

Modelling of DC Properties of graphite/polymer composite Prepared in Bulk and Membrane Forms

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Abstract— Graphite/IIR composites were prepared in both bulk and membrane forms. The insulator – conductor transition was studied according to the percolation theory where three different models were tested. It was found that only Fournier equation achieved the best fitting for all samples and also that the value of critical volume fraction of filler ϕ_c has increased with temperature for all samples. Also, the dependence of conductivity on temperature was studied, where it was found that samples loaded with graphite contents less than the percolation threshold exhibited higher positive temperature coefficient of conductivity (PTC).

Index Terms— Graphite, Butyl rubber, Membrane, DC properties

1 INTRODUCTION

Conductive polymer composite materials (CPCMs) deserved interest in several application fields [1], [2], [3], [4]. Typically, CPCMs are fabricated by melt and rolling mix of conductive fillers and polymers. A composite consisting of conductive fillers and an insulating polymer becomes electrically conductive as the filler content exceeds a certain critical value, which is generally attributed to percolation phenomenon [5], [6], [7]. This critical value is called the percolation threshold, at which, the conductivity can change drastically by several orders of magnitude for small variations of the filler content. Many efforts have been devoted to reduce the percolation threshold of CPCMs [8], [9]. It is worth mentioning that the value of percolation threshold is greatly affected by the properties of the fillers and the polymer matrices, processing methods, and dispersion of the fillers within matrices.

There are several theoretical models that can predict and describe the percolation threshold and electrical conductivity as a function of many factors. One of these theoretical models is a statistical one, which uses the percolation theory to predict that the conductivity is based on the probability of particle contacts within the composite. i.e., models proposed by Kirkpatrick [10], Zallen and McLachlan [11].

Study of thermal-sensitive behavior of some CPCMs is quite attractive for sensor applications. In many composites, the resistivity changes gradually with increasing temperature. Depending on different polymers, different types, concentrations and properties of fillers as well as their interactions, the temperature coefficient of resistance may be positive (PTC), negative (NTC) or zero, which is the combined result of several processes that the composites undergo at high temperature [12].

Electrically conducting polymers containing graphite have been studied extensively because of their potential applications in light emitting devices, batteries, electromagnetic shielding, anti-static and corrosion resistant coatings, and other functional applications [13], [14], [15], [16], [17]. Among the conducting polymeric composites, one main objective in its design from both economical and processing viewpoints is to minimize the filler concentration. We have achieved that by using two processing methods corresponding to two samples forms, namely: bulk and membrane form where the comparison between them was investigated. For the description of the insulator – conductor transition, i.e. percolation threshold, three different approaches were studied. An important thermal-sensitive feature of some CPCMs is that, the resistivity increases with temperature over a certain temperature range, which is known as positive temperature coefficient, (PTC) effect that also investigated.

2. EXPERIMENTAL

2.1 Materials and Sample preparation

Butyl rubber (IIR) which were supplied by TRENCO, Alexandria, Egypt and graphite powder (50 μm) which supplied by Merck, Germany were used in this study. All samples were prepared according to the following method with the compositions shown in Table (1). Ingredients of the rubber composites were mixed on a 2-roll mill of 170 mm diameter, working distance 300-mm, speed of slow roll being 24 rpm and gear ratio 1.4. The compounded rubber was divided into two groups; the first group was left for 24 hours before vulcanization. The vulcanization process was performed at $153 \pm 2^\circ\text{C}$ under a pressure of 150 bar for 15 minutes. By this way the bulky samples were prepared with average thickness 0.3 cm. The second group was dissolved in methylbenzene to obtain a highly concentrated solution. Subsequently, each gelatinous solution was shaped into membrane in a form of circle (7 cm in diameter) by means of a stainless steel dish. After slowly drying, a smooth and uniform thin composite membrane was resulted in about 0.7 mm in thickness. Then all composite membranes were vulcanized under pressure of 294 bar, at temperature of 153°C , and time of 30 minutes, the

Table (1): Composition of IIR composite

Ingredients	Quantity (phr ^a)
IIR	100
Graphite	0, 10, 20, 30, 40, 50, 60, 80,100
Processing oil	10
Stearic acid	1.5
Zinc oxide	5
MBTS ^b	1.5
PBN ^c	1
Sulfur	2

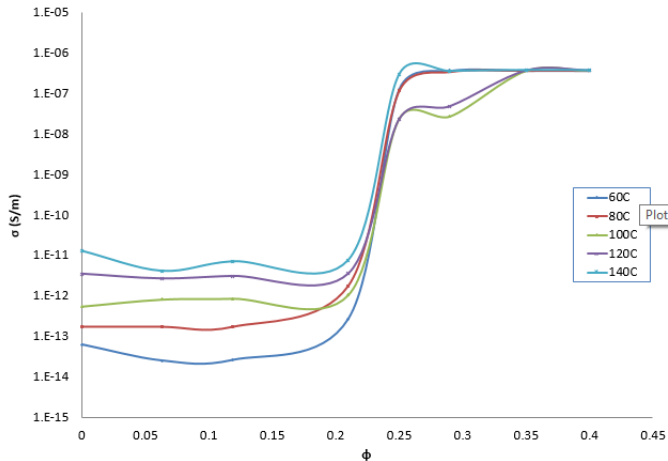


Fig.(1) DC conductivity as function of the volume fraction of filler for graphite/NR composites (bulk samples).

final membranes have average thickness 0.2 mm for IIR samples. Finally to ensure reproducibility of the results, both groups were aged at 70°C for 10 days.

3. MEASUREMENTS

All samples were in the form of disks of about 0.3 cm thick and 1.0 cm in diameter for bulk samples while of 0.4 - 0.2 mm thick and 1.1 cm in diameter for membranes samples. The samples were sandwiched between two brass electrodes after painting their two faces by silver paste to ensure an Ohmic contact with the electrodes. All measurements were made using a Keithly digital electrometer type 616, also a regulated electric oven was used to control the temperature of the sample which was detected by using sensitive thermocouple.

4. RESULTS AND DISCUSSION

a. Effect of graphite content:

Incorporating conductive filler into insulating polymer matrix results in a small increase in the conductivity of the composite with the filler loading. As the filler loading increases, a region is attained at which the conductivity increases drastically by many orders of magnitude for a small increase in the filler loading. This region is referred to as the percolation region and the so called insulator – conductor transition takes place [18], [19], [20], [21], [22].

The conductivity behavior of graphite/IIR composites in both bulk and membrane form are presented in figures (1-2) respectively as a function

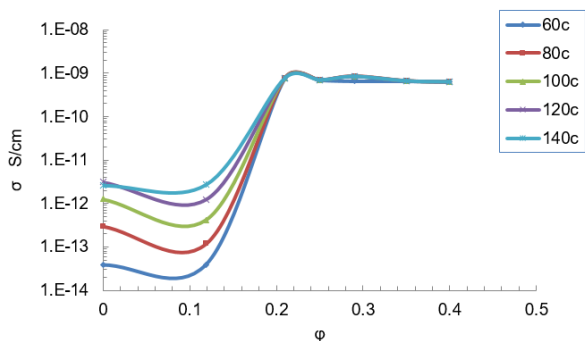


Fig.(2) DC conductivity as function of the volume fraction of filler for graphite/IIR composites (membrane samples).

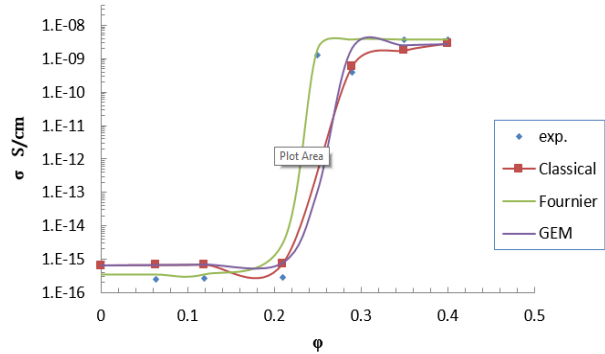


Fig. (3) Comparison between the fits of equation (1), (3) & (4) respectively.

of the volume fraction of filler (at different temperatures: 60, 80, 100, 120, and 140°C). The percolation threshold ϕ_c was found to be less than 0.12 for membrane state and higher than 0.25 for bulk state.

To account for the experimental data, three different models have been used. First, the classical percolation theory [23], which can be expressed in the form

$$\sigma_{DC} = \sigma_{OP} \left(\frac{\phi - \phi_c}{1 - \phi_c} \right)^t \quad \phi > \phi_c, \quad (1)$$

$$\sigma_{DC} = \sigma_{OM} \left(\frac{\phi_c - \phi}{\phi_c} \right)^{-s} \quad \phi < \phi_c, \quad (2)$$

Where t and s are fitting parameters. Second, the general effective medium (GEM) theory; given by:

$$(1 - \phi) \frac{\sigma_{OM}^{1/s} - \sigma_{DC}^{1/s}}{\sigma_{OM}^{1/s} + z \sigma_{DC}^{1/s}} + \phi \frac{\sigma_{OP}^{1/t} - \sigma_{DC}^{1/t}}{\sigma_{OP}^{1/t} + z \sigma_{DC}^{1/t}} = 0 \quad (3)$$

Where $z = (1 - \phi_c)/\phi_c$; and finally, Fournier equation [24]:

$$\text{Log}(\sigma_{DC}) = \text{Log}(\sigma_{OM}) + \frac{(\text{Log} \sigma_{OP} - \text{Log} \sigma_{OM})}{1 + \exp\{b(\phi - \phi_c)\}} \quad (4)$$

Where b is an empirical parameter that directs the change in conductance across the percolation threshold. For all equation σ_{OP} and σ_{OM} are values of the conductivities of filler particles and polymer matrix respectively, ϕ is the volume fraction of the conducting filler and ϕ_c is the percolation threshold. The critical exponent $t = 2$ and $s = 0.73$ are usually taken for 3D systems.

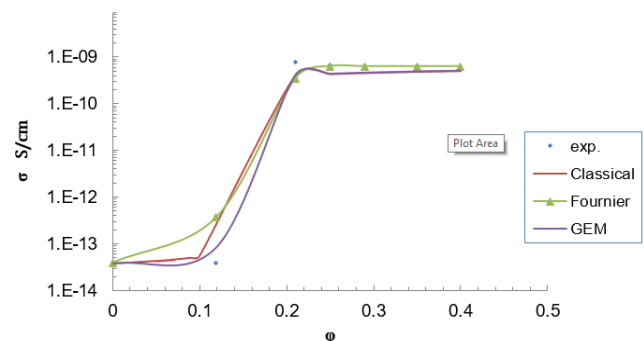


Fig.(4) Comparison between the fits of equations (1), (3) & (4) respectively.

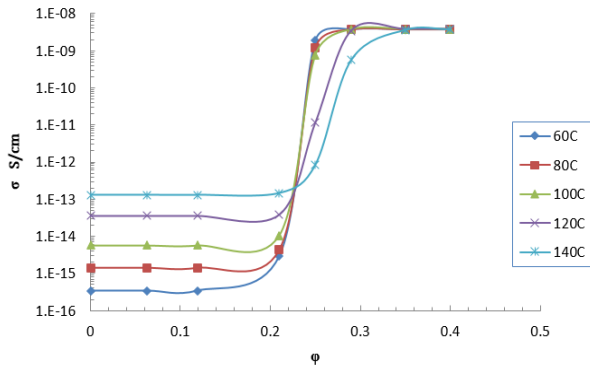


Fig.(5) Effect of temperature on the percolation concentration of graphite/IIR composite in Bulk form

As seen in Table (2), many parameters can influence the percolation concentration, ϕ_c , e.g. filler/matrix interactions, filler shape or filler distribution. They would effectively explain the difference between bulk and membrane states.

Table (2): The fitting parameters of equations (1)-(4)

		$\sigma_{0M}(S/m)$	$\sigma_{0P}(S/m)$	ϕ_c	b	t	s
Classic	IIR	6.44×10^{-14}	3.77×10^{-7}	0.25	-----	1.2	0.07
	IIRm	3.81×10^{-14}	6.30×10^{-7}	0.119	-----	0.2	0.2
Fournier	IIR	3.44×10^{-14}	3.77×10^{-7}	0.225	125	-----	-----
	IIRm	3.81×10^{-12}	6.30×10^{-8}	0.08	70	-----	-----
GEM	IIR	6.44×10^{-14}	3.77×10^{-7}	0.25	-----	0.2	0.1
	IIRm	3.81×10^{-12}	6.30×10^{-8}	0.119	-----	0.2	0.1

Figures (3-4) compare the fitting of dc conductivities versus graphite concentration. The fitting parameters are given in table (2).

Obviously, the classical percolation and the GEM fitting curves overlap and give better approximation for experimental points well above the percolation threshold. Meanwhile, Fournier equation is valid at all volume concentrations and the experimental results were correctly fitted as seen in figures (3-4). Table (3) represents fitting parameters of Fournier equations as a function of temperature, type of rubber matrix and bulk or membrane state of the composites (as obtained from figures (3-4)). It is noticed that ϕ_c increases with increasing temperature and the bulk form has a higher ϕ_c values than the membrane form.

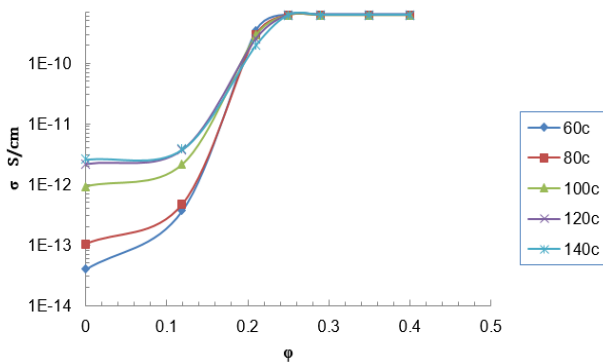


Fig.(6) Effect of temperature on the percolation concentration of graphite/IIR composite in membrane form.

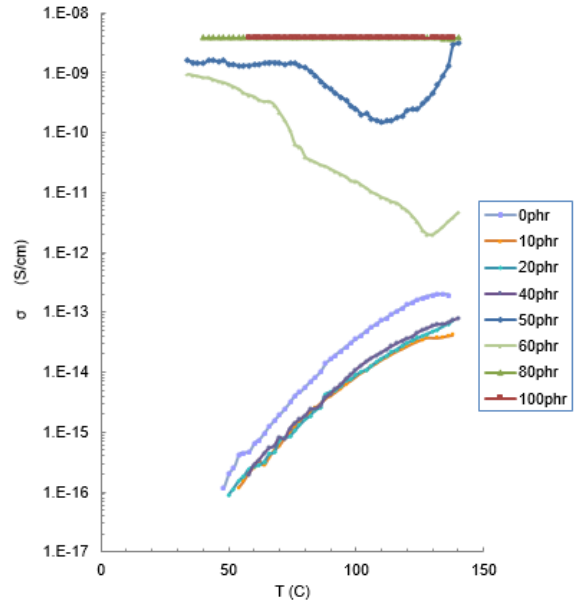


Fig. (7) Variation of conductivity with temperature of graphite/IIR composite in bulk form

As the temperature increases, the real volume fraction, ϕ , of graphite decreases due to the much high thermal expansion coefficient of the rubber matrix. This conclusion confirms the suggestion of X-S. Yi *et al* [25] that the loading level of filler $\phi(T)$ shows volume fraction dilution with matrix thermal expansion at the loading level (at room temperature).

Figures (5-6) represent the effect of temperature on the percolation concentration of the $\sigma - \phi$ curves. It is obvious that the percolation threshold shifts to higher filler volume fraction due to the increasing effect of the thermal expansion. So, for a given conductivity value, the quantitative volume fraction dilution effect caused by the matrix thermal expansion can only be compensated by adding the same quantity of conductive filler.

b. Effect of temperature

The effect of temperature on conductive rubber composite is shown through figures (7-8). Obviously from these figures the conductivity increases with temperature (for graphite loading ≤ 50 for IIR matrix in the bulk form and ≤ 20 for IIR in the membrane form) up to 140 °C. This positive temperature coefficient (PTC) is also observed in the composite

Table (3): The fitting parameters of Fournier equations

Temp.(°C)	Bulk		membrane	
	ϕ_c	b	ϕ_c	b
60	0.225	125	0.08	70
80	0.23	125	0.085	70
100	0.234	125	0.09	70
120	0.25	125	0.095	70
140	0.27	75	0.1	70

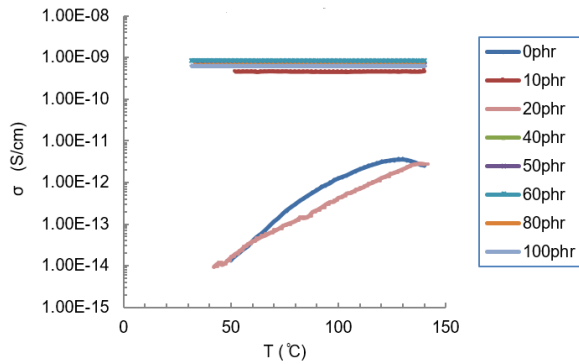


Fig.(8) Variation of conductivity with temperature of graphite/IIR composite in membrane form

systems based on NBR, EPDM, and their blends [26]. The magnitude of change, as well as the rate of change, in conductivity is the highest for pure IIR bulk based systems and the least for the IIR membrane based composites system. The relative change of the conductivity with temperature also depends on the amount of graphite loading (as shown in Table (4)) against temperature for all system. All samples show a pronounced PTC transition, which strongly indicates that the thermal volume expansion is one of the dominant factors responsible for the detected switch behavior [27].

A main mechanism of PTC effect for these polymer composites has been suggested, which implies that when these materials are exposed to an elevated temperature, the thermal expansion or thermal stress breaks some conducting paths in the conducting network, and thus the contribution of the thermal activation process of the polymer matrix is predominant [28], [29].

Table (4): Relative change of the conductivity with temperature

IIR Graphite content (phr)	TCC (C ⁻¹) bulk			TCC membranes		
	T = 30-80°C	80-110°C	110-140°C	30-80°C	80-110°C	110-40°C
0	9.3 × 10 ⁻³	0.034	8.29 × 10 ⁻³	0.0134	0.028	-0.032
10	0.015	0.024	0.016	----	----	----
20	0.012		0.021	0.65		0.085
40	0.0152		0.025	----	----	----
50	-0.028		0.546	----	----	----
60	-0.022	-0.068	-0.13	-5.95 × 10 ⁻⁴		
80	-5.51 × 10 ⁻³		-6.65 × 10 ⁻⁴	----	----	----

The increase of conductivity with temperature is attributed mainly to three reasons: the first is that the thermal emission of electrons through the gap between neighboring graphite particles when the particles are separated by a distance which do not amount to physical contact this leads to an increase in conductivity with rise of temperature. The second reason is that the rearrangement of small graphite particles takes place during heating, which lead to formation of more conductive networks.

This enhances the process of conduction. The third is that; during heating where oxidative cross linking at the surface takes place [30], and hence promotes conductivity. This is due to the incorporation of polar carbonyl groups. This could be due to the free electron pairs in collaboration with the flowing current.

5. CONCLUSIONS

The percolation threshold ϕ_c was found to be less than 0.12 for the graphite /IIR (membrane state) and much higher than 0.25 for the graphite/IIR (bulk state). Also, the value of ϕ_c increases with temperature for all samples. Moreover the Fournier equation achieved the best fitting for all samples in both graphite/IIR. The IIR matrix exhibited a high value of the temperature coefficient of conductivity (TCC). The highest value of TCC was obtained in membrane form (i.e. the membrane form is more thermo-sensitive than the bulk one).

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