J Mater Sci: Mater Electron (2008) 19:1079–1085
DOI 10.1007/s10854-007-9470-7

Thermoelectric power and AC electrical properties of PAN-based carbon fiber composites

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Received: 20 August 2007 / Accepted: 29 October 2007 / Published online: 5 December 2007

Abstract The thermoelectric power and AC electrical properties of conductive polymer composites made of polycarbonate filled with randomly distributed PAN-based carbon fibers of different concentration: 0, 5, 10, 18, and 30 wt% were studied. The thermoelectric power was measured as a function of temperature in the frequency range from 200 kHz to 12 MHz. It was found that the observed Seebeck coefficient and thermoelectric activation energy depend on temperature, frequency and fiber concentration. The Seebeck coefficient calculated using the electrical transport theory of semiconductors decreases with both increasing temperature and carbon fiber content. The thermoelectric power results revealed that the composites function electrically as semiconductors. Dielectric constants and AC conductivity were calculated from impedance and phase angle measurements. It was found that both increase with increasing temperature. The activation energy and relaxation time decrease with increasing temperature measured and applied frequency. The thermoelectric power results indicated that electrical conduction in bulk composites is produced from a combination of transport processes involving: electrons, holes, ions and charged impurity motion in addition to protonic migration.

1 Introduction

The conductivity of polymers could be increased by incorporating them with some conductive filler particles such as copper, silver, carbon fibers, and metallic ions or complexes. Conductive polymer composites are used in numerous technological applications [1–3]. The development of new advanced materials is mainly oriented towards the fiber filled composites. Fibers such as metallic, carbon fibers and glass embedded in thermoplastic polymers are examples of widely used conductive composites [4–7].

The above-mentioned fibers embedded in the amorphous polycarbonate (PC) matrix makes them a vital components in some electrical accessories and some marine applications [8, 9]. Polyacrylonitrile (PAN)-based carbon fibers have low electrical resistivity ($\sim 1{,}500\ \mu\Omega$ cm) measured along the fiber direction. PAN-based carbon fibers consists of graphite crystallites tilted with an angle of about 23° with respect to fiber axis. Previously, we found that they have a type of electrical conduction similar to that of the semiconducting materials [10, 11].

Recently, a study on the Hall effect and DC electrical properties of PAN-based fibers/PC composites was carried out [12]. It was found that the dependence of the electrical conductivity on temperature is described by two-stage conduction process with a semiconducting type of behavior and two activation energies. Also it was found from Hall effect measurements that those composites function as a *p*-type material at low fiber content, and as *n*-type material at high fiber content. Considering the filled carbon fibers as a

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random semiconductor, the electrical conduction observed for various composites were described in terms of the band structure and the observed morphology [12, 13].

The present work reports the result of a continued research work aimed to get a full picture of the electrical conduction in both DC and AC measurements of the Seebeck effect, dielectric constants, and AC conductivity as a function of temperature, fiber concentration and applied electric field frequency.

2 Experimental measurements

2.1 Composite preparation

The material used in the present work is PAN-based carbon fibers/polycarbonate composites. The fibers were produced by Celeanese company in USA. They were chopped into short pieces of 0.2–2 mm in length and dispersed randomly in polycarbonate resin. The procedure of composite preparation by Brabender and compression molding technique was described elsewhere [14, 15]. The composites obtained were in sheet form of 1.5 mm thickness and fiber concentrations of: 5, 10, 18, and 30 wt%. The morphology and structure isotropy of the prepared composites were studied using SEM and X-ray diffraction. The obtained X-ray diffraction patterns from the composites were concentric rings indicating isotropy in the prepared composite. Concerning the fibers distribution and morphology, Fig. 1 shows scanning electron micrographs of fractured surface of the specimen of 30 wt% PAN-based carbon fibers. It can be seen from the fractured surfaces that the fibers are randomly distributed and in good adhesion to PC matrix.

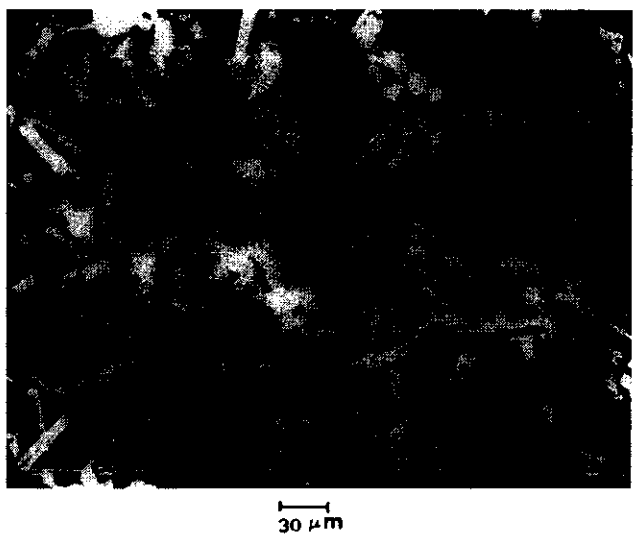

Fig. 1 SEM micrograph of 30 wt% carbon fibers composite

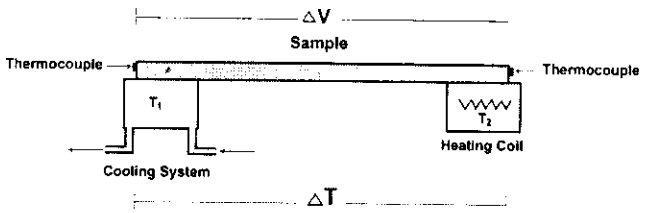

Fig. 2 Setup sketch of thermoelectric power measurement

2.2 Thermoelectric measurements

The used composite sample were in strips form with dimensions 4 × 0.5 cm. A temperature gradient ΔT was established between the ends of the strip, and the resulting potential difference ΔV was measured for different values of ΔT, which enabled the calculation of thermopower (Seebeck coefficient S).

Figure 2 shows the sketch of the setup used for measuring the thermopower of the prepared composites. Two thermocouples are fixed on the strip ends for measuring the temperatures T_1 and T_2. The produced potential difference ΔV was then measured. The temperature difference ΔT is produced from a heating coil and cooling line located at the ends of the sample.

2.3 Impedance measurements

Disk sample of 20.0 mm in diameter and 3.0 mm thick were cut from the molded plates of all composites for electrical measurements, which were carried out after applying a silver coating to each surface of all test samples. Each sample was then sandwiched between two copper circular disks to ensure a good electrical contact with the copper electrodes connected to an impedance analyser. Impedance and the phase angle were measured by varying the applied frequency using Hewlett Packard model 4192A impedance analyzer.

Fractured surface of the composites were prepared for scanning electron microscopy (SEM) which showed that the distribution of the carbon fibers is fairly random, as shown in Fig. 1.

The real component (ε') and the imaginary component (ε'') of the complex dielectric constant (ε^*) are related to impedance (Z) and phase angle (ϕ) as:

$$\varepsilon' = Z_i/2\pi f C_0 Z^2 \quad (1)$$

$$\varepsilon'' = Z_r/2\pi f C_0 Z^2 \quad (2)$$

where, f is the applied frequency, $C_0 = \varepsilon_0 A/T$ is the electrodes capacitance, T the specimen thickness, ε_0 the permitivity of free space, A the area of the disk, Z_i and Z_r are the imaginary and real components of the complex

impedance (Z) expressed in terms of the phase angle (ϕ) as ($Z = Z_r - iZ_i$, $Z_i = Z\sin\phi$) and $Z_r = Z\cos\phi$). The AC electrical conductivity (σ_{AC}) was calculated from the relation:

$$\sigma_{AC} = 2\pi f\, \varepsilon_0 \varepsilon'' \tag{3}$$

The activation energy (E_a) of the conduction process is calculated by Arrhenius equation,

$$\sigma_{AC} = \sigma_0 \exp(-E_a/k_B T) \tag{4}$$

where σ_0 is a material constant, T is the temperature in Kelvin, and k_B is Boltzman constant [14–17].

3 Results and discussion

The material used in this study was PAN-based carbon fiber/polycarbonate composites with fiber content: 5, 10, 18 and 30 wt%. The PAN-based carbon fibers were chosen because they have high electrical conductivity along the fiber direction. The random fibers (or the graphite crystals) distribution in polycarbonate matrix allows the investigated composites to be considered as a random semiconductor. This is based on the temperature dependence of the electrical conductivity of single PAN carbon fibers which showed a two-stage conduction process similar to a semiconductor behavior with two low activation energies [10].

3.1 The thermoelectric power results

Thermoelectric power or Seebeck effect is one of the methods which give information about the type of the charge carriers and the mechanism of the electrical conduction that takes place in a particular solid. If a temperature gradiant is established between the ends of a solid in a closed circuit then a thermocurrent is produced and affects the charge carriers in the solid and redistribute them. The produced potential difference ΔV in an open circuit (Fig. 2) is proportional to the temperature difference ΔT as:

$$\Delta V = S\Delta T \tag{5}$$

where S is called Seebeck coefficient. The sign of S expresses the type of the charge carriers in the electrical conduction: if the sign is negative then the solid functions as n-type semiconductor, and if the sign is positive then it functions as p-type semiconductor.

When the ends of composite sample exposed to different temperatures $\Delta T = (T_2 - T_1)$ a potential difference ΔV is produced along the sample due to temperature gradient. The Seebeck coefficient S can be calculated from the relation: $S = \frac{\Delta V}{\Delta T}$. Furthermore, S can be related to the activation energy (E_s) of the thermoelectric effect [18] as:

$$S = \frac{k}{e}\left[\frac{E_s}{kT} + A\right] \tag{6}$$

where k is Boltzman constant, e carrier charge, and A is a constant, S decreases with temperature in case of p-doped semiconductors [19].

The values of S and E_s were calculated for the PAN-based carbon fiber composites as a function of carbon concentration and temperature. It was found that the Seebeck coefficient decreases as the carbon fibers content (or the charge carriers density) increases as indicated in Table 1. Also, it decreases with increasing temperature as shown in Fig. 3. This figure represents the temperature dependence of S at low and high temperature ranges yielding two slopes corresponding to two activation energies determined from Eq. 6. The average values of the two activation energies E_s are plotted in Fig. 4 for various carbon fibers contents, where E_s decreases from 0.70 eV to 0.35 eV as the carbon fiber concentration increases to 30 wt%, i.e. to half its value for the neat polycarbonate.

The decrease of both S and Es with increasing carbon content is consistent with the behavior of the Hall coefficient and thermal activation energy observed in our recent study [12] on the DC electrical behavior of those carbon

Table 1 S-value at 35 °C

Composite (wt%)	$S \times 10^{-4}$ V/K
0	3.0
5	2.9
10	2.4
18	1.9
30	1.8

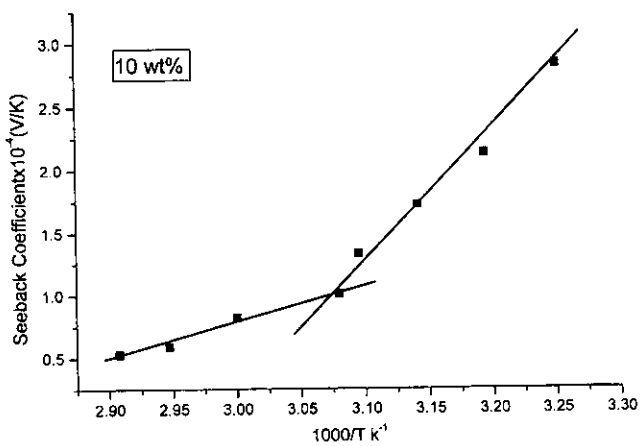

Fig. 3 The dependence of the Seebeck coefficient on the reciprocal temperature

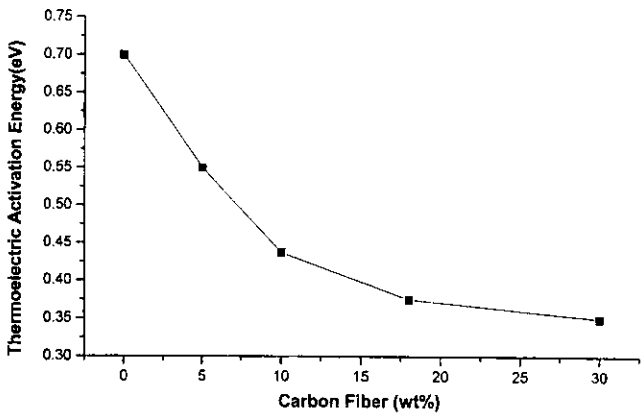

Fig. 4 Variation of the thermoelectric activation energy with carbon fiber content

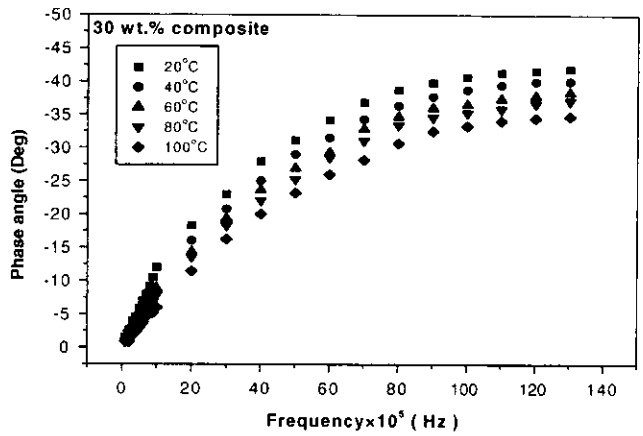

Fig. 5 The curve of phase angle versus frequency

fibers. The decrease of Seebeck coefficient with increasing carbon fiber content (or charge carriers density) is attributed to the decrease of the potential difference ΔV between the hot and cold ends of the composite sample.

The observed decrease of S with increasing temperature as shown in Fig. 3 confirms that the 10 wt% composite sample functions as p-type semiconductor dominated by holes transport in the conduction process since S has positive values. The Seeback coefficient at 35 °C is about $2 \times 10^{-4} V/K$ which is higher by a hundred time than that observed for metals of order of magnitude $10^{-6} V/K$. In case of metals S is proportional with temperature [18, 19], while in semiconductors it decreases with temperature as shown in Eq. 6 and Fig. 3. Similar results were reported by Patel [20] on the thermopower and electrical transport of chelate polymers containing metallic ions, where polychelates function as p-type semiconductor with holes as majority charge carries.

It is worth to mention that the behavior of the thermoelectric power of the composite is attributed to randomly distributed graphite crystallites arranged nearly along the fiber axis [11]. Also the Seebeck coefficient is very sensitive to the relaxation time of the electrical conduction process, a quantity that is very difficult to accurately calculate, so the experimental values of Seeback coefficient are hard to predict or interpret [21].

3.2 The AC electrical results

There was an interest to investigate the temperature dependence of the AC electrical properties of a composite made of 30 wt% of PAN-based carbon fibers embedded in polycarbonate matrix. Impedance spectroscopy was used in characterizing the thermal AC electrical conduction of the composite sample. Impedance measurements were conducted on the composite of high content of carbon fibers (30 wt%) and in the frequency range from 200 kHz to 12 MHz.

The variation of the phase angle with frequency at temperature range (20–100 °C) is shown in Fig. 5, where the negative values of the phase angle decrease with increasing temperature, i.e. the composite becomes less capacitive with increasing temperature. Thus the capacitive composite can be represented by parallel networks connected in series [22]. The impedance behavior with frequency at different temperatures is shown in Fig. 6. It can be noticed that the decrease of impedance with increasing both frequency and temperature results in a negative temperature coefficient of resistance similar to semiconductors [16]. High impedance values at low frequency may result from space charge polarization in the composite bulk, causing some potential barriers which, in turn, increase the impedance [14, 23].

Figure 7 shows Cole–Cole plots of the imaginary component (Z_i) versus the real component (Z_r) of the complex impedance for composite specimen (30 wt%) at different temperatures. The impedance construction plots are distorted semicircles exhibiting different electrical conduction

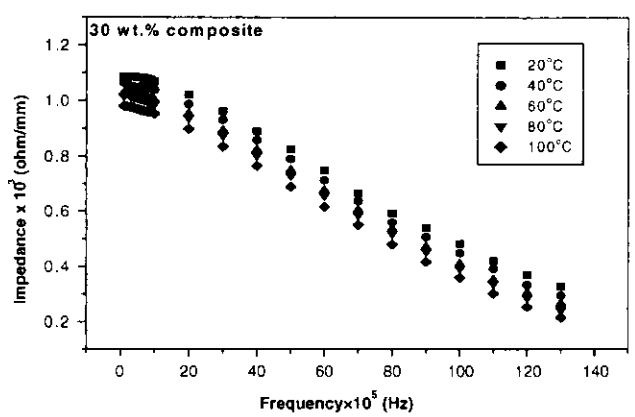

Fig. 6 Impedance dependence on frequency

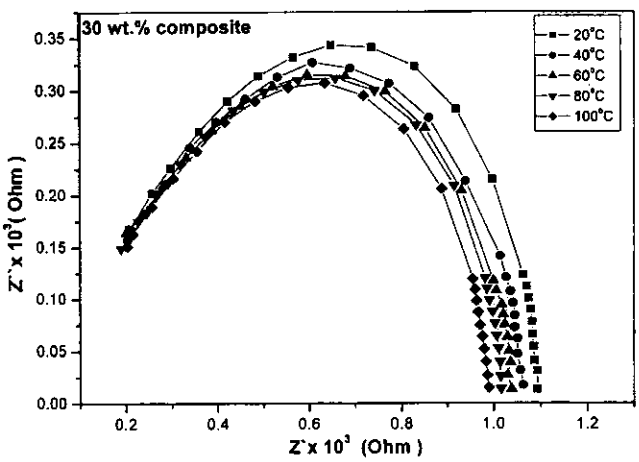

Fig. 7 Cole–Cole plots at different frequencies and temperatures

processes with spectrum of relaxation time. The figure shows that the real component (Z_r) of the bulk resistance of the composite decreases with increasing temperature, i.e. the composite material becomes less resistive or more conductive [7]. The relaxation time (τ) of the conduction process was determined by approximating these plots to semicircles using the relation $\omega_{max}\ \tau = 1$, where ω_{max} is the angular frequency at maximum values of (Z_i) observed on the constructed plots. Figure 8 shows that the observed relaxation time (τ) decreases with increasing temperature. This may be attributed to ionic mobility, which increases as temperature increases, or to electrons and impurities existing in the carbon fibers as we indicated in elemental analysis carried out by X-ray fluorescence [10] and γ-ray analysis [24].

The dielectric constant (ε') as a function of temperature is shown in Fig. 9 at different frequencies. The (ε') values were calculated from impedance data (equation 1, 2). It can be seen that the (ε') increases with increasing temperature and decreases with increasing applied electric field frequency. The dielectric loss (ε'') variation with temperature

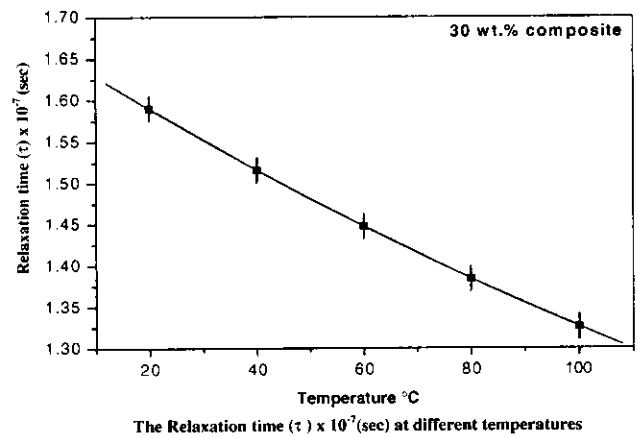

Fig. 8 The curve of relaxation time versus temperature

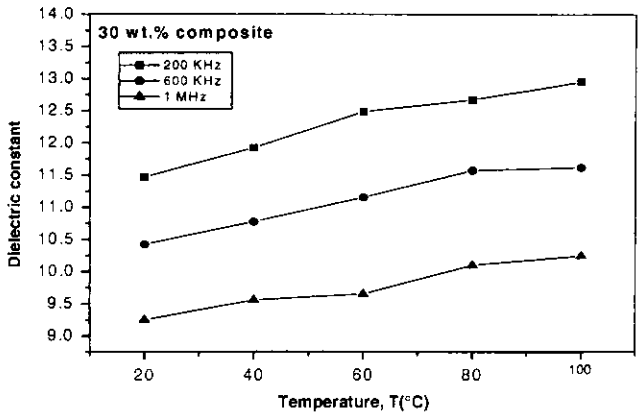

Fig. 9 The dependence of the dielectric constant (ε') on temperature

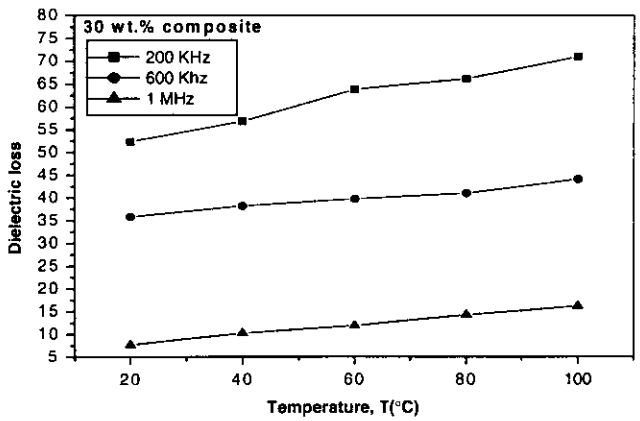

Fig. 10 The dependence of the dielectric loss (ε'') on temperature

is shown in Fig. 10 at different frequencies. The dielectric loss increases with increasing temperature and exhibits a lower values at higher frequency. The enhancement of the dielectric loss and dielectric constant with increasing temperature can be attributed to ionic conduction, contribution from electrons and impurities in bulk of the carbon fibers.

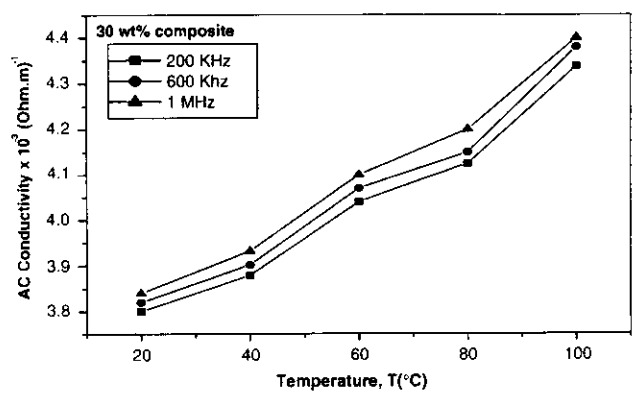

Fig. 11 The variation of AC conductivity with temperature

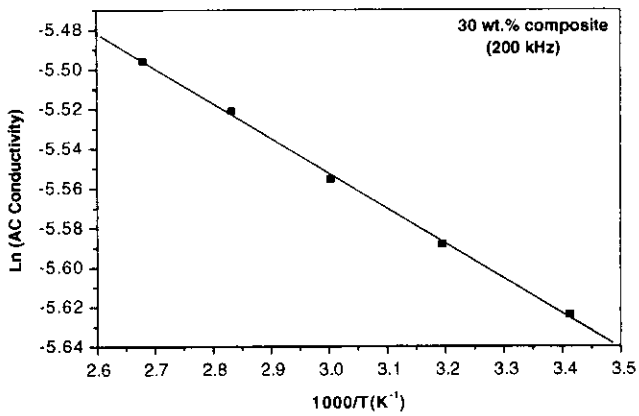

Fig. 12 Variation of $\mathrm{Ln}\sigma_{AC}$ with $1/T$ for the composite

Figure 11 represents the AC conductivity σ_{AC} versus temperature at different frequencies. It was found that σ_{AC} calculated from Eq. 3 increases with increasing temperature due to thermal activation in both the ionic conductivity and electrons mobility. Thus the electronic and ionic conduction mechanisms are operative in this conductive polymer composite, especially at higher temperatures. The induced AC conductivity at higher frequency, as shown in Fig. 11, reveals the role of the d-electrons in the conduction mechanism [20]. Using Eq. 4, the thermally activation energy (E_a) was calculated from the slope of the straight line of $\mathrm{Ln}\sigma_{AC}$ versus ($1000/T$) shown in Fig. 12. The dependence of (E_a) on frequency for thermally activated (ionic and electronic) conduction process is indicated in Table 2. The decrease in the activation energy values reflects enhancement in electrical conductivity due to impurities, electrons, ionic conduction and protonic migration process. These processes affect the charge carriers transport in the bulk composite.

4 Conclusion

PAN-based carbon fiber/polycarbonate composites were prepared by compression molding. The thermoelectric power, dielectric constants, and AC conductivity were studied as a function of carbon fibers concentration, temperature and applied field frequency. The overall thermoelectric behavior of the prepared composites is attributed to a combination of electrical conduction processes including electrons, ions, charged impurity motion in addition to protonic migration. Furthermore, the study of Seebeck effect for these composites revealed that they are regarded as p-type semiconductors and have hopping transport mechanism

Table 2 Dependence of activation energy on frequency

Applied frequency (kHz)	$E_a \times 10^{-2}$ eV
200	1.53
400	1.47
600	1.43
800	1.40
1000	1.39

Acknowledgement One of us (A. M. Zihlif) is very grateful to the International Center for Theoretical Physics (ICTP) in Trieste-Italy for support and cooperation.

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