HOPPING CONDUCTIVITY IN – POLYMER MATRIX - GRANULAR METAL COMPOSITES

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ABSTRACT

Charge transport properties, such as temperature dependent dc conductivity and frequency dependent conductance, of polymer matrix – metal particles composites are investigated in the present study. Both dc and ac conductivity are examined with varying parameters the filler content, temperature and frequency in the case of ac field. The conductive filler concentration remains in all systems lower than the critical value or percolation threshold, which determines the insulator to conductor transition. The temperature and frequency dependence of conductivity gives evidence for the charge carriers transport mechanism via the occurred agreement of experimental results and the employed hopping models (variable range hopping model and random free-energy barrier model).

1. INTRODUCTION

Composites systems consisting of an insulating matrix and randomly dispersed fine conductive particles have generated significant research interest, mostly, due to their electrical and electromagnetic performance [1]. The primary applications for conductive phase-polymer host composites refer to electromagnetic interference (EMI) shielding, radio frequency interference (RFI) shielding and electrostatic dissipation of charges (ESD). Furthermore, conductive polymer composites are used as electrical conductive adhesives and circuit elements in microelectronics [2] and have been reported to possess anticorrosive behaviour as metal components coatings [3].

Composite materials of an amorphous polymeric matrix and randomly dispersed metal particles are considered as heterogeneous disordered systems [4,5,6]. The electrical performance of granular materials, as these systems are sometimes referred to, is directly related to the permittivity and conductivity of the constituent phases, the size, shape and volume fraction of the inclusions and can be experimentally investigated by means of Dielectric Spectroscopy (DS) and dc conductivity measurements [1,7,8].

The majority of the available studies refers to binary systems, where the initial low concentration of the conductive phase is gradually increased in order to achieve a conductive or semi-conductive behaviour. The concentration of the inclusions has been proved to be a crucial parameter, governing the insulator to conductor transition of the composites. When the filler content is low, the mean distance between metal particles or clusters is sufficient large and conductance is restricted by the presence of the dielectric matrix. On the other hand, by increasing the conductive phase content the metal "islands" get closer and at a critical concentration of the filler a physical path is formed, through which the current can flow percolating the whole system. The insulator to conductor transition is described by means of percolation theory, where a critical concentration of the conductive filler is necessary for the sharp increase of conductivity [4]. Percolation theory defines the insulator to conductor transition according to the equation

$$\sigma \sim (P - P_c)^{\alpha} \qquad (1)$$

where P_c is the critical concentration or percolation threshold and a is the critical exponent [8,9]. However, the resulting description is valid only in the short vicinity of percolation threshold or above it. In any other case and by considering the insulating nature of the matrix, the observed conductivity should be originated by the transportation of charge carriers between neighbouring isolated conductive sites [1,10]. Most of the experimental work carried out [4,5] concerns the sharp increase of conductivity in the transition range, and is conducted by means of dc measurements. Although considerable conductivity has been recorded below percolation threshold [1,7], scarce attention has been given to the corresponding conductance mechanisms [1,11,12].

In the present study dc and ac conductivity of composite systems consisted of an epoxy resin matrix and metal particles is examined with varying parameters the filler content, temperature and frequency in the case of the ac field. In order to investigate further, the physical origin of the occurring charge transport in granular metal composite systems, well below the percolation threshold, different hopping models have been employed and applied on both dc and ac data. The examined models are the Variable Range Hopping (VRH) model proposed by Mott [13,14] and the Random Free-Energy Barrier model (also referred to as the symmetric hopping model) proposed by Dyre [6,15].

2. EXPERIMENTAL

A commercially available bisphenol type epoxy resin (D.E.R 321, Dow Chemicals) was used as a prepolymer with epoxy equivalent 182-192 and viscosity 5-7 P at 25 ^{o}C. As curing agent a cycloaliphatic amine (Chemmammine CA7 Henkel) at 30 phr (parts per hundred) was employed. While the above systems were still in the liquid state, various amounts of metal powder were added for the production of the composite samples. Iron powder from Ferak Art 21930 was used after drying at 100^{o}C for 48 hours, without any treatment and surface modification. Grains had the shape of a spheroid, with the mean diameter varying between 0.3 and 6 μm. The Iron particles content in the produced specimens was varying from 0 to 60 phr or from 1.5 to 17.0 % in volume fraction. A detailed description of the preparation procedure can be found elsewhere [1,7]. Dielectric measurements were performed by means of a Video bridge T-2100 (Electro-Scientific Industries Inc.) in the frequency range 10 Hz-3 kHz, and by an Impedance Analyser LF 4192 A (Hewllet Packard) in the frequency range 3 kHz -13 MHz. Both instruments were interfaced to a PC for simultaneous control and automated data acquisition. Direct current conductivity measurements were performed using the high resistance meter HP4339A of Hewlett-Packard according to ASTM D257-91 specifications. The test cell was a three terminal guarded system constructed according to the ASTM D150-92 specifications [1,7]. Temperature was varied from ambient to 140 ^{o}C.

3. RESULTS

The direct current conductivity, of all the examined composites, versus the Iron particles content is shown in Fig.1 at temperatures varying from 35 to 120 ^{o}C. Conductivity is slightly increasing with Iron content at any examined temperature. The absence of an abrupt increase in the conductivity values as a function of filler content signifies that the conductor to insulator transition has not been achieved in the present set of composite systems. Leading thus, to the reasonable conclusion that the concentration of metal particles for all the systems, is well below the percolation threshold and any further investigation of conductivity or charge transport mechanisms should not be carried out inside the scheme of percolation theory. In the same figure, a considerable increase of conductivity as temperature is raised, at constant conductive filler content, is also present. Conductivity values alter by almost four orders of magnitude with temperature, indicating a thermally activated process. In systems with

conductive impurities, charge transport is a rate determined effect, which can be described by the emission or absorption of a phonon each time a charge carrier moves from one site to another [13,14,16]. The temperature dependence of conductivity can be expressed as follows

$$\sigma(T) = \sigma_0 \exp\left[-\frac{E_A}{k_B T}\right] \tag{2}$$

where σ_0 is conductivity at infinite temperature a parameter lightly dependent on temperature, E_A is the activation energy and k_B the Boltzmann constant.

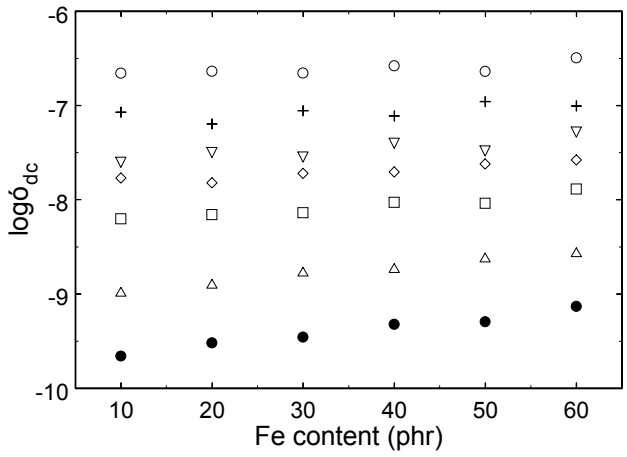

Fig. 1. The dc conductivity ($\log\sigma_{dc}$) versus the Iron content of composites, at various temperatures: (•) 35°C, (Δ) 50°C, (□) 70°C, (◊) 80°C, (▽) 90°C, (+) 100°C and (O) 120°C.

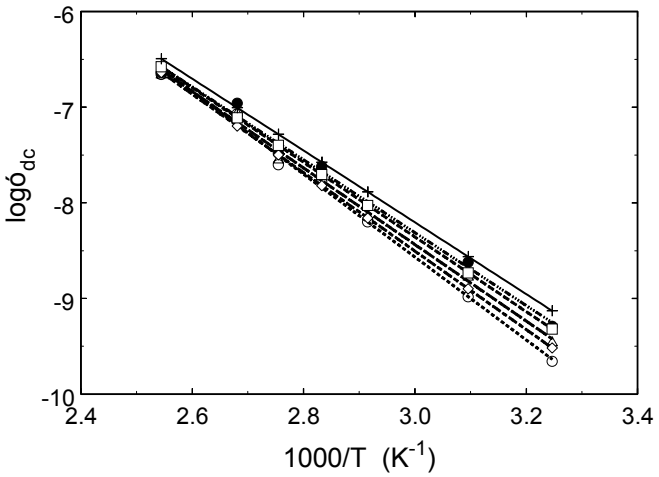

Fig. 2. The dc conductivity ($\log\sigma_{dc}$) versus the reciprocal of temperature ($1000/T$) of the composites with: (O) 10, (◊) 20, (Δ) 30, (□) 40, (•) 50, (+) 60 phr in Iron content.

Eq. (2) is valid for insulators and semiconductors, extrapolating conductivity to zero when temperature tends to zero. Fig. 2 provides plots of dc conductivity as a function of reciprocal temperature for all the examined systems. Experimental data are satisfactory linear fitted,

revealing the Arrhenious type or the single thermally activated process. From the linear fits the activation energy can be easily derived for each composite system, Table 1. The values of activation energy are decreasing as the conductive filler increases. The activation energy reflects the microstructure of the composites being a function of the mean radius of metal islands and the mean interparticle separation [17]. Thus, the formation of metal clusters inside the specimens and the reduction of interparticle separation by increasing the volume fraction of the conductive phase results in lowering the corresponding values of activation energy. Furthermore, the parameter σ_0 can be considered as constant, since the influence of temperature on σ_0 appears to be negligible with respect to the temperature dependence of the exponential factor in Eq. (2). Finally, the agreement between experimental data and Eq. (2) offers a secondary indication that no physical conductive network has been formed in the composites and hence there is no ohmic contribution to the overall dc conductivity.

Table 1. Specimen's content in Iron particles and the corresponding values of activation energy.

Fe (phr)	Fe volume fraction (%)	E_A (eV)
10	1.5	0.858
20	2.5	0.812
30	5.7	0.792
40	8.1	0.773
50	11.0	0.755
60	17.0	0.743

4. DISCUSSION

If the conductive particles are in contact, inside the insulating matrix, percolation paths should exist through the entire system and thus metallic type conduction is expected to occur. In that case σ_{dc} should tend to a finite value as $T \to 0$ and Eq. (2) should be far from being applicable on experimental data. The manifested absence of any physical contact of the inclusions, or any conductive path through which current can percolate the whole system, prompts to investigate conductivity in the field of another charge carrier transport mechanism.

Aiming to examine further the electrical transport properties of the polymer-metal particles systems at concentrations of the conductive phase well below the percolation threshold, two different hopping models have been employed and discussed. The Variable Range Hopping (VRH) model proposed by Mott [13,14] and the Random Free-Energy Barrier model (also referred to as the symmetric hopping model) proposed by Dyre [6,15]. The term hopping refers to sudden displacement of a charge carrier from one position to another neighbouring and in general includes both jumps over a potential barrier and quantum mechanical tunnelling [18,19].

4.1 Variable Range Hopping model

The temperature dependence of dc conductivity and the inherent charge transport mechanism in amorphous and disordered materials can be described by means of VRH model. The VRH mechanism, originally proposed by Mott, is a phonon assisted charge carrier transport process [13,14]. The charge carrier moves (hops) from a localized state to a nearby localized state of different energy, or to a localized state of similar energy with spatial separation from the initial site. If i and j denote the initial and the final state, the transition rate Γ_{ij}, according to Mott [14,20] can be expressed as

$$\Gamma_{ij} = \nu_0 \exp(-2\alpha R_{ij}) \exp\left(-\frac{\Delta E_{ij}}{k_B T}\right) \quad (3)$$

where α^{-1} is the decay length of the localized wave function, R_{ij} the hopping distance, ΔE_{ij} the energy difference between the two states, k_B is the Boltzmann constant and ν_0 a constant depending on the strength of the charge carrier-phonon interaction, which can be considered [20] to represent the number of hop attempts per unit time. At considerable low temperatures where $k_B T$ is small compared to ΔE_{ij} the second exponent of Eq. (3) tends to zero and according to VRH prediction carriers do not jump to the nearest site but to the energetically favourable. The VRH description is considered as equally applicable to charge carriers as electrons, holes, polarons or bilolarons provided that the suitable wavefunction is employed. If the interaction between electrons is neglected, the dependence on temperature of dc conductivity follows the formula

$$\sigma(T) = A \exp\left[-\left(\frac{T_0}{T}\right)^{\gamma}\right] \quad (4)$$

where the parameter A can be considered as the limiting value of conductivity at infinite temperature, T_0 is the characteristic temperature that determines the thermally activated hopping among localized states at different energies and considered as a measure of disorder [21] and the exponent γ is related to the dimensionality d of the transport process via $\gamma = 1/(1+d)$, where d =1,2,3. In the conventional VRH model the parameters A and T_0 are functions of localization length and density of states. There is an extensive literature [13,14,18] on the pre-exponential factor A. The parameter A depends on the assumptions made about the electron-phonon interaction [13], and in most of the cases is considered as constant although is slightly affected by temperature.

The applicability of the VRH model is examined by plotting the experimental results as $\log \sigma T^{1/2} = f(T^{-\gamma})$. In general the least square fitted curves provide a first hand indication not only for the nature of the charge transport mechanism but also for the dimensionality of the process. In the present study, γ is assumed to be equal to 1/4 for two reasons: (i) the examined systems are bulk polymer specimens (with thickness ~ 3mm) incorporating randomly distributed conductive particles, hence it is reasonable to consider that they are characterised by a 3-D conduction process, (ii) the quality factor R^2 describing the linear fit is closer to unity when γ= 1/4 is employed rather than γ= 1/3, Fig. 3.

4.2 Random Free-Energy Barrier model

The random free-energy barrier model (also referred to as the symmetric hopping model) proposed by Dyre [6,15], describes the frequency dependent conductivity, over a wide range of frequencies, in disordered solids at constant temperature. This model is based on the ascertainment that dc conductivity is thermally activated, $\sigma_{dc} \propto \exp\left(-\frac{\Delta E_{dc}}{kT}\right)$, and ac conductivity is less temperature dependent. The latter suggests that ac conduction is dominated by processes with activation energies smaller than ΔE_{dc}. In this model, the assumed as non-interacting charge carriers remain at sites with minimum energy. Occasionally, a charge carrier acquires by heating from its environment, sufficient energy to

overcome the energy barrier ΔE and to jump to the nearest-neighbour site. The jump rate (or the jump probability per unit time) between two neighbouring sites *i* and *j* is given [6,15] by

$$\Gamma_{ij} = \nu_0 \exp\left(-\frac{\Delta E}{k_B T}\right) \tag{5}$$

where ΔE the barrier to overcome or activation energy can vary randomly and ν_0 is the attempt frequency. The term "symmetric" refers to the fact that the jump rate is the same for jumps forward and backwards across a given barrier, that is $\Gamma_{ij} = \Gamma_{ji}$. By employing a continuous time random walk approximation and the above mentioned assumptions, Dyre [15] derived the following equation for ac conductivity in disordered solids:

$$\sigma_{ac}(\omega) = \sigma_{dc}\left[\frac{j\omega\tau}{\ln(1+j\omega\tau)}\right] \tag{6}$$

where, σ_{dc} , ω and τ are the direct current conductivity, the angular frequency and the relaxation time respectively. The random free-energy barrier model has been found to be in agreement with experimental data for a large number of disordered solids [6,15].

4.3 Hopping models and experimental data

The ac conductivity of all samples has been calculated from the dielectric losses according to the relation

$$\sigma^* = j\varepsilon_0\omega\varepsilon^*(\omega) = j\varepsilon_0\omega(\varepsilon' - j\varepsilon'') = \varepsilon_0\omega\varepsilon'' + j\varepsilon_0\omega\varepsilon' \tag{7}$$

The real part of $\sigma^*(\omega)$ is given by

$$\sigma_{ac} = \varepsilon_0\omega\varepsilon'' \tag{8}$$

where, ε_0 = 8.85 x 10^{-12} F·m^{-1} is the permittivity of the free space and $\omega = 2\pi f$ the angular frequency.

In Fig. 3 dc and ac, at constant frequency, conductivity data are presented as a function of temperature. In all cases data are well described by linear curves, implying hopping as the origin of the recorded conduction process. It should be noted that this is the first time, up to the best of the author's knowledge, where the VRH model is applied on isochronal ac conductivity data. The frequency and composition dependent values of T_0, as derived from the linear curve fits, are listed in Table 2. The values of T_0 are high for all the examined specimens indicating the insulating (low conductivity) nature of the systems. A weak diminishing tendency, which appears with increasing conductive filler content is in accordance with experimental results from different systems with varying conductivity [11,16]. Finally, conductivity values are increasing with frequency since alternating current conductivity sums all dissipative effects including an actual ohmic conductivity caused by migrating charge carriers as well as a frequency dielectric dispersion [22].

The log $\sigma(\omega)$ versus log f plots given in Figure 4, for the composites with 10 and 50 phr in Iron content, help to reveal further the ac behaviour of the systems. It is evident that ac conductivity is both frequency and temperature dependent and increases, up to five orders of magnitude, with increasing frequency and temperature. However the influence of temperature

is more pronounced in the low frequency range, while at the high frequencies edge the values of $\sigma_{ac}(\omega)$ display proximity. At low frequencies where the applied electric field, forces the charge carriers to drift over large distances, as temperature is increased, a tendency to retain almost constant values is recorded. When frequency is raised the mean displacement of the charge carriers is reduced and the real part of conductivity, after reaching a certain critical frequency f_c, follows the law $\sigma_{ac}(\omega) \sim \omega^s$ with $0 \le s \le 1$ characterizing hopping conduction [6,18]. The critical frequency f_c has been found to be dependent on temperature and conductive filler volume fraction [7,8,15].

Table 2. Values of T_0 as resulted from the linear fits of VRH model in Figure 3.

f (Hz)	T_0 (K)		
	Composite with 10 phr in Fe content	Composite with 30 phr in Fe content	Composite with 50 phr in Fe content
dc	6.55×10^{10}	4.79×10^{10}	3.96×10^{10}
10^2	4.36×10^{10}	3.73×10^{10}	3.55×10^{10}
10^3	2.01×10^{10}	1.54×10^{10}	1.39×10^{10}
10^4	3.25×10^{9}	2.77×10^{9}	2.34×10^{9}
10^5	1.47×10^{8}	1.92×10^{8}	1.71×10^{8}
10^6	3.24×10^{7}	4.67×10^{7}	4.48×10^{7}

In general at a constant temperature ac conductivity can be expressed as [18]

$$\sigma(\omega) = \sigma_{dc} + A(\omega)^s \tag{9}$$

where σ_{dc} is the $\omega \to 0$ limiting value of $\sigma(\omega)$ and A, s parameters depending on temperature and filler content [8,15]. Eq. (9) is often called "the ac universality law" since it has been found to satisfactorily describe the ac response of numerous different types of materials, which can be classified as disordered solids [6,15].

In Fig. 4 Eq. (6) is used in a predictive way. As it can be seen, it qualitatively follows the dispersion of ac conductivity. In the low frequency edge reveals the tendency of conductivity to achieve a constant value, while in the high frequency region verifies the exponential law of conductivity. In the low and intermediate frequency regime and at high temperatures, the produced curves deviate from experimental data by not being able to describe the recorded relaxation and pointing out that in the vicinity of the relaxation peaks the power law is not applicable [1].

The analysis carried out concludes, that the employed hopping models describe, satisfactorily, conductivity in the examined composites systems. A common feature of both models is their applicability on disordered materials, where the examined systems are also classified. Each model provides a description of conductivity under the influence of a different parameter. The VRH model reveals the influence of temperature on conductivity when the frequency of the applied field remains constant. The random free-energy barrier model shows the influence of frequency on conductivity at constant temperature. In both cases, electrical conduction in polymer matrix-granular metal composites, below the percolation threshold, appears to be resulting from charge carriers hopping between isolated metallic grains.

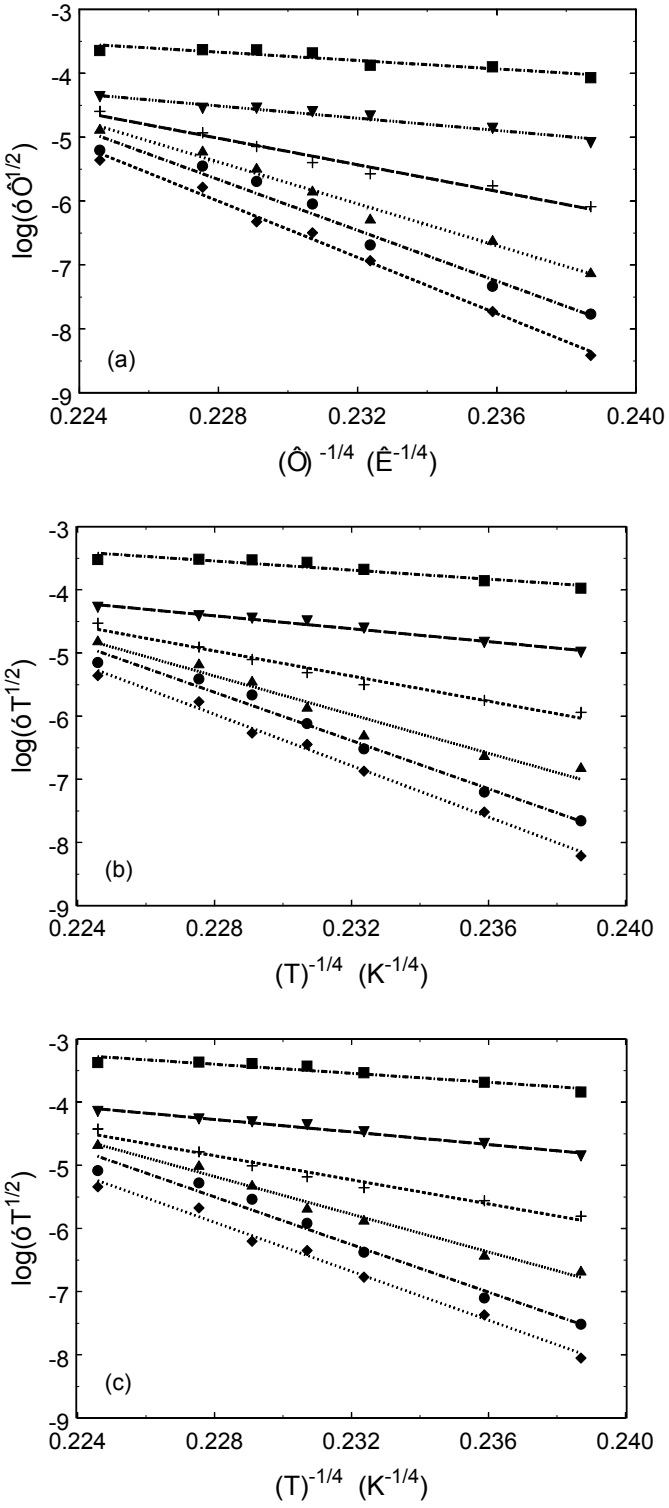

Fig.3. Conductivity data of the composites with (a) 10, (b) 30 and (c) 50 phr in Iron content, as described by the Variable Range Hopping model for a 3-D transport mechanism. (♦) dc, (●) 10^2 Hz, (▲) 10^3 Hz, (+) 10^4 Hz, (▼) 10^5 Hz, (■) 10^6 Hz.

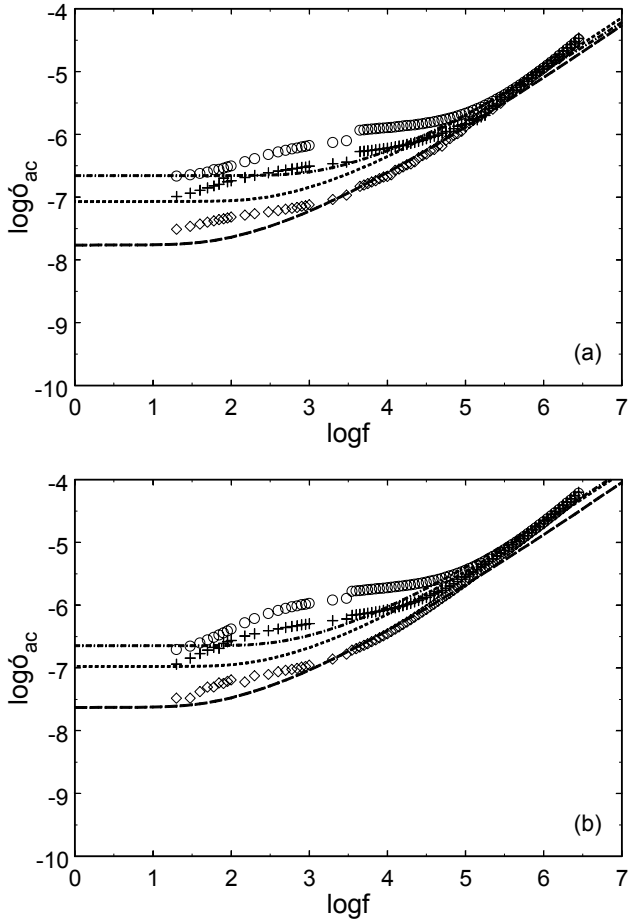

Fig. 4. The ac conductivity ($\log\sigma_{ac}$) versus log$f$ of the composites with (a) 10 and (b) 50 phr in Iron content, at various temperatures: (◊) 80 °C, (+) 100 °C, (O) 120 °C. Dashed lines are produced by the random free-energy barrier model, the used values of dc conductivity were the measured and found to be (a) 1.7 x 10^{-8}, 8.5 x 10^{-8} and 2.2 x 10^{-7} $(\Omega\text{-m})^{-1}$ and (b) 2.40 x 10^{-8}, 1.10 x 10^{-7} and 2.30 x 10^{-7} $(\Omega\text{-m})^{-1}$ respectively to each of the examined temperatures.

5. CONCLUSIONS

The physical origin of both dc and ac conductivity of polymer matrix – Iron particles composites, below the percolation threshold, has been investigated in the present study. The variable range hopping model and the random free-energy barrier model have been employed in order to reveal the mechanism of charge carriers transport under the influence of temperature and frequency of the applied field. Both models are in good agreement with experimental data suggesting hopping transport of carriers as responsible for the recorded performance.

ACKNOWLEDGEMENTS

The author would like to thank Prof. G. M. Tsangaris (Department of Materials Science and Technology, School of Chemical Engineering, National Technical University of Athens, Greece) for providing access to experimental data and facilities.

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