Electrical transport properties of CB/epoxy polymer composites

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Conductivity measurements were made on carbon black/epoxy-resin composites over the temperature range from 22 to 70 °C (T_g ≈83 °C) and for volume fractions of carbon black from 0.1 to 3.0%. The temperature effects on the electricall conductivity of these heterogeneous materials are analysed by Mott's variable range hopping model, in order to understand their conduction transport mechanism. Using this model we were able to calculate meaningful values for the density of states, hopping distance and hopping energy. The calculated Mott's parameters of epoxy-resin doped with carbon black were found to be consistent with the Mott's requirement. The effect of the addition of carbon black particles was to reduce the density of states near the Fermi level.

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1. Introduction

In recent years, the electrical properties and electromagnetic performance of carbon black/polymer composite blends have been extensively studied [1-7] owing to their significance in technology as well as in fundamental science. Electrically, conducting polymers are an important class of materials with potential applications. The primary uses of conductive polymer host composites include interference shielding and electrostatic dissipation of charges [8-10]. In addition to this, conducting polymer composites are used as electrically conductive adhesives and circuit elements in microelectronics [11]. The electrical performance of composite materials is closely related to the conductivity of the constituent components: the size, shape and volume concentrations of the particles. They can be experimentally tested via conductivity measurements [12]. Polymer epoxy matrix composites are principally electrical insulators owing to their low concentration of free charge carriers. Hence, their electrical response is essentially associated with relaxation occurrences that are affected by an alternating current (AC) field. The observed relaxation processes are linked to dipolar orientation effects or space charge migration [13-14]. Charge mobility and interfacial polarisation are deemed as the genesis of dielectric effects. At lower temperatures, polar side groups enhance the electrical performance of the system. Interfacial polarisation is the result of the heterogeneity of the system, e.g., mobile charges assembled at the polymer-filler interface form large dipoles. The volume concentration of the conductive charges has been proved to be a crucial parameter governing the electrical behaviour of the polymer composites [15]. When the filler content is low, the mean distance between charge particles or clusters is large and conductance is limited by the presence of the dielectric polymer matrix. At a critical volume fraction (or percolating threshold) of the filler, a physical path is formed in a way that the current can flow, percolating the whole system.

This paper presents a study of the effect of carbon black particles (CB) on the electrical properties of an epoxy-resin (DGEBF) polymer. The electrical conductivity as a function of temperature was used to study the charge transport mechanism in the composites. The various Mott's parameters were estimated for samples exhibiting variable range hoping conduction in the low temperature region.

2. Experimental

The three-dimensional randomly mixed conductor/insulator that we studied consists of small carbon black particles (produced by Cabot Co) embedded in an insulating epoxy-resin matrix DGEBF: Diglycidylic Ether of Bisphenol F (from Ciba Geigy Co.). The mixture of DGEBF and CB particles was processed with an amine curing agent (4,9-dioxadodecan-1,12-diamine, equivalent weight=81, supplied by BASF). The ratio, by weight, of the mixture of the DGEBF and CB particles to the amine curing agent was adjusted to achieve stoichiometry [16-18]. The carbon black particles had an average size 11 nm, DC conductivity 350 $(\Omega.m)^{-1}$, density 1.89 $g.cm^{-3}$, specific surface area 639 $m^2.g^{-1}$ and percolation threshold $\Phi_c \approx$ 2.75%. The epoxy-resin matrix had a DC conductivity of 1.4 10^{-14} $(\Omega.m)^{-1}$, density of 1.19 $g.cm^{-3}$ and glass transition temperature of $T_g \approx 83$ °C [19]. The mechanical mixing operation that was used to fabricate samples with specific CB volume concentration Φ, has been previously

described in detail elsewhere [20, 21]. The resin, the hardener, and fillers were out gassed and stirred in a vacuum chamber at room temperature for 24 h. The CB loading, Φ, was varied from 0.1 to 3.0 %.

The AC conductance and capacitance were measured by using a Hewlett Packard 4194A Impedance Analyzer. The DC conductivity was obtained from the AC conductivity by extrapolation ($\omega \rightarrow 0$). Estimating relative error on the conductivity is $\Delta\sigma/\sigma \leq 3$ %.

3. Results and discussion

In the composite materials, the DC electrical conduction takes place by charge hopping between and along the polymeric chains. The DC conductivity shown as $log\,\sigma_{DC}$ versus T in Fig. 1 increases slowly with temperature in the range from 295 to 343 K. This suggests that the conduction is due to variable range hopping in the localised states near the Fermi level.

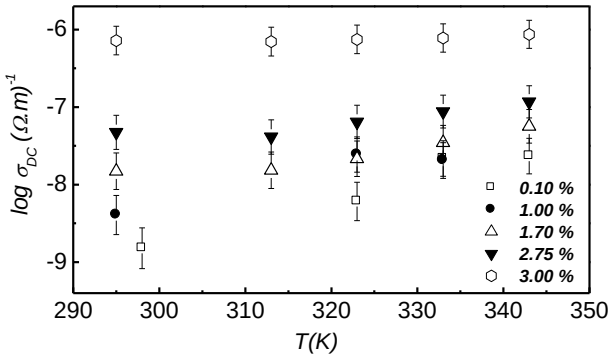

Fig. 1. $log\,\sigma_{DC}$ versus T at several concentrations of CB in the epoxy-resin composite. The estimated error bars represent the uncertainty of DC conductivity measurements.

A model that can be used to describe the conduction process is that one originally developed for amorphous silicon by Mott–Davis [22]. When applied to conducting polymers, it assumes that charge transport originates from localized or fixed states within the polymer chain. The charge transfer between the chains takes place by hopping, referred to as phonon assisted hopping, between two localized states. Lattice vibrations enhance this process of tunneling from one localized state to another. Plots of DC conductivity versus temperature can be parameterised by Mott's Variable Range Hopping conduction model, characterised by the expression

$$\sigma_{DC}(T) = \frac{\sigma_o}{T^{1/2}} \exp\left[-\left(\frac{T_o}{T}\right)^{1/4}\right] \qquad (1)$$

and the Mott characteristic temperature T_o

$$T_o = \lambda\alpha^3 / kN(E_F) \qquad (2)$$

where $N(E_F)$ is the density of localized states at the Fermi level (E_F), and α describe the spatial extent of localized wave function. The characteristic temperature T_o can be associated with the effective energy barrier between localized molecular chains [23]. High value of T_o implies strong localisation of carriers inside the molecular chains, resulting in the decrease of the conductivity [23].

The pre-exponential term σ_o of equation (1), as obtained by various workers [24, 25], is given by:

$$\sigma_o = 3e^2 \upsilon_{ph} \left[N(E_F)/8\pi\alpha k\right]^{1/2} \qquad (3)$$

where e is the electron charge ($1.602\ 10^{-19}$ C), k is Boltzmann's constant (8.616×10^{-5} eV.K^{-1}) and υ_{ph} the Debye frequency ($\approx 10^{13}$ *Hz*). A solution of equations (2) and (3) yields to

$$\alpha = 21.12\ \sigma_o\, T_o^{1/2} \qquad (4)$$

and

$$N(E_F) = 1.97 \times 10^9\ \sigma_o^3\ T_o^{1/2} \qquad (5)$$

The average hopping distance, R_{hop}, between two localised states and the hopping energy, W_{hop}, are given by the following equations [24]:

$$R_{hop} = \left[9/8\pi\alpha kTN(E_F)\right]^{1/4} \qquad (6)$$

and

$$W_{hop} = 3/\left(4\pi\ R^3 N(E_F)\right) \qquad (7)$$

The low-temperature conductivity data were replotted as $ln(\sigma_{DC}.T^{1/2})$ versus $T^{-1/4}$ in Fig. 2. Various Mott's parameters, such as T_o, σ_o, α, $N(E_F)$, R_{hop} and W_{hop} were calculated from equations (1) to (7), and resumed in Table 1.

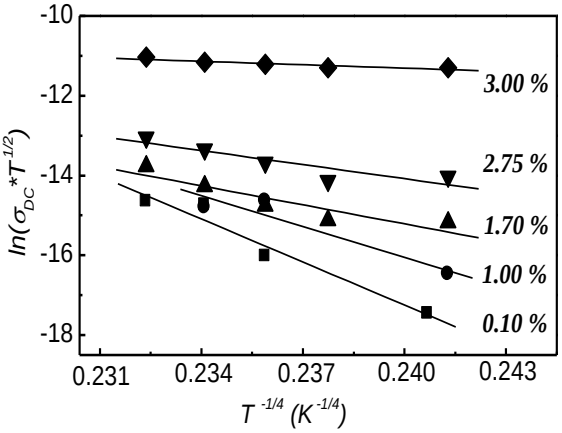

Fig. 2. $ln(\sigma_{DC}.T^{-1/2})$ versus $T^{-1/4}$ for various concentrations of CB in the epoxy-resin composites. The solid lines represent the best linear fits to the data with the correlation coefficient r between 0.90 and 0.98. The values of parameters σ_o and T_o resulting from the calculated slopes are reported in Table 1.

Table 1. Mott's parameters of carbon black/epoxy-resin in the temperature range from 295 to 343 K. The errors in R_{hop} and W_{hop} are the standard deviations.

Φ(%)	σ_o (S.cm^{-1}.K$^{1/2}$)	T_o (K)	α (cm^{-1})	$N(E_F)$ (eV^{-1} cm^{-3})	R_{hop}(cm) at. 298 K	$\alpha.R_{hop}$ at. 298 K	W_{hop}(eV) at. 298 K
0.10	$9.25\ 10^{29}$	$1.66\ 10^{10}$	$2.52\ 10^{34}$	$2.01\ 10^{98}$	$(1.28\pm0.05)\ 10^{-33}$	32.26	0.55±0.12
1.00	$3.49\ 10^{19}$	$4.43\ 10^{9}$	$4.86\ 10^{23}$	$5.43\ 10^{66}$	$(4.79\pm0.18)\ 10^{-23}$	23.28	0.40±0.09
1.70	$3.58\ 10^{9}$	$6.39\ 10^{8}$	$1.91\ 10^{13}$	$2.28\ 10^{36}$	$(7.52\pm0.28)\ 10^{-13}$	14.36	0.25±0.05
2.75	$1.46\ 10^{6}$	$1.87\ 10^{8}$	$4.22\ 10^{9}$	$8.38\ 10^{25}$	$(2.50\pm0.10)\ 10^{-9}$	10.55	0.18±0.04
3.00	$1.83\ 10^{-2}$	$6.52\ 10^{5}$	$3.12\ 10^{2}$	$9.75\ 10^{6}$	$(8.23\pm0.31)\ 10^{-3}$	2.57	0.04±0.01

It is obvious from the table above that $\alpha.R_{hop} \geq 2.57$ and $W_{hop} \geq 0.04$ eV. Hence, the present measurements are in fair agreement with the Mott and Davis conditions for variable range hopping conduction which are $\alpha.R_{hop} >> 1$ and $W_{hop} >> kT$ [25]. The density of localised states $N(E_F)$ decreases with increasing carbon black concentration in the epoxy-resin matrix (Fig. 3). The effect of the addition of carbon black particles is to reduce the density of states near the Fermi level and increase the localisation length α^{-1} enhancing the spatial extent of the localized states.

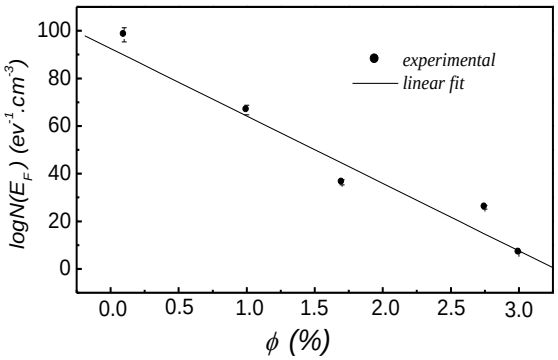

Fig. 3. Density of states as a function of CB concentrations loaded in epoxy-resin matrix. The estimated error bars represent the uncertainty in estimating the density of localized states $N(E_F)$. The solid line represents the best linear fits to the data.

From Table 1, the parameters T_o and σ_o have higher values for lower doped samples and consequently higher $N(E_F)$ values compared with the theoretical values of approximately 10^{19}–10^{20} cm^{-3} eV^{-1} [26] which can be explained by the fact that these composites are not conducting materials. From Figs. 4 and 5 it appears that the hopping distance, R_{hop}, decreases and hopping energy, W_{hop}, increases with temperature, for different volume fractions of CB loaded in the epoxy-resin matrix. This type of behaviour may be due to the increase of the disorder of the system with temperature, so that conduction takes place by hopping of carriers to states locations close to the initial state and between chains, resulting in decreased R_{hop} value. Similarly, W_{hop} increases because with the increase of disorder more energy is required by the carriers to make a transition between two states in the hopping process.

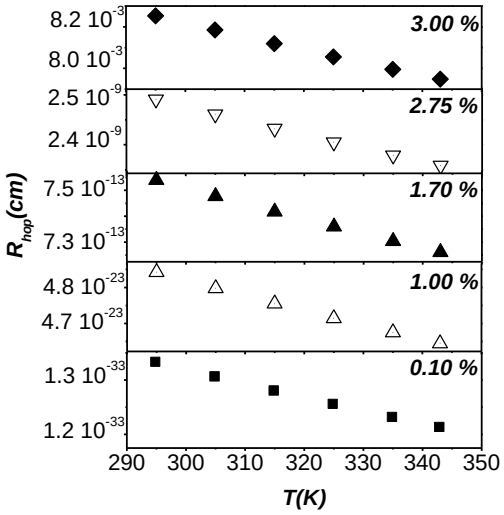

Fig. 4. Hopping distance as a function of temperature fordifferent concentrations of CB loaded in epoxy-resin matrix.

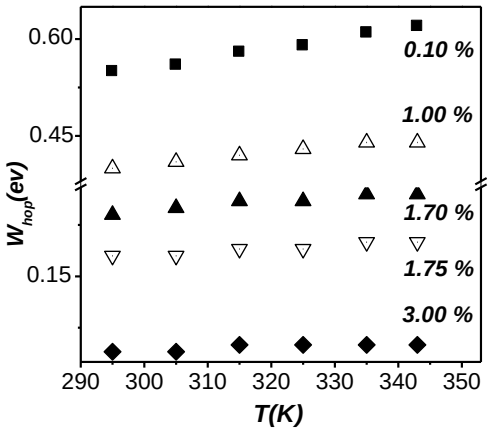

Fig. 5. Hopping energy as a function of temperature for different concentrations of CB loaded in epoxy-resin matrix.

4. Conclusions

From the above results and discussion, we conclude that hopping conduction was taking place in the carbon black/epoxy-resin matrix composites over the entire temperature range of investigation. The incorporation of carbon black into the epoxy-resin matrix resulted in a sharp decrease in the density of localised states near the Fermi level. In the range of temperature from 22 to 70 °C, that is, below the glass transition, we found that the conductivity was due to variable range hopping in the localized states at the Fermi level, which is in agreement with Mott's variable range hopping conduction.

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