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Material properties

# Temperature dependence of electrical properties in conductive polymer composites

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ABSTRACT

Conductive graphite and carbon black filled composites have been prepared using polypropylene, poly(buthylene-terephtalate) and polycarbonate as matrix, and the effect of temperature on conductivity has been studied. Conductivity of graphite filled composites changed significantly as temperature and filler content increased while the conductivity of carbon black filled composites was insensitive to temperature change. To understand the differences in the conductivity change of composites containing different amount of fillers, apparent thermal expansion of composites was measured and it was found that graphite reduced the thermal expansion of composites more than carbon black. The contradiction was solved by analyzing the current–voltage characteristic of composites. It revealed that the conduction mechanism of graphite filled composites was dominated by ohmic conduction, however, in carbon black filled composites the characteristic charge transport process was tunneling and hopping conduction. Thermal activation of tunneling and hopping conduction compensated for the heat expansion of carbon black filled composites.



## 1. Introduction

Development of conductive polymer composites (CPCs) is very promising and these materials have been increasingly studied widely. Due to their corrosion resistance and low density, CPCs may replace metals in several applications [1–4]. The operating temperature of products that contain CPC is not necessarily ambient, thus it is very important to examine the temperature dependence of the electrical properties of CPCs, and that is a rather complex issue.

Each type of resistivity varies with temperature. Positive temperature coefficient of resistance (PTCR) of CPCs has a switching effect in self-limited heating systems or current limited electric circuits [5,6]. In applications like bi- or monopolar plates in proton exchange membrane fuel cells (PEMFCs), it is very important to reach low resistivity even in higher temperature ranges (60–80 °C or 130–200 °C). Therefore, resistance is not allowed to increase with temperature, otherwise cell efficiency decreases at operating temperature [7–9].

Basically, conductive polymer composites have positive temperature coefficients of resistance. However, the type, amount and dispersion state of the fillers, the thermal activation of the fillers' electrons and the oxidation of the matrix material (formation of polar groups) affect this property significantly [10,11].

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Alexander [12] and Mohiuddin et al. [7] found that carbon black and carbon nanotube filled composites had lower resistance at higher temperatures. This means that these composites had negative temperature coefficients of resistance (NTCR) thus, their conductivity increased as temperature rose because of the thermal activation of electrons. Contrary to this, Costa [13], Del Rio [14] and Nakano et al. [5] found that the conductivity of carbon black filled composites decreased as temperature increased. CPCs consist of an insulating polymer matrix and conductive fillers that have significantly lower thermal expansion coefficients than polymers [15]. Different thermal expansion of the matrix and the fillers can disrupt the conductive network in the composite, and hence decrease electrical conductivity. However, in the case of larger amounts of filler, they are so close to each other that, in spite of heating, the disruption of a conductive route leads to the formation of another one [6,8].

The current–voltage characteristic of composites refers to the electric charge transport mechanism in the composite. If the characteristic is linear, electron transport is mainly ohmic conduction. In this case, resistivity rises as temperature increases; this means that the same current values are connected to even higher voltage values. If the characteristic differs from linear and shows an exponential behavior, charge transport takes place by tunneling and hopping conduction. In the case of tunneling and hopping conduction, the exponential nature of the current–voltage characteristic strengthens as temperature increases [16–19].

In this study, electrical properties of graphite and carbon black filled CPCs were studied as a function of temperature. Polymers and carbon fillers have rather different thermal expansion coefficients, thus thermal expansion studies were carried out. Current–voltage characteristic of composites was analyzed to understand the dominant charge transport mechanism in the composites.

## 2. Experimental

### 2.1. Materials

Tipplen H949A polypropylene (TVK Plc., Hungary) with an melt volume rate (MVR) value of 50 $cm^3$/10 min; Pocan B 1305 poly(butylene-terephthalate) (Lanxess) with an MVR value of 47 $cm^3$/10 min and Apec 1695 polycarbonate (Bayer) with an MVR value of 45 $cm^3$/10 min were used as matrices. The graphite powder used for increasing conductivity (Carbosint Ltd., Hungary) was crystalline natural graphite powder. The type of carbon black used was Ketjenblack EC-600 JD (AkzoNobel). The properties of fillers are summarized in Table 1 (density and other values were provided by the manufacturers).

The various compositions were mixed in a Brabender kneader at 240°C (PP), 250°C (PBT) and 340°C (PC) for 12 min at 20 rpm. From the melt-mixed materials, 80x80x2 mm plates were compression molded at 250°C (PP), 260°C (PBT) and at 345°C (PC) at 160 bar in a Collin P 200E press.

**Table 1**
Properties of fillers used [20,21].

| | Graphite powder (G) | Carbon black (CB) |
|---|---|---|
| Apparent bulk density (g/$cm^3$) | 0.40 | 0.11 |
| Density (g/$cm^3$) | 2.24 | 1.80 |
| Average particle size (μm) | diameter: 10–20<br>thickness: 0.1–1 | 0.035 |
| Specific surface ($m^2$/g) | 6 | 1400 |
| Conductivity (S/cm) | 400–1250 | 2.5–200 |

The compositions used in the examinations of conductivity and mechanical properties are shown in Table 2.

### 2.2. Test methods

In this study, comparative tests were performed since trends and changes of properties relative to each other were considered.

Conductivity was measured on 120x120x2 mm plates using a four-probe resistivity testing method [22–24] with a data acquisition Agilent 34970A and module 34901A in the following temperature ranges: −20–130°C (PP), 30–130°C (PBT) and 30–160°C (PC), with 10°C temperature increments. A special head was prepared for this measurement; four gold-plated Ingun probes were embedded 2 cm from each other in an insulator plate. The surface of the samples was cleaned with acetone before conductivity tests were performed. A current of 10 μA was applied during the measurements. Conductivity was calculated using Equation (1):

$$\sigma = \left(\frac{\pi \cdot w}{\ln 2} \cdot R \cdot F_1 \cdot F_2\right)^{-1} \quad (1)$$

where $\sigma$ is conductivity, $w$ is specimen width, $R$ is resistivity measured and $F_1 \cdot F_2$ is a geometrical factor which in this case is 1 because the ratio of the distance of the probes and specimen width is higher than 2 [22–24].

Further electrical characterization of the specimens was carried out by means of current–voltage characteristics analysis. Current was generated by a GW Insteak GPS-4303 power supply from 0.01 to 0.15 A with increments of 0.01 A. The voltage was measured with an Agilent 34970A data acquisition and module 34901A.

**Table 2**
Compositions and notations of CPCs.

| Notation | | | PBT/PP/PC (vol%) | G (vol%) | CB (vol%) |
|---|---|---|---|---|---|
| Matrix | Filler | Composition | | | |
| PBT orPP or PC | CB | 96.8 polymer +3.2CB | 96.8 | 0 | 3.2 |
| | | 94.1 polymer +4.9CB | 94.1 | 0 | 4.9 |
| | | 93.3 polymer +6.7CB | 93.3 | 0 | 6.7 |
| | | 91.8 polymer +8.2CB | 91.8 | 0 | 8.2 |
| | G | 78.0 polymer +22.0G | 78.0 | 22.0 | 0 |
| | | 70.3 polymer +29.7G | 70.3 | 29.7 | 0 |
| | | 61.2 polymer +38.8G | 61.2 | 38.8 | 0 |
| | | 40.4 polymer +49.6G | 40.4 | 49.6 | 0 |
| | | 37.2 polymer +62.8G | 37.2 | 62.8 | 0 |