Temperature sensing potential of shear oriented polymer composites

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Abstract

Conductive polymer composites with anistotropic characteristics exhibit electrical properties that are direction dependent. In this paper properties of a composite based on the matrix composed of low density polyethylene (LDPE) blend with polycarbonate (PC) and carbon black (CB) as a filler have been presented. The composite was extruded with a twin screw extruder and formed into thin sheets that were subdued to a cold orientation. The samples for measurements were collected in a direction perpendicular and parallel to the shear flow. Mechanical and electrical properties in both directions were evaluated. The electrical properties were measured within a temperature range of 40-110ºC in order to determine the application potential of such composites as temperature sensors.

1. Introduction

The operating temperature is a factor contributing significantly to changes in the sensor signal. Electrically conductive polymer composites, and conductive polymers frequently exhibit a positive temperature coefficient of resistance (PTCR effect) representing a sudden increase in the electrical resistance within a defined temperature range. This effect is controlled within narrow limits and the use of PCTR materials as temperature sensors is difficult. Termistors were manufactured commonly of PTCR ceramics, mostly $BaTiO_3$. However, the use of these materials at room temperature is difficult, due to a large resistance, severely restricting a flow of the electric current. Therefore, recently developed thermistors consist of the electrically conductive polymer composites. Such thermistors are successfully used both for the high and low voltage applications [1]. Morphology has a major effect to the electrical properties of these composites. Depending on a size of the electrically conductive filler particles a continuous electrically conductive network in the matrix polymer can be created at relatively low filler concentration. This effect is best observed for the nano-size filler particles. The composite processing parameters such as time, temperature and pressure influence the polymer composite phase structure, thus affecting its electrical properties. Due to a low interfacial interactions, a change in the processing parameters may have a significant impact on the polymer crystallinity or a filler aggregation which may cause variations in the electrical parameters of the composites. Sadchev et al. [2] studied an effect of processing parameters on the electrical properties of poly(vinyl chloride) (PVC) filled with graphite. The composites were prepared by covering the polymer particles with a graphite layer and then sintering. The main advantage of preparing composites in this manner rather than by a melt compounding was a prior location of graphite at the interface of each PVC particle which in theory allows for a continuous network at a relatively low percolation treshold.

The negative temperature coefficient of resistance (NTCR effect) is difficult to achieve in the conventional polymer composites. Murugaraj et al. [3] have described preparation of NTCR material by means of in-situ polymerization of BTDA-ODA polyimide in the presence of carbon nanoparticles (carbon black Vulcan XC72 the average size of 30 nm). The test specimens were prepared by film casting. The samples exhibited a decrease in the electrical conductivity with a temperature increase, which allowed them to be classified as potential thermistors, but their sensitivity to temperature should be improved .

One can conclude from literature [1-5] that a temperature sensitivity of the electrical conductivity of polymer/carbon filler composites is related to following factors:

- increase in the thermal conductivity with an activation of the charge carrier effect,
- difference in the thermal expansion of a filler and a matrix, that causes a deterioration of the electrical conductivity,
- filler aggregation degree,
- cross-linking degree of a polymer, that substantially affects the electron hopping process.

In order to develop a new type of thermistor it seems promising to search for the composites exhibiting a different electrical conductivity in different directions. Such anisotropic electrically conductive polymer composites (ACPC) have a high application potential, such as field emitters or sensors [6-8] and to our knowledge it is not fully exploited. Different types of approaches are used to obtain ACPC. Tai et al. [6] proposed to obtain the one-dimensional electrically conductive structure in a polymer matrix by an electric field to provide a desired carbon black particles location. Another approach has been described in [9], where the authors obtained ACPC by compressing an anisotropic graphite subjected to pyrolysis and subsequent activation. The most widely used filler for this type of material are carbon nanotubes due to their high length to cross section ratio, good mechanical properties and excellent electrical conductivity. For example, Dai et al. [10] developed a composite filled with perpendicularly arranged carbon nanotubes for detection of gases. The materials exhibited a good selectivity, high sensitivity and excellent resistance to environmental conditions.

2. Experimental

2.1. Materials used and composite preparation

Polycarbonate (PC) Makrolon 3208 from BASF, high density poyethylene (HDPE) Lupolen 3721C (Basell Orlen) and carbon black (PC) Ketjenblack EC-300J (Akzo Nobel) were used.

The composites containing 2, 4, 6 and 7.77 wt.% of carbon black and a polymer matrix composed of HDPE/PC blend (3/1 volume ratio) were prepared by means of a two step procedure. At first the filler was suspended in methyl alcohol and sonicated for 1,5 h to improve a carbon black dispersion. It was then deposited onto PE granules and the alcohol was evaporated. The second step was admixing of polycarbonate during melt processing, that has been conducted using a twin screw extruder from Thermo-Fisher equipped with a slit die. The extrusion temperature profile was set to 180-240 °C, with a screw speed of 40 RPM.

The sheets produced were transferred to a calendar (Thermo-Fisher) using set of rolls to maintain a required elongation ratio.

2.2. Electrical properties measurement

The composite samples were cut in a direction parallel and perpendicular to orientation (described as 0 and 90º, respectively). Resistivity measurements were conducted using a two probes method, whereas the actual value measured was the voltage, as it is proportional to the resistivity at constant current. Every sample had a contact covered with a thin gold layer for minimizing a surface resistivity, thus forming a sensing probe.

Keithley 2000 multimeter (Keithley Inc.) combined with GW-Instek voltage source were used to measure the electrical response of samples to a change in temperature.

Each sample with electrodes attached was placed in a heating chamber for about 3 minutes for the voltage stabilization. After reaching stability the data were collected along with a temperature change in the chamber. The temperature range was 45-105ºC and each sample underwent a complete heating and cooling cycle, after that it was disposed of.

3. Results and discussion

The data collected have been presented as a relative voltage U/U_0 which is the voltage measured divided by a baseline.

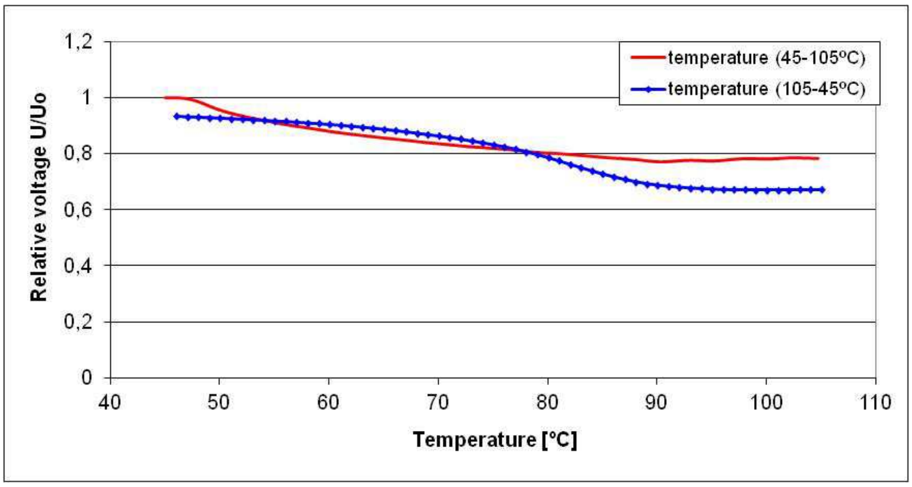

Figure 1. Relative voltage change as a function of temperature for composite containing 4% of carbon black (direction 0º).

All test materials exhibited the PTCR effect, as their resistance increased with a temperature increase. Relative voltage curves for the composite containing 4% of carbon black and cut along to the deformation direction have shown a decrease in the voltage of about 30% with the temperature increase (Figure 1). In the applied temperature range there was no thermal degradation of a composite matrix, therefore the sensor response was based primarily on the changes in a location of the electrically conductive filler pathways, resulting from the phase structure of PC/HDPE blends. The cooling curves confirmed this assumption as the voltage values returned to the level prior to the test, but a recovery was not complete. The sensor exposed to elevated temperature and then cooled down exhibited a hysteresis resulting from the incomplete reconstruction of conductive pathways, thus evidencing that the morphology changes were partially irreversible.

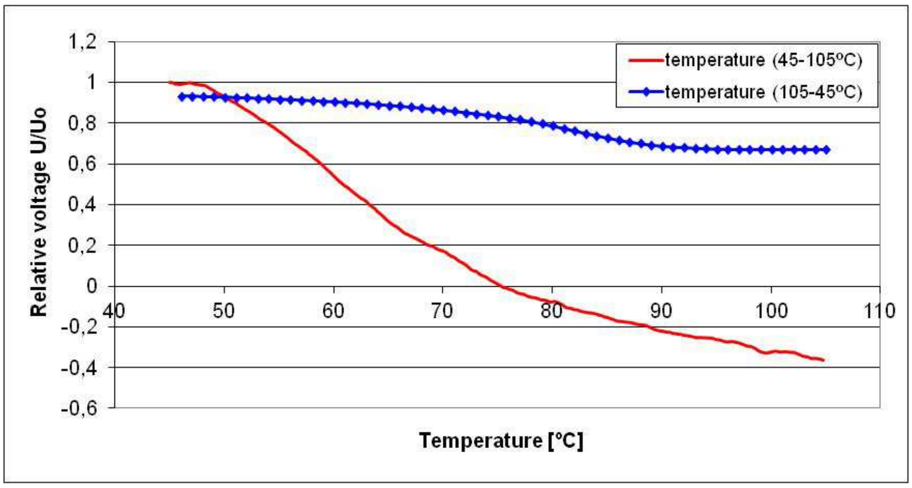

Figure 2. Relative voltage change in function of temperature for composite containing 4% of carbon black (direction 90°).

The samples containing 4% of carbon black cut perpendicular to the deformation direction have shown a significant sensitivity to the temperature changes (Figure 2). This is due to two factors, mainly a content of the filler is close to the percolation threshold (defined in previous studies at approximately 3%), moreover during orientation of the sheet the electrical conductivity of the composite was reduced along the axis perpendicular to the direction of deformation. In a selected temperature range the composite exhibited a complete voltage drop during heating.

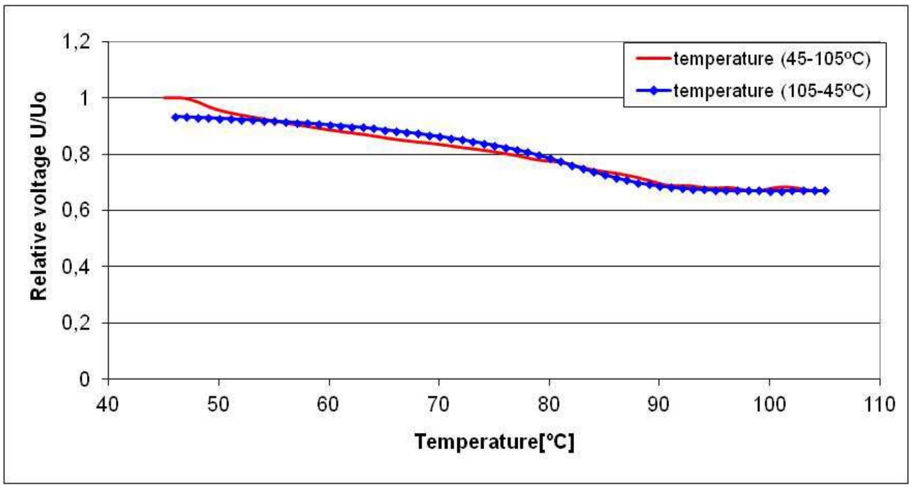

Figure 3. Relative voltage change in function of temperature for composite containing 6% of carbon black (direction 0°).

The samples cut along the deformation direction containing 6% of CB, exhibited PTCR effect, similar to other investigated materials. The voltage reduction with a temperature increase was visible, but it was less significant compared to the material with a filler content being close to the percolation threshold. That was due to a higher number of the electrically conductive pathways in a polymer matrix, causing the sensor signal to be less sensitive to the temperature changes. Apart from this, the material exhibited also an effect of incomplete CB pathways recovery during the cooling cycle.

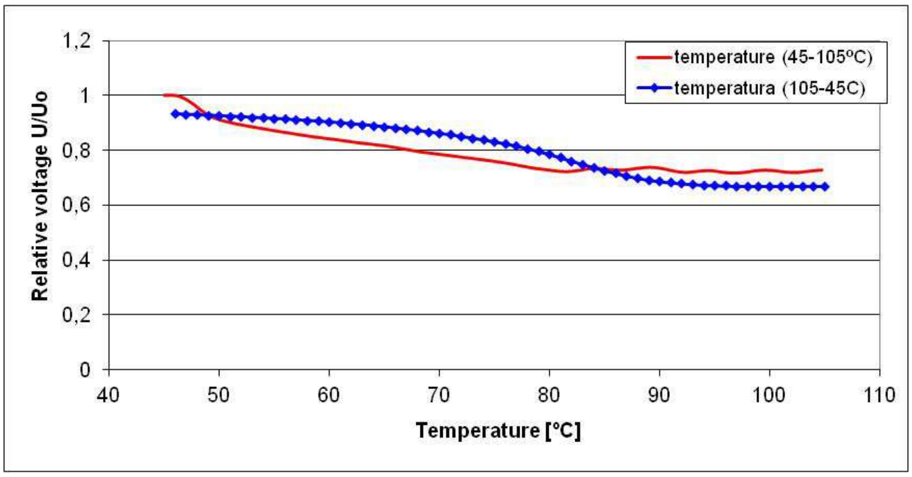

Figure 4. Relative voltage change in function of temperature for composite containing 6% of carbon black (direction 90°).

The samples containing 6% of carbon black cut perpendicular to the direction of orientation (Figure 9) have shown higher sensitivity to the temperature changes when compared to samples of direction 0°. That was due to the orientation of carbon black pathways during extrusion that resulted in a reduction of the composite electrical conductivity. The measured signal ratio reached 40% of the baseline during heating and, like in the other materials an incomplete recovery during the cooling cycle was observed.

4. Conclusions

- The materials have shown a high potential for thermosensitive applications in a temperature range up to 105°C.
- Character of the sensor signal strongly depends on the conductive filler concentration.
- Temperature sensitivity of the material can be tailored for specific applications by means of the filler percolation threshold in a polymer matrix and with the orientation parameters.

5. Acknowledgments

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6. References

1. McLachlan DS, Heaney MB. *Complex ac conductivity of a carbon black composite as a function of frequency, composition, and temperature.* Phys. Rev. B., 60(18):12746, 1999.
2. Sachdev VK, Mehra NC, Mehra RM. *Study of pre-localized graphite/polyvinyl chloride electroconductive composites for sensors.* Phys. Stat. Sol. (a)., 201(9):2089-2098, 2004
3. Murugaraj P, Mainwaring D, Mora-Huertas N. *Thermistor behaviour in a semiconducting polymer–nanoparticle composite film.* J. Phys. D: Appl. Phys.,

39(10):2072-2078. 2006

4. Sau KP, Chaki TK, Khastgir D. *Electrical and mechanical properties of conducting carbon black filled composites based on rubber and rubber blends*. J. Appl. Polym. Sci., 71(6):887-895, 1999
5. Song Y, Zheng Q, Yi X. *Reversible nonlinear conduction in high-density polyethylene/acetylene carbon black composites at various ambient temperatures*. J. Polym. Sci. B Polym. Phys. 4;42(7):1212-1217, 2004
6. Tai X, Wu G, Tominaga Y, Asai S, Sumita M. *An approach to one-dimensional conductive polymer composites*. J. Polym. Sci. B Polym. Phys. 1;43(2):184-189, 2005
7. Jung YJ, Kar S, Talapatra S, Soldano C, Viswanathan G, Li X, et al. *Aligned Carbon Nanotube−Polymer Hybrid Architectures for Diverse Flexible Electronic Applications*. Nano Letters., 6(3):413-418, 2006
8. Yu G, Cao A, Lieber CM. *Large-area blown bubble films of aligned nanowires and carbon nanotubes*. Nat Nano. 2(6):372-377, 2007
9. Celzard A, Krzesiñska M, Bégin D, Marêché JF, Puricelli S, Furdin G. *Preparation, electrical and elastic properties of new anisotropic expanded graphite-based composites*. Carbon., 40(4):557-566, 2002
10. Wei C, Dai L, Roy A, Tolle TB. *Multifunctional chemical vapor sensors of aligned carbon nanotube and polymer composites*. J. Am. Chem. Soc. 128(5):1412-1413, 2006