The weight fraction of the carbon blacks ranged from 0.0 up to 20 wt % with the epoxy resin. By discharging a high voltage through the composite it was found that the resistivity of the composite decreased. Epoxy-carbon black composites show significant differences from the neat epoxy resin measured in the frequency range. Conductivity percolation threshold was found when carbon blacks is added in the range of 1 and 2 wt%. It was found that the epoxy/ carbon black composites have better thermal properties than the neat epoxy.

Keywords: Thermal conductivity, electrical conductivity, carbon black, epoxy

دراسة الخواص الحرارية والكهربائية لراتنج الايبوكسي المدعم بمسحوق الكاربون

الخلاصة

يمكن تحقيق التوصيل الحراري والكهربائي للبوليمرات العازله وذلك باستخدام دقائق مثل المعادن والكاربون الاسود . حيث يشار للمواد الناتجه بالمواد المتراكبه الموصله ذات الاساس البوليمري . في هذا البحث تم دراسه خواص التوصيل الحراري والكهربائي لراتنج الايبوكسي المدعم بأسود الكاربون بنسب مئويه وزنيه تتراوح من 0 الى 20 % .وجد عند امرار فولتيه عاليه خلال النماذج المدعمة حدوث انخفاض واضح في المقاومه النوعيه مقارنه بنماذج الايبوكسي غير المدعمه بأسود الكاربون . لوحظ حدوث ظاهرة (percolation threshold) عند النسب الوزنيه لاسود الكاربون من 1-2% . ووجد تحسن في خواص التوصيل الحراري لمتراكبات الايبوكسي المدعم باسود الكاربون مقارنه بالايبوكسي غير المدعم

Nomenclature

A	Across sectional area (mm^2)	t	Temperature (^oK)
CB	Carbon black	v	Volume fraction of filler (%)
d	Thickness of the sample (mm)	v_c	Critical volume fraction
DC	Direct current	ΔV	Critical volume fraction
K	Thermal conductivity (W/ m-K)	**Greek Letters**	
I	Current (ampere)	σ	Electrical conductivity (s/cm)
R	Electrical resistivity (Ω. Cm)		

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1. Introduction

Plastics and polymers are inherently low in thermal and electrical conductivity. For this reason applications that require conductive properties, which could also benefit from the use of polymer because of their light weight, high strength/weight ratio, easy mold ability, etc, can not take advantage of this desirable material. Research is in progress on inherently conductive polymers, and some polymers with reasonable conductivity values are commercially available [1]. However, at the present time admixing inert, conductive fillers into non-conductive polymers remains very effective and economical way to produce an electrically or thermally conductive polymer component.

Electrical conductivity can be achieved by incorporation of highly conductive fillers, such as carbon-black (CB) particles, carbon fibers, metallic fillers, or intrinsically conducting polymers [2].

Graphite and carbon black offer the benefit of low density and cost when compared to metallic substances used for the same function. Graphite and carbon black also have an advantage in that they are typically inert and compatible with most if not all polymer systems. Carbon materials provide electrical conduction through the π bonding system that exists between adjacent carbon atoms in the carbon/graphite structure, (π bonds are covalent chemical bonds where two lobes of one involved electron orbital overlap two lobes of the other involved electron orbital). Thermal conduction is affected by overlapping sigma bonds which are part of the same molecular bonding system. Regardless of whether or not the conduction is thermal or electrical, electrons provide the pathway for energy transfer, sigma bonds (σ bonds) are the strongest type of covalent chemical bond .In a sigma bond, orbital overlap is always along the intermuclear axis so the bond is centered directly between the two nuclei.

The DC conductivity is related to the formation of a network of filler particles within the matrix; it increases sharply at a characteristic conducting particle concentration (v_c) known as the percolation threshold [3].

The different percolation behavior can be explained by taking into account the chemical reaction between the CB particles and the polymer. This interaction depends on the relative difference of the acidity/ basicity of the polymer and the CB particles. The acidity/basicity with and without CB particles was measured by visual titration. Hydrogen ions may be transferred from the CB surface to the polymer or reverse resulting in an electrical charging of the CB particles. The CB charge is observed by applying an electric field and detecting the moving of the particles by optical microscopy. In addition the agglomeration of the particles is limited by the ionic conductivity of the polymer [4].

2. Theory

In order to achieve conduction in filled polymer systems, conductive pathways of filler particles are required throughout the polymer matrix so as to allow electrons to move freely through the material. Percolation theory quantitatively relates the electrical conductivity of the composite to the volume fraction of the filler. The critical volume fraction v_c, also called the percolation threshold, is the lowest concentration of filler that forms continuous conductive pathways throughout the polymer matrix [5]. The composite conductivity increases slowly with increasing filler concentration until the critical volume fraction is reached. At a very sharp jump in conductivity is obtained over a very small concentration range, referred to as the critical region. In the critical region the conductivity σ, and concentration have a power-law relationship as given by

$$\sigma \infty (v - v_c)^t \qquad (1)$$

Where v is the volume fraction of fillers, the power-law index t is a function of the interactions between the polymer and the matrix [6]. The critical region ends when all the filler particles are involved in at least one conductive pathway and higher filler concentrations only achieve moderate changes in conductivity. The idea of percolation networks is shown in Figure (1), for low aspect-ratio additives such as carbon black [7]. For a fixed intrinsic conductivity and geometry, the conductivity of a composite undergoes a classic curve as a function of loading as seen in Figure (2) Below the threshold loading, volume resistivity is very high, but decreases suddenly and significantly above the threshold, as particles form long touching chains.

Published literature is rich with investigations of mechanical properties of composites [8]. Several publications like Hashin [9], Caruso et al [10], Muralidhar [11], Springer and Tsai [12] addressing different theoretical approaches for predicting thermal conductivity of composite materials have been noted. However, one of the publications [8] has discussed both transverse and axial thermal conductivity of a carbon black composite. A non-linear increase in the thermal conductivity was reported with the increase of carbon black volume fraction and no theoretical models are able to predict this non- linearity.

Carlos Alberto Baldan et al [13] prepared carbon black-filled epoxy composites using different carbon black ratios below and above the percolation limit and the samples were characterized during the cure process by dielectric impedance spectroscopy and by DC conductivity. The results present distinct behavior during the cure process because of the effect of the conducting filler on the matrix microstructure. Filled samples below the conductive percolation threshold should be monitored by dielectric spectroscopy analysis whereas samples above that limit displays conductive behavior during all the curing stages**.**

The aim of this paper is to study the conduction mechanism of a composite consisting of an epoxy resin as a matrix and carbon black as a conductive filler**.**

3. Experiments part

3.1 Materials

The matrix used in this study was an Epoxy resin (Epon 828), this resin is an undiluted difunctional bisphenol A/epichlorohydrin derived liquid epoxy resin manufactured by Shell Chemical Company. TETA (tri ethylene tetra amine) is used as curing agent product of (Ciba Co.) trade name CY956. The filler component was carbon black with apparent density (0.451 g/cm^3), 4.8 % moisture content, and ash content (9.4%). The details of the carbon black preparation have been described by Najat et al. [14].

3.2 Preparations of CB/epoxy composites

The first step consists of mixing the resin with the desired amount of CB (up to 20 wt %) for 1 h at 500 rpm using a dissolver disk at room temperature. This step induced a good dispersion of the CB particles within the epoxy resin and reduced the size of the CB agglomerates. Samples were cured after mix up with the appropriate combination ratios component A (TETA) and component B (Resin and CBs) in the ratio of A: B = 1:5 by weight, using a mechanical stirrer to insure the complete mixing of the two components. The additive was thoroughly mixed in the resin and molded into 40 cm diameter discs of a thickness approximately 10 mm using Teflon molds as showing in figure (3).

3.3 Electrical and thermal conductivity measurements

The electrical properties of an epoxy resin filled with carbon fibers were studied, by discharging a high voltage through the composite. DC Electrical conductivity was measured by the standard four-probe method at ambient conditions [15].In this method; four equally spaced probes are placed on the sample. A current source provides constantly increasing current I_0. When I_0 is passing though the two outer probes, the resulting voltage drop ΔV across the two inner probes is measured by the voltmeter. The electrical conductivity was obtained as the slope of voltage vs. current. The

specimens had 10 mm diameter and 1 mm thickness.
The resistance of the sample can be obtained by the following equation:

$$R = \frac{\Delta V}{I_o} \qquad (2)$$

The thermal conductivity measured in this work using Lee's disc apparatus [16]. Figure (4) shows the arrangement of this apparatus. This method was based on the heat supplied to the apparatus in the steady state, this being equal to the energy emitted from the exposed surface. When the electrical heater is turned on (Apply the 1 volt to the heater as soon as possible), heat will flow from the heater into discs 1 and 2 and from 2 across the sample to 3. The heat will be lost to the room by emission and convection from the rim and end of 1 and 3 and from the rim of 2 and the rim of the heater. The rate of heat loss from the sample is small compared with the heat loss from the copper discs. The rate of loss of heat of a particular disc will be proportional to the temperature difference between the disc and its surroundings, provided this temperature difference is small (Newton's law of cooling). The temperature of the three discs will increase till the rate of heat loss to the room is equal to the rate of heat generation in the electrical heater. When this occurs equilibrium has been reached, thermal conductivity calculated by the following equation:
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$$K = \frac{ed(A_3(t_3 - t))}{A(t_2 - t_3)} \qquad (3)$$

t_1, t_2 and t_3 are the temperatures of the three discs.
t is the room temperature
A1, A2 and A3 are the emitting areas of the three discs (The amount of heat crossing the sample is the amount of heat emitted from disc 3.
A across a sample of the material of uniform cross-section mm^2.
K is the thermal conductivity in (W/ m-K).
e is a constant which measures the heat loss per unit area of copper.
d is the thickness of the sample.
The sample was a cylinder with 40 mm diameter and 5 mm length.

4. Result and discussion

4.1 Electrical Conductivity

The electrical properties changing when CBs particles are added to the epoxy. The composites behavior evolves from insulating material characteristics to those of conductive materials. The effective utilization of carbon black in composite applications depends strongly on the ability to homogeneously disperse them throughout the matrix without destroying their integrity. The electrical conductivity of a material is defined as:

$$s = \frac{1}{R} \qquad (4)$$

where R is the resistivity which is commonly expressed in Ω. cm and the unit for electrical conductivity σ is s/cm. Figure (5) shows the effect of CBs content on resistivity. At very low concentrations of CBs the resistivity gradually decreases with increasing CBs content. The resistivity lower is caused by enrichment of higher conductive material components (According to percolation theory, electrical paths are made up of conductive inclusions in the direct-contact structure based on Ohmic behaviour and the percolation threshold values strongly depend on the shape of particles) [17]. However, at 2 wt%, a sizeable reduction in resistivity, is observed. This stepwise change in resistivity is a result of the formation of an interconnected structure of carbon black and can be regarded as an electrical percolation threshold. This simply means that at concentrations between 1 and 2 wt% CBs, a very high percentage of electrons are permitted to flow through the sample due to the creation of an interconnecting conductive pathway.(When the CBs are embedded into epoxy resin with up to 2 wt.%, the electrical conductivity increases by six orders of magnitude)[18]. At concentrations above 2 wt% CBs, the resistivities are low and decrease marginally with increasing CBs content, and after 10% of CBs addition no change has been detected in the increase of electrical conductivity. These observations are in very good agreement with the [7, 13]. Interestingly, the measured values are in accordance with values given by Hagerstrom and Greene [19] who found a volume resistivity of 10^2 Ohm-cm for 5 wt% multi walled nanotubes (MWNT) in polymer composite (PC).

4.2 Thermal conductivity

The thermal conductivity of a composite depends on many parameters including 1) Type of additives; 2) Additives percentage; and 3) Resin type. The parameters of major influence on thermal conductivity are Additives percentage and conductivity properties of both resin and additives. Additive like carbon black was directly mixed with the resin and the effect of addition of this additive on thermal conductivity was determined. Different samples with 1 wt% to 20 wt% were mixed in the resin for testing and results are listed in table (1) and graphically plotted in Figures (6) Addition of carbon black significantly increases the thermal conductivity. For example, 10 wt% and 20 wt% respectively result in 100% and 120% increase in thermal conductivity over neat resin. No percolation threshold of thermal conductivity is observed because the ratio of thermal conductivities of CBs and polymer matrix is not higher than$10^4$16].

It was observed that after 20 wt% of CBs addition the increased in thermal conductivity is slightly small.

5. Conclusion

Electrical, and thermal properties of CB/ epoxy composites were experimentally examined as the CBs loading was increased up to 20 wt.-%. A percolation threshold less than 2.0 wt.-percent are obtained. Addition of carbon black significantly increases the thermal conductivity. The CBs yield much higher electrical and thermal conductivity than the neat epoxy resin.

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Table (1) Thermal conductivity and electrical resistivity values of epoxy resin filled with carbon black

Electrical resistivity (Ω. Cm)	Thermal Conductivity (W/m K)	Carbon Black (wt %)
10^14	0.12	0
0.9*10^14	0.14	0.5
0.8*10^14	0.15	1
10^5	0.17	2
31622.77	0.19	3
10000	0.214	5
7943.28	0.24	10
7943.28	0.252	15
7943.28	0.264	20

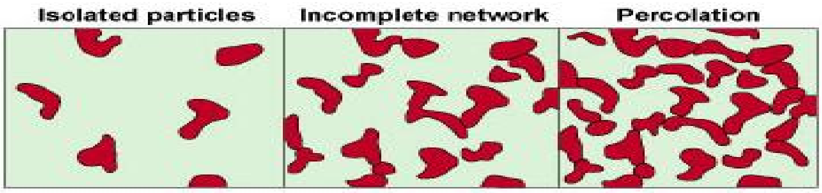

Fig (1) Percolation networks of carbon black [7].

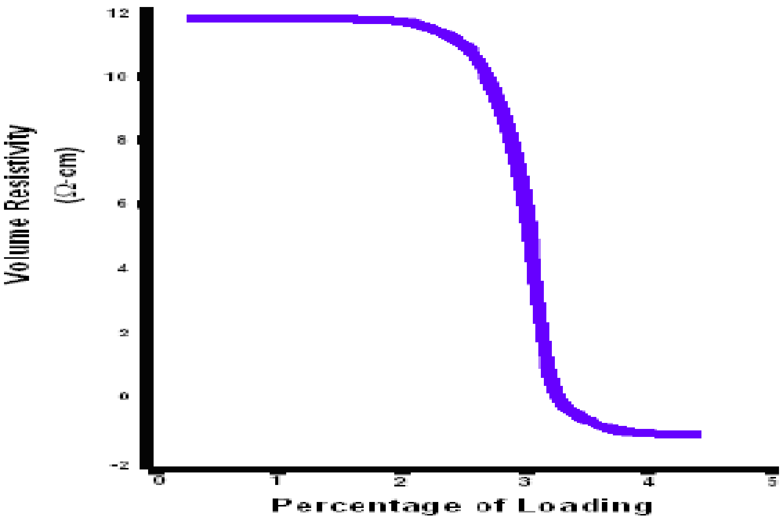

Fig (2) Percolation networks of carbon black [7].

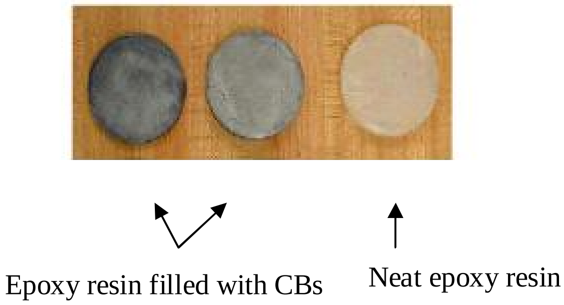

Fig (3) Epoxy resin cast with and without additives poured in Teflon mould

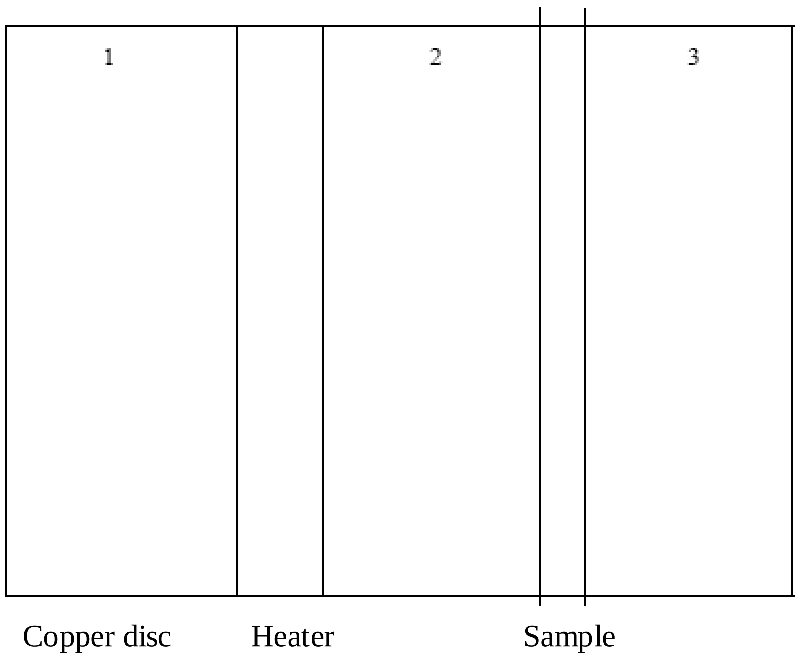

Fig (4): Experiment arrangement of the Lees disc apparatus

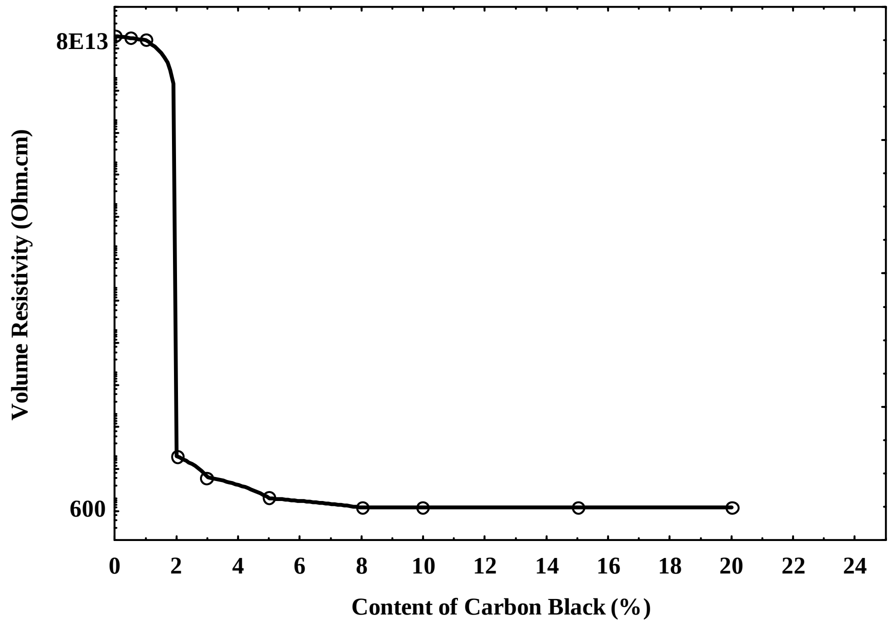

Figure (5) Effect of CBs content on resistivity

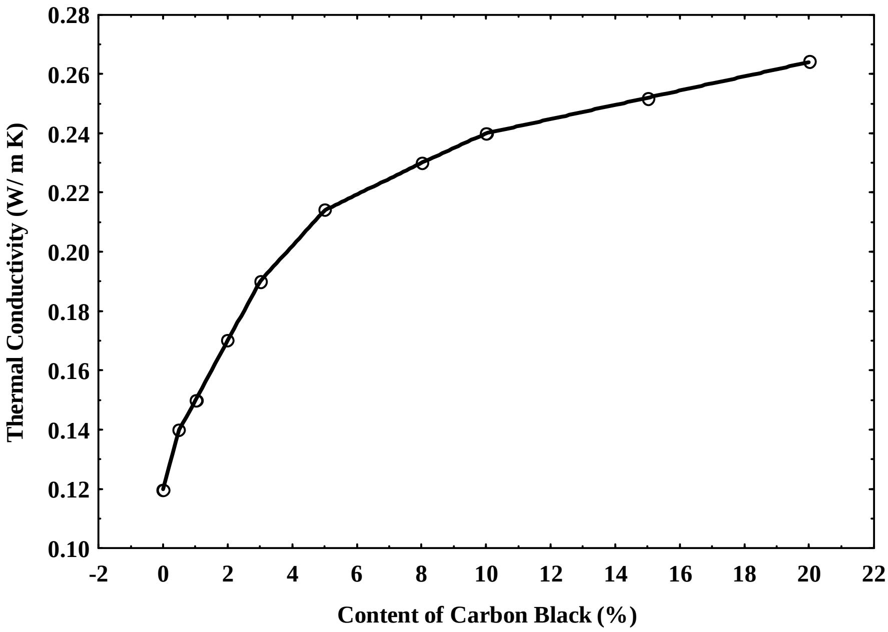

Figure (6) Effect of CBs content on thermal conductivity