Tuneable PTC effect in polymer-wax-carbon composite resistors

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Abstract: The resistivity dependence on temperature of composite resistors made of carbon fillers dispersed in an organic matrix are known to be strongly affected by the matrix thermal expansion. High positive temperature coefficient (PTC) effects, i.e. essentially switching from resistive to quasi-insulating behaviour, can be caused by phase changes in the matrix and the assorted volume expansion, a behaviour that has been previously shown with both simple organic waxes (low temperatures) and semicrystalline polymers (higher temperatures, used commercially in resettable fuses). However, waxes become very liquid upon melting, possibly resulting in carbon sedimentation, and tunability of semicrystalline polymers is limited. In this work, we therefore study composite resistors with a mixed polymer-wax matrix, the polymer imparting high viscosity in the liquid state and a variety of waxes allowing a high tunability of the behaviour. It is shown that the resulting resistors exhibit strong PTC effects, linked with the melting and crystallisation of the wax component.

Key words: thick-film resistors, polymer-carbon composites, PTC effect, resettable fuses

1. INTRODUCTION

Besides high-reliability thick-film cermet resistors [1], composite resistive materials based on organic matrices [2], mainly on different forms of carbon [3], have many useful industrial properties and allow convenient low-temperature processing. Especially, for thick-film conductive and resistive materials, the use of organic resin matrices allows compatibility with a wide range of substrates, albeit at the cost of lower stability than their cermet analogues [4,5].

One particularly interesting feature of such composite resistors (both in bulk and thin-film form) is the possibility of introducing a steep increase in resistivity above a given temperature: a "switching" PTC effect, as opposed to the more linear one used for instance in platinum temperature sensors. This abrupt jump in resistivity is due to a 1st-order phase change in the matrix, i.e. mostly melting, as has been shown for model systems of exfoliated graphite or carbon nanotubes in hexadecane or even water [6]. However, such composites, whose matrix consists solely of small molecules, are not expected to be stable over many cycles, as the high fluidity of the molecular matrix in the molten state allows extensive particle rearrangements or even sedimentation.

Practical PTC composites applicable to resettable fuses [7] and self-limiting heaters [8] therefore are based on polymers, which are highly viscous in the molten state. The main materials used are forms of high-density polyethylene (HDPE), which can achieve a quite high level of crystallinity and yield practical transition temperatures in the 120-140°C range [9-11], in line with the melting range of the crystallites. However, HDPE does not lend itself well to thick-film processing, and its transition temperature cannot be easily tuned.

In this work, we therefore explore a mixed approach [8,12], akin to hot-melt adhesives, between a molecular [6] and polymer [9-11] matrix, whereby an amorphous polymer (ethylcellulose, EC) well-suited as a screen-printing vehicle is combined with a molecular crystalline wax (1-octadecanol, stearyl alcohol, C18E0).

- At high temperature, the wax melts and acts as a solvent for the matrix. However, due to the long-chain solvent and dissolved long-chain polymer, viscosity remains high and precludes sedimentation.
Upon cooling, the wax crystallises out of the polymer, which solidifies both the now crystalline wax and the polymer, due to the now separate wax no longer acting as a plasticiser. Using this hot-melt matrix and graphite powder as a conductive phase, we expect a jump in resistance near the melting point of the wax, ~59°C.

2. EXPERIMENTAL

2.1. Materials and sample preparation

Ethylcellulose (EC-4-48, 4 cps grade, 48% hydroxyl) and octadecanol (C18E0) were purchased from Sigma-Aldrich, and synthetic near-spherical graphite (KS4, < 4 µm) was obtained from TIMCAL (Tab. 1). First, the matrix was prepared by dissolving EC-4-48 powder into liquid C18E0 (~100°C with constant stirring), with a 1:3 mass, which yields a waxy solid that is tougher than C18E0 alone at room temperature. Various amounts of graphite were then included by hand mixing in the re-molten matrix.

For these preliminary experiments, the composites were not formulated in solvents for conventional screen printing. Instead, resistive strips were screen-printed directly (~1.5 mm width, ~50 µm thickness) in the hot state onto test patterns on alumina substrates, by hand through a metal mask. Resistor lengths, as defined by the Ag electrodes (ESL 9912K, ElectroScience Laboratories, USA) ranged from 0.3 to 5.0 mm (Fig. 1).

Tab. 1. Used materials (density according to supplier).

<table>
<thead>
<tr>
<th>Material</th>
<th>Code</th>
<th>Supplier</th>
<th>Density [kg/m³]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylcellulose</td>
<td>EC / EC-4-48</td>
<td>Sigma-Aldrich</td>
<td>1'140</td>
</tr>
<tr>
<td>1-Octadecanol</td>
<td>C18E0</td>
<td>Sigma-Aldrich</td>
<td>812</td>
</tr>
<tr>
<td>Graphite, synthetic, &lt;4 µm</td>
<td>KS4</td>
<td>TIMCAL</td>
<td>2'255</td>
</tr>
</tbody>
</table>

Fig. 1. The used resistive test patterns (numbers on the resistive strip: effective resistor lengths, all dimensions in mm).

2.2. Measurements

The samples were subjected to two heating cycles:

- A first temperature cycle was performed from 25°C to 80°C, in regular 5 K steps.
- A second cycle was then carried out, starting at 25°C, then 40°C, then 47-58°C in 1 K steps.

Measurements were performed both during the heating and cooling phases (3 per temperature and altogether 18 resistors per composition). For each point, the temperature was stabilised for ~3 min before taking the measurement.
3. RESULTS AND DISCUSSIONS

The evolution of the resistivity of the samples is shown in Fig. 2, for both thermal cycles. Several observations may be made:

- As expected, sample resistivity decreases with filler loading.
- At low temperature, resistivity increases smoothly with temperature, and then very fast around the melting point of the wax, above which conductivity is essentially lost (resistance not measureable, resistivity $>10^4 \Omega \cdot m$). Upon cooling below the melting point of the wax, conductivity is regained. Resistivity then decreases smoothly with further cooling towards room temperature.
- The resistivity evolves throughout the cycles. Especially, the second cycle, with slow cooling through the crystallisation range of the wax, results in much lower resistivity at the end of the cycle. Also, upon slow cooling in the second cycle, resistivity decreases in two steps: a) decrease from very high ($>10^4 \Omega \cdot m$) to $\sim 10 \Omega \cdot m$, as in the 1st cycle, and b) a second decrease around 50°C, highlighted with an arrow in Fig. 2.
- As expected, our samples, exhibit 'switching' PTC characteristics, with a switch temperature correlating reasonably well with the melting point of the wax. An exact match is not expected, as the transformation is not simple melting of a pure phase, but also involves the polymer, and transformation of the EC-C18E0 polymer-wax system. Assuming that the crystalline C18E0 phase does not dissolve any EC, the evolution of the matrix can therefore be written as:

$$EC \text{ (amorphous, with little dissolved C18E0)} + C18E0 \xleftarrow{\beta} \leftrightarrow \text{liquid (EC + C18E0)}$$

As such, the transformation is not expected to occur at a single temperature, even at equilibrium, but rather occur over a temperature range. With further cooling below the point at which crystalline C18E0 appears, progressively more C18E0 is expected to crystallise out of EC. The system is further complicated by the existence of several solid phases for C18E0 [13].

Furthermore, as the EC phase becomes highly viscous, kinetics also play a strong role, as seen when comparing both graphs. Although temperature changes were done in steps (change, stabilisation and measurement), one can nevertheless give average cooling rates around 50°C, the temperature of the feature seen in the 2nd cycle: 30 K/h for the 1st cycle, and 9 K/h for the 2nd. Apparently, the slower cooling gives more time for crystallisation, resulting in a lower resistivity. This hypothesis is confirmed when comparing the end of the 1st cycle with the beginning of the 2nd: in the 16-day period between both measurements, resistivity noticeably decreased, indicating that slow crystallisation takes place even at room temperature if the sample was cooled relatively fast.

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4. CONCLUSIONS

The resistivity of composites consisting of a mixed polymer-wax matrix filled with graphite conductive phase exhibits 'switching' PTC characteristics around the melting point of the wax, within a certain range of filler concentrations, brought about by the phase behaviour of the polymer-wax system. The results are very promising, as the system may be tuned simply by changing the type of wax. However, the results also highlight the complex behaviour of these composites, and further studies are needed to elucidate their equilibrium and kinetic characteristics.

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