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Simulation of Electrical and Thermal Behavior of Poly(propylene) / Carbon Filler Conductive Polymer Composites

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Summary: PP-carbon CPC show interesting thermo-electrical properties, smooth resistivity increase with temperature up to 150°C and consequently high power dissipation on a wide temperature range. The addition of short carbon fibers to PP already formulated with carbon black increases sharply the electrical conductivity of the CPC but does not have much influence on thermal conductivity as it could have been expected from the favorable aspect ratio of the fibers. The simulations of the thermo-electrical behavior of the CPC under tension put into evidence a temperature gradient at high heat flux due to the low thermal conductivity, which may damage the material itself.

Keywords: conductive polymer composite; conductivity models; fillers; simulations; thermal and electrical properties

Introduction

Conductive polymer composites (CPC) resulting from the association of an insulating polymer matrix with electrical conductive fillers (carbon black, carbon fibers, metal particles), exhibit several interesting features due to their electrical resistivity variation with thermal solicitations, the so called PTC effect (positive temperature coefficient) [1]. Besides the numerous advantages of CPC, their low thermal conductivity resulting from their high insulating polymer content is a drawback to achieve high thermal efficiency and allow good heat dissipation. Indeed, the crossing of electric direct current through the charged polymer induces internal power dissipation by joule effect, which can generate temperature gradients very important in the material. The objective of this study is that way to quantify the effect of different fillers and to understand the different phenomena involved during ohmic heating with CPC. In this paper, the results obtained with Poly(propylene) containing carbon black and carbon fibers are presented.

In a first step, the effect of filler content on electrical and thermal conductivities is quantified. Then, the coupling of electrical and thermal phenomena is studied.

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Experiments of ohmic heating are performed on extruded tapes samples. The objective is to validate the values obtained for the thermo-physical parameters and to well understand the material behavior when it is subjected to electrical potential difference as it is the case in ohmic heating.

Materials and methods

Materials. The desired CPC composition was adjusted blending a poly(propylene) master batch containing 30% w/w special P carbon black from PREMIX (TP 6504) with a pure poly(propylene) from TOTAL (3181). THORAYCA T300 long carbon fibers sized with an epoxy agent were obtained from THORAY and cut by APPLY CARBON to obtain short carbon fibers (SCF) with a mean diameter of 8.7 ± 1.7 μm and a length distribution of 1700 ± 0.3 μm. Carbon black filled poly(ethylene-co-ethyl acrylate) (EEA-CB) was LE 7704 from BOREALIS. The main thermal characteristics of the polymers are recalled in Table 1.

Blending. Depending on the sample thickness required for each characterization technique, the blending process chosen was either a BRABENDER LAB STATION internal mixer to obtain 10 mm thick molded pads, or a BRABENDER LAB STATION twin screw extruder to obtain 3 mm thick tapes. To obtain a good dispersion of the SCF in the CPC a two step process was used: a first blend in a twin screw extruder followed by a second in a single screw extruder (after grinding).

Table 1: Polymers characteristics.

	T_g (°C)	$T_{c,n}$ (°C)	T_m (°C)	k ($W.m^{-1}.K^{-1}$)	ρ (Ω.cm)	X (%)
PP	- 10 ± 3	114.4 ± 0.5	166.4 ± 0.5	0.24	10^{11}	52.5
EEA	- 33 ± 3	83 ± 0.5	99.5 ± 0.5	0.26	10^{15}	20

Methods. Electrical resistivity evolution with temperature was measured by a four probe technique. After connection the sample ($2 \times 10 \times 70$ mm^3) was placed in an oven [2]. The specific heat capacity C_p ($J.kg^{-1}.K^{-1}$) was measured using a METTLER TOLEDO DSC 822 differential scanning calorimeter. A three-curve analysis method was used, with sapphire as reference material. The density d was determined with a pycnometer at room temperature and the density variation as a function of temperature was obtained by a TA Instrument DMA 2980 dynamic mechanical analyzer with the compression accessory.

Thermal diffusivity α was determined by the laser flash method. Thermal conductivity k as a function of temperature was deduced from the parameters (α, d, C_p) using equation 1.

$$k = \alpha\, d\, C_p \qquad (1)$$

The effective thermal conductivity as a function of filler content was measured by a guarded hot plate method at 50°C. The samples were 10 mm thick pads of 60 × 60 mm^2 section.

Electrical and thermal properties

Electrical properties. Figure 1 shows that an important resistivity decrease can be obtained by addition of carbon black up to 17.5% v/v CB. Over this content, the curve reaches a plateau and introducing more CB in PP won't decrease the CPC resistivity, but adding carbon fibers up to 5% v/v allows to overcome this limit and to gain 0.75 decade of conductivity.

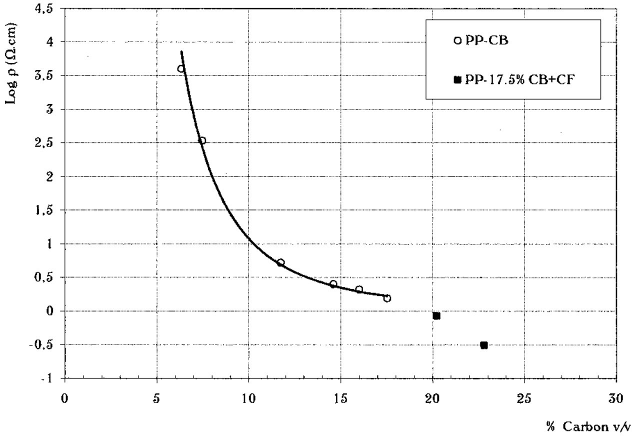

Figure 1. Evolution of PP resistivity with CB content and SCF content over 17.5% v/v CB.

In Figure 2 the variation of the electrical resistivity of PP CPC for three filler contents (30% w/w CB, 30% w/w CB + 5% w/w SCF and 30% w/w CB + 10% w/w SCF) is compared to that of EEA CPC with 27.75% w/w CB. Very different electrical behaviors can be observed: PP CPC resistivity increases smoothly from 40 to 160°C of about one decade while for EEA CPC, a stronger PTC effect is observed (about 2.5 decades between 40 and 100°C). More, the room temperature resistivity of the former is much lower, ρ # 0.3 Ω.cm for PP + 30%CB + 10%SCF compared to EEA + 27.75%CB, ρ # 215 Ω.cm. This important difference can mainly be explained by the dispersion level of the filler in the matrix, a good dispersion of the filler leads to a lower conductivity, and by the structure of the filler, a highly structured filler is more conductive for the same content. Related the melting of the matrix, the switching temperature is observed at about 80°C for EEA CPC and suggested to be at about 160°C for PP CPC.

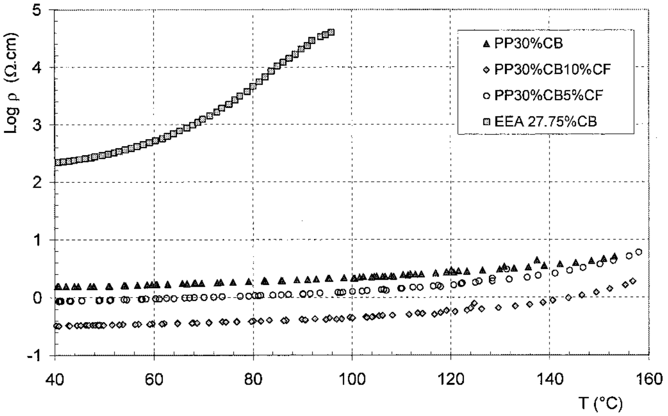

Figure 2. Evolution of electrical resistivity versus temperature.

Thermal properties. The influence of fillers on the thermal conductivity was first investigated (Figure 3). It can first be noticed that the two CPC have similar evolutions of thermal conductivity whatever the filler nature. It can be seen that the effective thermal conductivity of CPC k can only be increased by a factor two over 25% v/v of fillers. On the other hand using higher filler contents unexpectedly also leads to an important modification of rheological properties of CPC, so that it is not realistic to use more than 30% v/v of filler to increase thermal conductivity. Several empirical models predicting the composite effective thermal conductivity k as a function of the filler volume content ϕ for known thermal conductivities of the matrix and the filler can be found in the literature [3]. A very good fitting of experimental data is obtained with MAXWELL [4] volume fraction for randomly distributed and non-interacting homogeneous spheres in a homogeneous medium. Some experimental considerations are taken into account in the LEWIS & NIELSEN model, through parameters linked to particles geometry and the maximum packing volume fraction. The fitting of experimental data with this later model provides two coefficients $A = 1.5$ and $\phi_m = 0.637$ [5] suggesting a random distribution of spherical shape. This result shows that introducing up to 5% v/v of cylindrical elements in the CPC does not modify the overall thermal conduction mode.

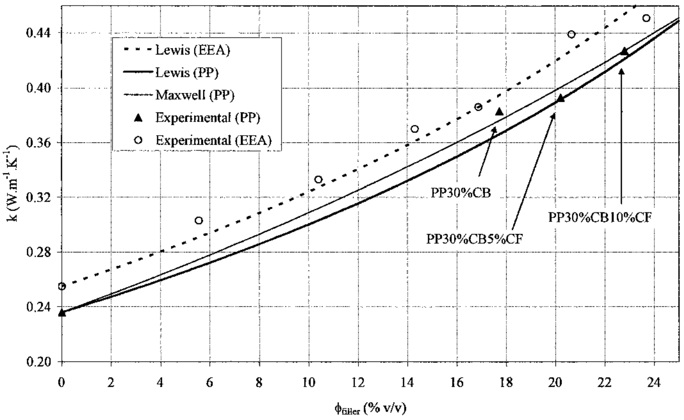

Figure 3. Effective thermal conductivity as a function of carbon volume fraction at 50°C.

Figure 4 represents the evolution of equivalent volume heat capacity (d C_p) and the thermal conductivity with temperature for PP-30% CB. As PP crystals melt over 120°C, a rough increase C_p is observed, this is why C_p has only been evaluated in the temperature range [20°C - 120°C] where the curve is approximately linear. The evolution of the thermal conductivity with temperature was derived from equation (1). The k value obtained at 50°C is in good agreement with that measured independently by the guarded hot plate method.

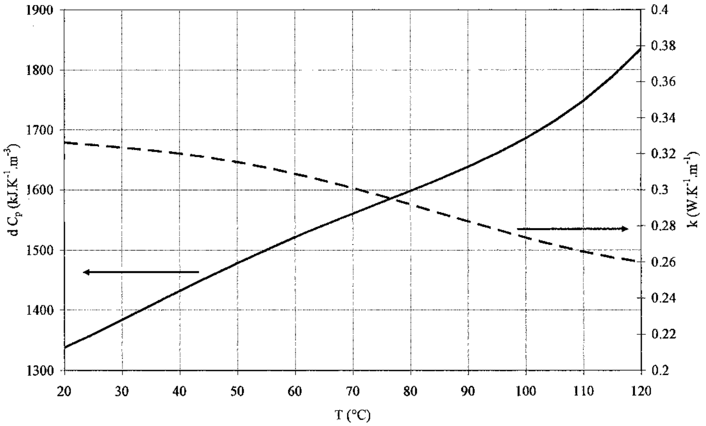

Figure 4. Thermal conductivity and volume heat capacity evolution with temperature for PP-30% w/w CB.

Simulation of electrical and thermal behavior of the CPC

Experimental and modeling work has been carried out on PP-30% CB extruded tapes subjected to direct current, as is the case during ohmic heating. Samples were extruded tapes (dimensions: 179 × 40 × 2.35 mm). They are disposed vertically on the edge and connected to current by two copper electrodes at each end according to a procedure already described in previous work [2]. In experimental study, the heat transfers at the vertical surface are natural convection and thermal radiation. The temperatures at the center of the material and at the surface were measured by type K thermocouples of 250 μm diameter.

Geometry and mathematical modeling. The geometry and the mesh of the problem are show in Figure 5. The voltage is applied directly to the ends.

The material is supposed isotropic and homogenous at the macroscopic scale. The governing equations for the electrical conduction and heat transfer in the material are [7]:

$$-\nabla \cdot (\sigma(T)\nabla V) = 0 \tag{2}$$

$$d(T)C_p(T)\frac{\partial T}{\partial t} = \nabla \cdot (k(T)\nabla T) + S(T) \qquad \text{with} \quad S(T) = \sigma E^2 \tag{3}$$

with $\sigma(T)$ the electrical conductivity function of temperature T; V, the voltage and S, the internal power generated by Joule effect.

The mathematical modeling is solved with the finite element method [8] using FEMLAB®.

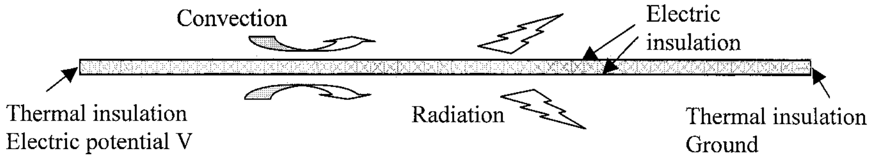

Figure 5. Longitudinal cross section, view from the top, of the extruded tape.

Confrontation of experimental data with simulating results. In order to compare experimental measurements with simulation, the voltage solicitation and air temperature with respect to time are directly read in an experimental file. Then, the thermo-physical data determined previously are brought into the model through polynomial equations. In Figure 6, the simulated intensity and temperature responses are in good agreement with experimental data. The electrical intensity was calculated from the current density J at half length of the tape. The intensity curve emphasizes the PTC effect, beginning close to 40°C and responsible for a temperature self-regulation effect. During a voltage step, the intensity instantaneously increases before it progressively decreases and reaches the steady state. It can be noticed that this phenomenon is reversed during cooling. The plotted temperatures are the experimental and simulated temperatures in the center of the tape. In this case, the heat flux is small (1 kW.m^{-2} for V = 25 V), so the thermal gradients in the material are lower than 2°C (Figure 7).

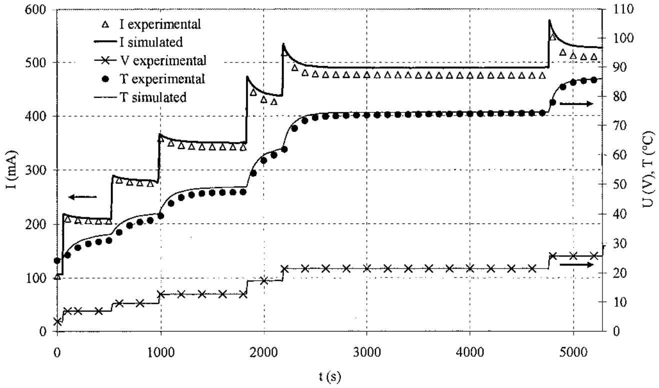

Figure 6. Comparison of experimental and simulated transient response of PP-30% w/w.

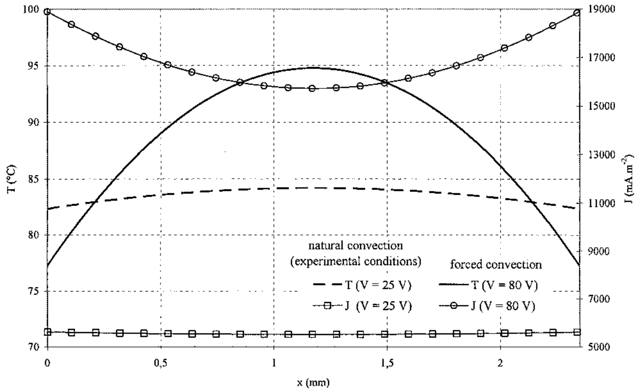

Figure 7. Current density and temperature profile through the thickness at two different voltage solicitations.

Additional information on the thermo-electrical behavior of the CPC can be deduced from Figure 7, where it appears that due to the presence of a thermal gradient between the surface and the core of the sample, the current density J is not constant in the thickness of the material. These plots obtained in stationary state conditions also show that the electrical power is generated at the surfaces (colder). The simulation validated for a low voltage (25 V) providing a low heat flux (around 1 $kW.m^{-2}$) allows extrapolating the behavior of the CPC at higher heat flux (9 $kW.m^{-2}$ / 80 V). This last simulation has been made in forced convection in order to obtain 85°C in the material. In this case the temperature gradient increases from one or two degrees to about twenty so that it may be necessary to increase the thermal conductivity of the CPC.

Conclusion

PP-carbon CPC show interesting thermo-electrical properties, smooth evolution of resistivity with temperature up to 150°C and consequently high power dissipation. The addition of SCF to PP already formulated with CB increases sharply the electrical conductivity of the CPC but does not have much influence on thermal conductivity as it could have been expected from the favorable aspect ratio of the fibers. The simulations put into evidence a thermal gradient increase with the heat flux which may damage the material itself. One way to reduce this gradient is to increase the thermal conductivity. But it has been shown that thermal conductivity can only be improved by a factor 2 for a filler volume fraction of 25%. Since carbon is both electrical and thermal conductor, this method also presents the drawback to increase simultaneously electrical and thermal conductivity. Moreover, the increase of electrical filler volume fraction tends to diminish the self-regulation effect due to a better stability of conductive chains through material. This is why future developments of this work will concern the use of thermally conducting and non-electrically conducting fillers.

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