Ethylene-octene copolymer and carbon black composite electro-thermal properties for self-regulating heating

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Abstract. Carbon black – ethylene-octene copolymer (EOC-CB) composite electro-thermal properties were investigated for using the composite as self-regulating heating material. The materials electrical resistance change with temperature change was investigated. Additionally, while a voltage of 30 V was applied, the sample temperature and electrical current strength was measured. The samples with 15 to 20 phr CB showed positive temperature coefficient of resistivity and could be used as self-regulating heating materials. For different concentrations of CB the achieved equilibrium temperatures were between 30°C to 60°C (with 30 V) and could be used to comfortably warm the human body.

1. Introduction
A lot of scientific effort has been put into the research of materials that exhibit positive temperature coefficient of resistivity (PTC). The electrical resistivity of materials with PTC effect increases nonlinearly with temperature [1]. This effect usually occurs with materials at their phase transition temperature – usually melting temperature – that for polymers is rather high compared to the human body’s temperature [2]. Materials that have PTC can be used as self-regulating heating materials. For these materials as long as a voltage is applied to the material, the temperature increases to an equilibrium temperature and stays at that temperature.

The mechanism of PTC is still not fully understood and explained. There are many models and theories [3–6], which try to explain the effect, but all struggle with some aspect of explanation of the experimentally acquired data. This is because it is almost impossible to ascertain of the models rightness or wrongness experimentally. Nevertheless, the widely accepted opinion is that electrical resistance in polymer composites can be described by the percolation theory – the electro-conducting particles form a conductive network throughout the polymer matrix, which is responsible for conductivity [7,8]. Between close particle aggregates, a thin polymer layer prevents direct conduction, but through this layer electron tunneling can occur [8,9]. The main effect responsible for increase in resistance with increased temperature is the matrix volume expansion, either due to the difference in coefficients of linear thermal expansion between polymer and particles or due to phase transition – mostly melting of crystalline regions. Therefore, the most accepted theory is based on electron tunneling – electrons tunnel through thin dielectric polymer layers, which are between particles. The tunneling probability is highly dependent on layer thickness, so if the polymer matrix expands, the resistance increases exponentially [10,11].
Many materials have been shown to exhibit PTC behavior. The most popular being high density polyethylene as matrix material [12–15], but other types of matrix materials are epoxy [16], polypropylene [17], poly(vinylidene fluoride) [18] with different types of filler, including carbon nanotubes [14,16,17], carbon nanofiber [12,13], Ni [18] and Ag nanoparticles [19]. The biggest downside to these materials is, that the PTC temperature is above 130°C, which is way too high to use as a self-regulating heating element for the human body.

In this paper we propose a new PTC exhibiting composite material made of ethylene-octene copolymer (EOC) and carbon black (CB). Our goal is to get the PTC peak temperature comparatively low – in the range of 50-60°C, so it can be used as a self-regulating warming device for the human body. The composite’s resistance vs temperature, particle distribution, and equilibrium temperatures for different phr (parts per hundred rubber) of CB have been characterized.

2. Materials and methods

The samples are prepared by mixing ethylene-octene copolymer (EOC) granules (38% octene content, Engage 8200, Dow) with carbon black (CB) powder (Printex XE-2, Evonik Industries) and dicumyl peroxide (crosslinking agent) on a heated two-roll mill (Labtech Engineering). Following that, the sample is vulcanized at 170°C under 6 kPa for 10 min. Silver paint (Spi supplies) electrodes are painted on the flat surface of the sample. The sample length is 95 mm (space between electrodes is 85 mm), the sample width 75 mm and thickness 0.7 mm. Samples with 10 - 30 phr of CB are prepared.

DSC measurements are made using Mettler Toledo instrument in a temperature range from 20 to 200 °C with speed 10°/min in a heating-cooling-heating regime.

The resistance dependence on temperature measurements are carried out in a SNOL 58/350 laboratory oven with an additional thermocouple attached to the sample. The temperature and current/resistance dependence on applied voltage are carried out in room temperature with a thermal insulator beneath the sample. The applied voltage is constant 30V.

For the electro conductivity measurements in microscale atomic force microscope (AFM) measurements (Smena, NT-MDT) are performed in contact mode using an electro conductive tip (CSG10/Pt, NT-MDT). A round sample of 18 mm diameter and 1 mm thickness is used. The mathematical processing to characterize the particle distribution in the composite matrix in microscale have been made as explained in [20]. In AFM electro-conducting mode the current between the AFM tip on the composite surface and the bottom electrode has been measured at an applied voltage of U = 1V. If the particles form a channel, which goes through the sample, then a current begins to flow and an increased intensity peak is observed. The electro conducting channel distribution dIndex is calculated by dividing the map into 9 squares and calculating the percentage of area taken up by electro conducting channels in each square. The size distribution sIndex is calculated by acquiring the channel size distribution, and evaluating agglomerate presence. The average of the two indexes is cIndex – which describes the sample overall.

3. Results and discussion

3.1. Thermal properties

Table 1. DSC measurement values for melting heat, crystallization heat and peak temperatures.

|            | Melting heat (Jg\(^{-1}\)) | Melting peak temperature (°C) | Crystallization heat (Jg\(^{-1}\)) | Crystallization peak temperature (°C) |
|------------|-----------------------------|-------------------------------|-----------------------------------|--------------------------------------|
| 10 phr     | -11.14                      | 59.72                         | 8.97                              | 37.46                                |
| 15 phr     | -10.28                      | 59.39                         | 7.37                              | 36.78                                |
| 20 phr     | -11.36                      | 58.88                         | 6.08                              | 39.78                                |
| 25 phr     | -9.48                       | 56.74                         | 5.03                              | 36.59                                |
| 30 phr     | -7.69                       | 54.54                         | 4.86                              | 39.45                                |
DSC thermograms of EOC-CB for the second heating cycle are shown in figure 1. As can be seen, the melting occurs at approximately 55 – 60°C, which is consistent with peroxide cured EOC in different literature [21]. During the cooling cycle the matrix undergoes crystallization at approximately 36 - 40°C. The values for melting heat, crystallization heat, and peak temperature are shown in table 1. The PTC effect is considered to be until around 55 °C when the matrix undergoes the most significant expansion. This is confirmed by resistance-temperature measurements (shown in figure 2). The highest relative resistance change maxima is for 10 phr, which has the smallest CB concentration and has the most crystalline matrix (see table 1). All the other samples show an increase in resistivity until 50°C, however the increase is relatively smaller, due to the large amount of CB preventing the polymer from having more crystalline regions. Contrarily, for the material to work as a heating element for voltages around 30 V and lower, the base resistance needs to be appropriately small. Samples with 10 phr did not undergo noticeable heating if 30 V were applied, so the next best concentration for our purposes seems to be in the range of 15 phr – 20 phr.

3.2. Electrical heating properties

A 15 phr sample heating experiment in the time scale is given in figure 3. First, base electrical resistance is measured for 30 seconds, then a constant voltage of 30 V is applied and the current strength is measured. After 25 minutes an equilibrium state is reached, in which the temperature of the sample does not increase significantly after that point. Then the voltage is switched off and the resistance of the sample while cooling/relaxing is measured. By increasing the temperature, the electrical resistance increases, however the calculated power (P = IU) decreases. This shows that the sample exhibits PTC effect. After 5 minutes of heating, the sample has already reached ~65% of the maximum equilibrium temperature, which shows that the sample heating rate is moderate (0.7°C/min). In figure 4, you can see the maximum temperature reached (equilibrium) while electrically heating the samples with 30 V for each filler load.

In figure 5, the current strength vs time for 15-25 phr CB samples is shown. For 15 and 20 phr of CB the current strength decreases (resistance increases) with time and temperature increase. The electro-conducting particle amount for 15 and 20 phr of CB is low enough so that the damage to the electro-conducting network done by thermal expansion is the dominant mechanism for sample electrical resistance increase (current strength decrease). For 25 phr of CB sample the current strength first drops slightly, but afterwards increases significantly. At higher loads of CB the mechanism for resistance change is interchanging between two effects – the thermal expansion with consecutive resistance increase and the resistance decrease due to formation of new conductive channels in the
region of melting when the temperature increases. If the filler load is sufficiently high, then the temperature increase results in an increased electrical current flow through the sample. In this case, the thermal fluctuation induced tunneling conduction takes place between electro-conducting particles and the electrical resistance is reduced [22].

![Temperature, resistance and power curves vs time for 15 phr CB samples. For the first 25 minutes the applied voltage is 30 V.](image3)

![Maximum temperature reached for different phr of CB samples while electrically heating with 30V.](image4)

![Current strength vs time, while electrically heating 15, 20 and 25 phr of CB samples.](image5)

![slIndex, dIndex, cIndex (left axis) and sample electrical resistance (right axis) depending on parallel samples.](image6)

3.3. Nano-scale characterization

The electro conducting channel distribution indexes for parallel samples for 20 and 30 phr, compared to 10 phr samples (figure 6), are quite largely dispersed, which can be explained by overload of CB particles. The effect is more pronounced for 30 phr samples with an electrical resistance under an ohm. These samples have a lot of filling material what makes them more electro-conducting and the channels fuse together on the AFM electro-conducting mode map (figure 7), reducing the slIndex values. Overall, for different phr samples the highest cIndex (mathematical average of the other two indexes) value is for samples with 20 phr CB, what seems to be the optimal concentration for particle distribution. This concentration showed promise also from the thermal point of view, so it seems to be
the best for a self-regulating heating material, as the electrical resistance is a couple of ohms and the dispersion is quite uniform.

4. Conclusions
In this paper we propose a new PTC exhibiting composite material made of ethylene-octene copolymer and carbon black. The composite’s most intense PTC effect is in the 30-50°C region that corresponds to maximal temperatures with 30 V at around 30-34°C for 20 phr samples, therefore it can be used as a self-regulating warming device for the human body. With a higher filler load, the required voltage to get an equilibrium temperature of around 38°C can be minimized, and as a result, the self-regulating device could be powered with a USB connection (5V, 0.5A).

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