In situ network structure, electrical and thermal properties of conductive epoxy resin–carbon black composites for electrical heater applications

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Abstract

Epoxy composites at high carbon black (CB) concentration exhibited good electrical and thermal stability, which can make them attractive for consideration in heating devices and conducting composite applications. The effect of CB on the network structure of epoxy composites, like volume fraction of epoxy network (\(V_r\)), the extent of CB reinforcing (\(\gamma\)), interparticle distance between conductive particles (IPD), epoxy–solvent interaction parameter (\(v\)), average number molecular weight between cross-links (\(M_c\)), number of elastically effective chains (NEC), cross-linking density (CLD) and scanning electron microscope (SEM), was investigated in details. The conductivity of an insulating epoxy matrix increases continuously with CB content and is well explained by percolation theory. The effects of different concentration of CB and sintering on the electrical conductivity of epoxy composite as a function of temperature during heating and cooling cycles were discussed. The conduction mechanism and negative temperature coefficient of conductivity (NTCC) of epoxy–CB composites were analyzed. The current–voltage–temperature and working power–temperature characteristics of these composites as a function of CB content were investigated. We attempt to contribute to a better understanding of the negative resistance phenomena in epoxy–CB composites. The nonlinear coefficient (\(\alpha\)), the size of conductive particles (SCP) and hopping distance (\(a_h\)) of charge carriers in epoxy–CB composites were evaluated. The thermal stability was tested by means of temperature–time curve at certain applied power, on and off, for one cycle. The characteristic thermal properties, like characteristic time growth (\(\tau_g\)), decay (\(\tau_d\)) and current (\(t_i\)) constants of epoxy as a function of CB content, were estimated. The specific heat (\(C_p\)) and amount of heat transferred by radiation and convection (\(h_r\)) were calculated based on energy balance concept as a function of CB content. The thermoelectric power (TEP) and thermal conductivity (\(k\)) as a function of temperature of epoxy–CB composite were discussed. In conclusion, the epoxy–CB composites show good thermal stability and they can be used as heating devices for consumer products.

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1. Introduction

Organic materials cannot be used alone for high performance applications because they have limited
properties. Therefore, organic/reinforcing filler composites are frequently employed in order to overcome the limitation. One of the widely used organic/reinforcing filler composites is an epoxy–carbon black (CB) and/or silica system [1–3]. Epoxy resins as organic have high strength, good stiffness, good thermal stability, excellent heat, moisture and chemical resistance; therefore, they are applied in the field of coatings, adhesives, casting, potting, composites, laminates and encapsulation of semiconductor devices [2–5]. However, the development of polymers with high electrical conductivity has opened up the possibility of new applications for polymers [6]. Polymer’s negative and positive temperature coefficient of conductivity (NTCC and PTCC) are examples of composites consisting of insulative polymer matrix and conductive filler. Conducting polymers can be obtained in two ways: by producing a polymer that is intrinsically conducting or can be made so by doping or by loading an electrically insulating matrix with conductive filler [7–10]. Carbon black, graphite or other conductive fillers are commonly used as a component of conductive and reinforcement polymer composites [11]. In fact, the electrical properties of conductive polymer composites depend on the nature of the polymer; the amount of filler, structure and porosity of filler; filler matrix interaction; mixing condition; etc. [4–12]. Therefore, for excellent physical and chemical properties, strong interfaces between polymer and fillers are needed. Nowadays, there is a great economic interest in NTCC and PTCC materials because of their technological applications as temperature or current sensors [13], flooring materials to dissipate static electric charge [14], pressure sensitive sensors which can be used for shockproof switches [15], sensors for measurement of vehicle weight to collect toll tax on roads [16], heater [17], antistatic coating \((\sigma = 10^{-6} - 10^{-5} \ \Omega^{-1} \ \text{cm}^{-1})\) and electromagnetic radiation shielding \((\sigma = 10^{-3} - 10^{-1} \ \Omega^{-1} \ \text{cm}^{-1})\) [18,19]. However, the exact mechanism of the PTCC and NTCC behaviors of polymer–CB composites is an unsolved issue [1–19].

Whenever such polymer composites are used as thermistor devices for electrical heater, they are subjected to repeated thermal cycles and it becomes necessary to understand how electrical conductivity changes with loading filler, repeated thermal cycles and applied working power. The power consumption of the thermistor devices is increasing, leading to raise the bulk temperature of the thermistor devices. It is, therefore, important to insure and understand the reliability under working power. To the best of our knowledge, no experimental work has been reported in the literature on the thermal stability of epoxy–CB composites under thermal cycles and working power. Thus, future application of these materials strongly depends on the success of improving their reliability with respect to thermal cycles and working power.

With this scope, the purpose of the present contribution is to present new data on the thermal stability under thermal cycles and working power. In addition, we attempt to give extensive experimental results that may lead to a better understanding of network structure, electrical and thermal properties of epoxy–CB composites for practical applications as heating devices and/or conducting composites.

2. Experimental

Polymer material used in this work was epoxy with a commercial type 815 and hardener type B002W produced by Yuka Shell Epoxy Chemical, Japan. The resin/hardening ratio was stoichiometric according to the manufacturers data sheets. The furnace carbon black, CB (Kunebo Chemical, Japan) with particle size 20 \(\mu\)m and surface area 120 m\(^2\) g\(^{-1}\) was used as a filler component in the composite. Five batches of CB/epoxy weight ratios are 4/6, 5/5, 6/4, 6.5/3.5, 7/3 and abbreviated as F4/6, F5/5, F6/4, F6.5/3.5 and F7/3, respectively. The green epoxy/hardener with different content of CB were prepared by centrifuging mixer (Matsuo, Japan) for 1 min at room temperature. The bulk samples of composite were obtained by casting the green composites on Teflon mould. Mosaic gold–copper electrodes were embedded into samples during preparation process to reduce the sample electrode contact resistance [2]. Then the epoxy–CB composites were cured in an oven at 80 °C for 3 h. Morphology study of the epoxy composites was conducted on Scanning Electron Microscopy (SEM, JSM-5310 LVB, JEOL). Hardness \(H_v\) has been determined using a universal testing machine (ASTM-D2240-
78). The density of epoxy–CB composites ($\rho_c$) was measured using the Archimedes methods [23]. Bulk electrical conductivity was measured through two-electrode technique [2]. The specimens with the attached gold–copper electrodes were placed in a special chamber where temperature was controlled in accordance with a desirable basic program. The heating and cooling rates were adjusted to about 1 °C/min. Original software was used to record the electrical conductivity with temperature interval 1 °C. the electrical conductivity ($\sigma$) is calculated according to the following equation: $\sigma=(I/V)(t/A)$, where $I$ is the electric current, $V$ the applied voltage, $t$ the thickness of the test epoxy–CB piece and $A$ the cross-sectional area.

The circuit used for measuring DC current–voltage characteristic was described elsewhere [1]. For sintering treatments, the samples were soaked in controlled chamber at 20 °C for 1 week in dry air. The thermodlectric power (TEP) measurements were made on computer-controlled equipment by gripping the samples between two blocks of the stainless steel. Two fine thermocouples were attached on the samples in order to measure the temperature gradient across these samples produced by heater attached to one of the stainless steel blocks. The Seebeck voltages at normal pressure were measured through the gold–cupper leads by Yokogawa portable data logger type P030. For the measurement of the power-dependent temperature, the sample was placed in controlled chamber at 20 °C. Computer controlled the temperature for each applied power. For the measurement thermal conductivity ($\lambda$), the electrical power was applied to the sample and once the thermal equilibrium was reached, the temperature was read by thermocouple. The electrical power was then changed in order to obtain a set of data. The thermal conductivity was obtained as a derivative of $W/cm K$.

### 3. Results and discussion

#### 3.1. Effect of carbon black on network structure

To verify the possibility that CB improves the network structure of the epoxy matrix, some physicochemical parameters were determined.

The volume fraction of epoxy network ($V_r$) has been determined by using the equilibrium swelling method [23]. The equation used for calculating the value of ($V_r$) in the swollen samples containing CB particles can be expressed by the following equation [2]:

$$V_r = \frac{(0.56e^{-\theta} + 0.44)\omega_0\rho_s}{\omega_0\rho_s + \omega_s\rho_r}$$

(1)

where $\theta$ is the concentration of CB in composites, $\omega_0$ is the weight of dry samples, $\rho_s$ is the weight of absorbed solvent, $\rho_s$ and $\rho_r$ are the densities of the solvent and epoxy, respectively.

The extent of CB reinforcing ($\gamma$) in epoxy composites is given by [21]:

$$\gamma = \left(1 - \frac{V_r}{\theta}\right) \div \left(\frac{\theta}{1 - \theta}\right)$$

(2)

The interparticle distance (IPD) between conductive particles is calculated by the equation [2]:

$$\text{IPD} = -D \left[ \left( \frac{k\pi}{6V_r} \right)^{1/3} - 1 \right]$$

(3)

where $D$ is the epoxy particle diameter and $k=1$ for cubic packing.

The epoxy–solvent interaction parameter ($\chi$) is given by the following equation [23]:

$$\chi = 0.431 - 0.311V_r - 0.036V_r^2$$

(4)

Fig. 1 shows the relationship between $V_r$, $\gamma$, IPD, $\chi$ and ($\rho_c$) for as-prepared and sintering samples at 80 °C for 1 week of epoxy–CB composites as a function of CB content. It is seen that $V_r$, $\gamma$ and $\rho_c$ increase, while IPD decreases for both batches with CB content increasing. This can be explained that the CB filled the free volume of epoxy mixture (i.e. reduced the interchain gaps between conductive particles) and created new conductive trajectories into epoxy composites. On the other hand, the values of $\chi$ decreases for both batches with increasing CB content and the level of sintering batch is lower than as-prepared batch. This ascribed to the higher interfacial interaction levels between CB and epoxy leading to a higher level of CB fracturing. This
supports that both CB and sintering improves the network density and interfacial adhesion in epoxy–CB matrix. To confirm, the number of elastically effective chains, in a network per unit volume, (NEC) is expressed by the following equation [19]:

$$NEC = \left(\frac{\rho_i N_A}{M_c}\right)$$

(5)

where $N_A$ is Avogadro’s number and $M_c$ the average number molecular weight between cross-links and can be determined by using the following equation [2]:

$$M_c = \frac{-\rho_i V_s V_f^{1/3}}{\ln(1 - V_f) + V_f + \chi V_f^2}$$

(6)

where $V_s$ is the molar volume of solvent used.

The cross-linking density (CLD) of epoxy composites was calculated by the following equation [2]:

$$CLD = \frac{1}{2M_c}$$

(7)

Fig. 2 displays the relation between NEC, $M_c$, CLD and hardness $H_v$ for two batches of epoxy composites as a function of CB content. It is clear that the NEC, CLD and $H_v$ increase, while $M_c$ decreases for the two batches and depends on CB content. The level of sintering batches is higher than as-prepared one. A possible reason for this may be that the CB filled by microviods is located at the interface of the epoxy matrix and, therefore, increases the intermolecular interaction and the network density of the epoxy matrix. Besides, the $H_v$ increases with increasing CB
content and the level of sintering batch is higher than as-prepared one. The reasons are that CB reduced the creep of the epoxy matrix and therein led to enhance the network structure stability within the epoxy matrix as confirmed by SEM. In our opinion and based on previous results, the higher and better level of physicochemical parameters for sintering batch compared to as-prepared batch reflects that the sintering acts as an additional cross-linking agent and/or charge carriers reservoir (i.e. creating a pinning center effect) into the epoxy matrix [23]. Therefore, the sintering process has a positive effect in the network density of the epoxy matrix.

3.2. Morphological investigation of epoxy–CB composites

The morphology of epoxy–CB composite was studied to elucidate the physical properties–structure relationship. SEM photographs of as-prepared epoxy for samples F4/6 and F7/3 are presented in Fig. 3a,b, respectively. In Fig. 3a, it is clear that there are large amounts of CB agglomerates and irregular/poor dispersion of CB within the epoxy matrix. This implies that the epoxy is less compatible and wetability with CB surface leads to poor interface between epoxy and CB. Therein, the CB structure within this epoxy is coarser and the absence of continuous conductive paths lead to low electrical conductivity as confirmed by conductivity measurements in the next section. Therefore, a high CB content is needed to form a CB network that generates continuous conducting composite. In contrast, the sample F7/3 in Fig. 3b exhibited better dispersed and high fracturing levels and structuring of the CB conductive particles within the epoxy matrix. One would expect that, if most of the CB particles were located at the epoxy interface, a continuous conductivity increase with increasing CB particles would be expected.

Fig. 2. Variation of $M_c$, NEC, CLD and $H_e$ for two batches of epoxy with different content of CB.

Fig. 3. SEM micrographs of as-prepared batch: (a) F4/6 batch contains 4:6 wt.% CB; (b) F7/3 batch contains 7:3 wt.% CB.
3.3. Determination of the carbon black percolation threshold

The electrical conductivity at 25 °C as a function of CB content for epoxy composites is presented in Fig. 5. It is clear that when the CB content is lower than 4 wt.%, the conductivity of composites changes slightly and the composites will present insulator properties. The conductive CB particles in the epoxy matrix are widely separated and form a finite cluster in the epoxy matrix. The conductive network paths cannot form due to the physical barriers between the gaps that hinder the flow of charge carriers through the epoxy matrix [6]. As the content of CB increases from 4 to 7 wt.%, the electrical conductivity of the composites increases continually from $3.4 \times 10^{-7}$ (Ω cm)$^{-1}$ to $3.4 \times 10^{-3}$ (Ω cm)$^{-1}$. We presume that once the volume fraction of CB reaches a critical value, namely the percolation threshold, $P_c$, the new fibrillar conductive and interpenetrating network structure starts to form. This indicates a phase transition from insulator to conductor and a three-dimensional morphology structure will be constructed in the epoxy matrix [10]. The value of $P_c$ for these composites is about 4.4 wt.%, which indicates good homogeneity and dispersion of CB in the epoxy matrix.

Fig. 4a,b shows the SEM photographs of sintering samples F4/6 and F7/3, respectively. The microstructure of the two batches indicates that the CB particles are finely dispersed; ordering, good interchain connectivity and large grains about 6 μm are observed after sintering. This indicates that the sintering enhances the quality in microstructure core and sinkability (i.e. increase the chains connectivity) of the epoxy matrix.

Fig. 4. SEM photographs of sintering batch at 80 °C for 1 week: (a) F4/6 batch contains 4:6 wt.% CB; (b) F7/3 batch contains 7:3 wt.% CB.

Fig. 5. Dependence of the electrical conductivity at 25 °C for the epoxy contains different content of CB for two batches.
Interestingly, the conductivity increases continuously with increasing CB content. The main reason is that CB improved the interface adhesion and quality of the conductive network structure within the epoxy matrix as confirmed by the network structure results and SEM.

The level of electrical conductivity for sintering batch is higher than as-prepared batch, which supports that the sintering maturates the conductive network density and increases the shrinkability among conductive filaments in the epoxy matrix [23].

We conclude that the electrical conductivity of epoxy–CB composites can be controlled on a molecular level to any desired utilization technology.

The packing fraction (PF) and the effective coordination number (ECN) are given by [17]:

$$PF = \frac{\theta_c}{P_c}, \text{ and } ECN = \frac{PF}{P_c}$$  \(\theta_c\)

where \(\theta_c\) is the critical value of volume fraction after percolation, which sharply change in conductivity.

The calculated values for PF and ECN are 0.93 and 2.12, respectively. These values indicate that the CB particles are arranged in closely packed spheres inside the epoxy matrix [2,23] as confirmed by SEM analysis in Fig. 3a,b.

The scaling law of the percolation clusters is expressed as follows [18]:

$$\sigma(T) = c \left( \frac{\theta - P_c}{1 - P_c} \right)^\eta$$  \(\eta\)

where \(c\) is the conductivity scale factor and \(\eta\) is the conductivity critical exponent, which accounts for the cluster size.

The weighted nonlinear square fits give a conductivity critical exponent, \(\eta = 2.36\), and a conductivity scale factor, \(c = 0.32 \times 10^{-3} \text{ (}\Omega \text{ cm)}^{-1}\). The values of \(\eta\) and \(c\) are similar to those found theoretically for the three-dimensional continuous percolation [19].

3.4. Temperature dependence electrical conductivity

Fig. 6 presents temperature dependencies of electrical conductivity \((\sigma - T)\) for as-prepared epoxy–CB composites during heating and cooling cycles. One can see that the conductivity of the specimens decreases as the temperature increases. These indicate the metal nature of the epoxy–CB composites [4]. Therefore, the conductivity decrease with temperature can be attributable to the predominant conduction in the CB particles. There are two possible reasons for decreasing conductivity with temperature. First, an increase in the gap between conductive chains due to the thermal expansion of the epoxy matrix may also give some contribution to the decrease in conductivity with temperature [2]. Second, near to the melting point of epoxy, the free volume increases rapidly and then results to the increase in the widening between conductive sites; the carrier’s mobility transfer is poorer; thus, the electrical conductivity decreases [8,23].

The change in electrical conductivity against temperature during temperature cycle exhibits irreversible process and the level of hysteresis decreases with increasing CB content. We speculate that the decrease of electrical conductivity after heating cycle is probably due to the deflocculating of conductive particles during cycle leading to the breakdown of the conductive filaments and/or stabilizing effect of conductive particles which decrease conduction.

Fig. 7 presents temperature dependencies of electrical conductivity \((\sigma - T)\) for sintering batch during
heating and cooling cycles. It is clear that the level and/or magnitude of electrical conductivity are higher than as-prepared batch. This ascribed to an expansion of the size of the conductive grains as confirmed by SEM in Fig. 4a,b and the reduction of the interchain distance among these grains. In addition, we speculate that sintering introduces some texturing of the conductive grains into the epoxy matrix and, thereby, contributes to an increase the electrical conductivity. It is interesting to mention that a lower level of hysteresis loop is observed for sintering batch and hysteresis decreases with increasing CB content. Another argument that is confirmed is that the introduction of both sintering process and CB into the epoxy matrix improves the thermal stability of network structural density and stabilizes the electrical network paths in the epoxy matrix [19].

The $\sigma-T$ curve was analyzed by applying two different models. According to the first, namely the Mott model, the electrical conductivity follows the relation [20]:

$$\sigma(T) = \sigma_m \exp - \left( \frac{T_0}{T} \right)^n$$  \hspace{1cm} (10)

where $\sigma_m$ is a moderately temperature-dependent pre-exponential factor, $T_0$ a characteristic temperature, $T$ the absolute temperature and $n$ the Mott that assumed a constant density of states; this gives $n = 1/4$ for the three-dimensional and $n = 1/2$ for the one-dimensional hopping conductivity.

It is found that the value $n = 1/4$ fits the data better than the value $n = 1/2$, which gives the Mott a three-dimensional variable range hopping law with a temperature-dependent $\sigma_m$.

The temperature parameter, $T_0$, and $\sigma_m$ for two batches of the epoxy matrix as a function of CB content are depicted in Fig. 8. The marked increases of $\sigma_m$ and the decreasing $T_0$ for the two batches indicate that the conducting paths change the geometrical characteristics (i.e. interchain distance among conductive sites) inside the epoxy matrix with increasing CB content [21,22]. These imply that before $P_c$, i.e. CB $\leq$ 4 wt.%, the epoxy conductive chains form a one-dimensional system. Therefore, a significant change of geometrical character of temperature dependence of the epoxy composite conductivity can be expected above 4 wt.% CB as confirmed in Section 3.3 and SEM.

The temperature parameter $T_0$ can serve for the estimation of the size of conducting CB particles
(SCP) in the nonconducting epoxy matrix by the following equation [15,23].

$$\text{SCP} = \frac{4eE_0}{K_BT_0}$$  \hspace{1cm} (11)

where $K_B$ is Boltzmann constant, $e$ the electron charge and $E_0$ the intensity of the electrical field in the sample and is about 50,000 V/cm$^3$.

The evaluated value of SCP for two batches as a function of CB content is shown in Fig. 8. From the examination of Fig. 8, it is seen that for the two batches the SCP increase with increasing CB content. These strongly supports that CB and sintering act as a carrier reservoir and accelerate the mobilization of charge carriers into the epoxy matrix [17,23].

According to the second approach, the activation energy, $E_a$, was estimated from slope of the plot of log $\sigma$ vs. reciprocal temperature using the Arrhenius law [7]:

$$\sigma = \sigma_0 \exp \left( - \frac{E_a}{K_BT} \right)$$  \hspace{1cm} (12)

where $\sigma_0$ is the pre-exponential factor that depends on type of CB and polymers.

The dependence of $E_a$ on the CB content for two batches is displayed in Fig. 9. As seen in Fig. 9, the values of $E_a$ for the two batches decrease with increasing CB content. This may be due to an increase of polarization energy and/or charge carriers density leading to a decrease of the domain boundary potential of CB aggregates into the epoxy matrix [10,18].

In order to elucidate the type of conduction mechanism in epoxy–CB composites, the hopping energy, $E_h$, can be calculated according to the following formula [23]:

$$\sigma \sqrt{T} = A \exp \left( - \frac{E_h}{K_BT} \right)$$  \hspace{1cm} (13)

where $A$ is a constant.

The estimated value of $E_a$ as a function of CB content for two batches is displayed in Fig. 9. The value of $E_a$ is quite close to the value of $E_h$; this means that the conduction mechanism in epoxy–CB composites is governed by small polaron hopping conduction mechanism [21,23].

3.5. Negative temperature coefficient of conductivity (NTCC)

The NTCC is one of the important parameters governing the variation of conductivity with temperature. The NTCC can be estimated according to the following equation [24]:

$$\text{NTCC} = \pm \left( \frac{d\sigma}{dT} \right) \left( \frac{1}{\sigma_0} \right)$$  \hspace{1cm} (14)

where $\sigma_0$ is the conductivity at room temperature.

The variation of NTCC at 70 °C vs. CB content for two batches are depicted in Fig. 9. The NTCC for both batches decrease with increasing CB content, while the level of NTCC for sintering batch is lower than as-prepared batch. This associates to CB and sintering maturates the network structure density and thermodynamic stability of the epoxy matrix [2,4].

3.6. Current–voltage characteristics

Fig. 10 presents the current–voltage–temperature characteristics of as-prepared epoxy with different concentration of CB. It is seen that for low applied voltage, the $I$–$V$ exhibits linear resistance and shows a positive slope, indicating Ohmic (i.e. linear) behavior without any remarkable change of the sample temperature. In fact, the samples behave as Ohmic resistor in which the current density is controlled by thermal
As the electric field increases, the behavior of \( I-V \) changes from linear to non-Ohmic (i.e., nonlinear). This is attributed to the change in the percolation conductive path across the epoxy matrix; thermal fluctuations due to significant Joule heating took place; and nonlinearity set in. Increasing the electric field above a certain voltage, namely hot voltage \( V_h \), depends on CB content; leads to an increase in the Joule heating effect and, consequently, increases in the sample temperature; and decreases the current, i.e., shows negative resistance \( (dI/dV) < 0 \).

We discuss the question why the negative resistance appears after the hot voltage. To clarify this phenomena, let us consider the electrical operation circuit of conductive particles inside the epoxy matrix that is described by the electric equivalent circuit in Fig. 10b [24]. We speculate that at high electric field, the whole polymer matrix is heated by Joule heating and, therefore, polymer matrix contains link and separate conductive phases. This may be due to rupture of conductive filaments and some inhomogeneity in microstructure of the epoxy matrix. At high electric field, the separated conductive filaments may have electrostatic capacity; therefore, the conductive filaments may charge as in the circuit in the Fig. 10b. The positively charged conductive filaments may generate Coulomb attractive forces among the separated filaments and repulsive forces among the linking conductive filaments and, thus, resistance may decrease and/or may increase [23,24]. This can be explained that the charge carriers in the hot area (i.e. the area after hot voltage) move easily to the positive electrode and, therefore, the resistance in that side decreases. On the other hand, the carrier’s vacancy concentration increases at the negative potential pole resulting in an increasing resistance. Therefore, we conclude that the negative resistance (i.e., resistance increases) is clearly generated by Coulomb attractive forces at high applied field in epoxy composites. Moreover, the resistance increases at hot voltage is mainly due to a break in filament interlinked by conductive particles at high electric field.

Fig. 11 shows the \( I-V-T \) characteristics of sintering batch for epoxy-CB composites. It is found that the level of current is higher compared to as-prepared batch. It is noticeable that the top of the hot voltage, \( V_h \), was shifted towards lower voltage. This implies
that a sintering process enhances the conductive network paths and the network structure density on the epoxy matrix.

The nonlinear coefficient ($\alpha$) can be determined by [14]:

$$I = GV^{\alpha} \quad (15)$$

where $G$ is a constant depending on CB content with conductance dimension.

The values of $\alpha$ for two batches as a function of CB content are displayed in Fig. 12. It is seen that the $\alpha$ values for the two batches decrease with increasing CB content. The level of $\alpha$ for sintering batch is lower than as-prepared batch and is strongly influenced by CB and sintering condition.

Finally, the ($I-V$) curve can serve for the estimation of the hopping distance, $a_h$, of the charge carriers at high electric field (i.e. $a_h eE > k_B T$). The electrical current density, $J$, is related to the applied field, $E$, by the approximation of hopping model [17]:

$$J = J_0 \sinh \left( \frac{a_h eE}{2RT} \right) \quad (16)$$

where $J_0$ is a constant which is dependent on CB content (A/cm²), $e$ the electronic charge and $R$ the gas constant.

The value of $a_h$ at 50 °C as a function of CB content for two batches is displayed in Fig. 12. It is seen that the value of $a_h$ decreases with increasing CB content. This reflects that the CB improves the interchain connectivity of conductive filaments and accelerates the mobilization of charge carriers into the epoxy matrix [1,5].

### 3.7. Temperature–time dependence and specific heat

For practical reasons, we focused our attention on the temperature–time behavior as a function of applied power for epoxy–CB composites. Fig. 13 presents the applied power–ultimate temperature dependence for as-prepared epoxy–CB composite. It can be seen that the ultimate temperature strongly depends on the CB content. It is interesting to mention that the level of temperature increases by Joule heating at the same electrical power applied. This clue implies that CB improves the tidiness of network structure and the thermal stability of the epoxy matrix.

In order to check the thermal stability of epoxy–CB composites, calculate some useful thermal parameters like specific heat, $C_p$, and amount of heat transfer by radiation and convection, $h_r$. The temperature–current–time dependence during an applied power of about 1.5 W/cm³, on and off, for both batches is displayed in Figs. 14a,b and 15, respectively. Comparing the two batches, it is clear that the magnitude of maximum temperature for sintering batch is higher than as-prepared batch under the same applied power. This observation clarifies that the sintering improves the thermodynamic stability of the epoxy matrix.
In Figs. 14a and 15, the $T$–$t$ curve can be divided into three stages, namely (I) the temperature growth (i.e. power on) stage, (II) the equilibrium stage (i.e. heat gain by working power = heat loss by radiation and convection) and (III) the temperature decay stage (i.e. power off).

In Stage I, the characteristic growth time constant ($\tau_g$) during applied power (i.e. temperature growth), calculated at $t = \tau_g$, can be expressed by an exponentially growth function on the form

$$\left(\frac{T(t) - T_r}{T_m - T_r}\right) = 1 - e^{-\frac{t}{\tau_g}}$$

(17)

where $T_r$ and $T_m$ are the initial and ultimate temperature, respectively.

In Stage II and according to the conservation law of energy, the amount of heat transfer by radiation and convection ($h_r$) is given by:

$$h_r = \frac{I_cV_0}{T_m - T_0}$$

(18)

where $V_0$ is the initial applied voltage and $I_c$ the steady state current as seen in Fig. 14b. The current–time curve in Fig. 14b can be described by the following empirical formula:

$$\left(\frac{I(t) - I_c}{I_m - I_c}\right) = e^{-t/t_i}$$

(19)

where $I_m$ is the maximum current and $t_i$ the characteristic current constant and depends on CB content and sintering process.

In Stage III, the characteristic decay time constant ($\tau_d$), i.e. the working power is switched off (temperature decay), is expressed by the following equation:

$$\left(\frac{T(t) - T_r}{T_m - T_r}\right) = e^{-\frac{t}{\tau_d}}$$

(20)

Fig. 16 presents the calculated values of $\tau_g$, $\tau_d$, $t_i$ and $h_r$ as a function of CB content for two batches. It is clear that $\tau_g$, $\tau_d$ and $t_i$ decrease, while $h_r$ increases with increasing CB content for the two batches. This means that the incorporation of both CB and sintering process in the epoxy matrix improves the ordering and architecture microstructure core of the epoxy matrix, which leads to improve their thermal stability [2,16].

It is interesting to mention that from the calculated values of $h_r$ per unit sample area per second, one can determine the optimum working conditions to warm a given volume at a given initial boundary condition.
The specific heat \((C_p)\) is calculated on the base of energy balance equation by using the following equation \([16,23]\):

\[
C_p = \frac{1}{m} \left[ A h r \tau_d \left( 1 - e^{-\frac{h}{k T_r}} \right) \right]
\]  

(21)

where \(m\) is the mass of the sample, \(A\) the area of the sample and \(t_0\) is the time required for the temperature of the sample to reach room temperature, \(T_r\).

The calculated values of \(C_p\) for two batches increase with increasing CB content as presented in Fig. 16. This supports that both CB and sintering improve the network density and microstructure stability of the epoxy matrix \([3]\).

3.8. Thermoelectric power (TEP)

The measurements of temperature dependence of TEP or Seebeck coefficient play a principal role in the determination of actual charge transport mechanism in solid. The temperature dependence of TEP for as-prepared epoxy with different CB content is presented in Fig. 17. As is seen in Fig. 17, the magnitude or level of TEP increases with increasing temperature and depends on the CB content. This implies that the TEP shows a nearly metallic behavior for all examined samples. Surprisingly, the TEP for sample F4/6 shows a negative TEP. This means that the conduction mechanism is an electron. For all of the other samples, the TEP is positive, which suggests conduction by holes rather than by electron. The negative TEP for sample F4/6 is ascribed to the weak interaction and the lower excitation energy between the conductive filaments in the epoxy matrix \([7]\). Indeed, the sample F4/6 shows two different regions: first, at low temperature about 53 °C, the dependence is linear. This is due to the change in microstructure of epoxy. The second stage starts at 56 °C and it exhibits linearity; this may be due to the thermal generation of charge carrier mobility \([2]\).

The thermoelectric power figure of merit TEPM is defined as \([22]\):

\[
\text{TEPM} = \frac{\sigma(TEP)^2}{\text{Thermal conductivity(}\lambda\text{)}}
\]  

(22)

In Eq. (22), \(\sigma(TEP)^2\) represents the power generated by the thermoelectric epoxy–CB composites and \(1/\lambda\) is a measure of its ability to sustain a temperature difference. The values of TEPM as a function of CB concentration are depicted in Fig. 17. It is seen that the TEPM increases with increasing CB content. This argument confirms that the incorporation of CB into
the epoxy matrix enhances their thermodynamic stability and network density.

3.9. Thermal conductivity

Thermal conductivity–temperature dependence of epoxy as a function of CB content is shown in Fig. 18. It is seen that all samples show an appreciable increase of $\lambda$ values upon increasing temperature and depend on CB content. This ascribed to the conductive paths and the network density increase with increasing CB content [12]. Also, some oriented and texturing regions within the microstructure core of epoxy composite will be formed with increasing CB content [4]. This leads to a decrease in the thermal resistance and means free path of phonons. Also, the segmental mobility of the epoxy matrix increases during heating results to an increasing thermal conductivity [16].

It can be concluded that the thermal properties depend mainly on the CB content in the epoxy matrix, i.e. epoxy–CB interface and temperature.

4. Conclusions

Based on the experimental data, the following conclusions can be drawn.

(1) Carbon black (CB) and sintering improve the network structure density of the epoxy matrix.

(2) The electrical conductivity of epoxy–CB composites increases continuously with increasing CB content and there is the possibility to realize the electrical conductivity of the epoxy composites according to desired utilization technology.

(3) The temperature dependence of electrical conductivity strongly depends on CB concentration and can be enhanced significantly with sintering process.

(4) The conduction mechanism of epoxy–CB composites is governed by hopping conduction process. The negative temperature coefficient of conductivity (NTCC) depends on both carbon black and sintering process.

(5) Current–voltage characteristics show non-Ohmic, i.e. (nonlinearity) at high voltage, and show a certain kind of switching effect. The negative resistance after hot voltage is generated by Coulomb attractive force.

(6) The values of the maximum temperature and characteristic time constants for heating and cooling curve depend on both CB concentration and sintering.

(7) Epoxy–CB composites show good thermal stability and they can be used as heating devices for consumer products.

(8) Thermoelectric power–temperature dependence shows that two types of carrier transport, electrons and holes, depend on CB concentration. The thermoelectric power, specific heat and thermal conductivity depend on network structure density.

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References
