

MAGNETICALLY TUNEABLE THERMOPLASTIC RESISTIVE COMPOSITES

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ABSTRACT:

Depending on the materials and processing parameters, composite materials consisting of an insulating matrix and a conductive filler may be electrically insulating, resistive or conducting. Previously, we had manufactured composites consisting of a resin and a conducting magnetic filler, and shown that polymerisation under magnetic field could achieve oriented conductors, with essentially unidirectional electrical conduction. In this work, we explore the possibility of replacing the resin matrix by a thermoplastic material, allowing in principle free reconfiguration of the filler by re-melting the matrix under different magnetic field strengths and orientations, and thereby tuning of the electrical transport properties. The formulation, fabrication and first results are reported on such materials, with an ethylcellulose - wax matrix and conducting powders based on Ag-coated Fe_3O_4 and Fe_2CoO_4 ferrites.

Keywords: thick-film technology, composites, conductors, magnetic materials.

1 INTRODUCTION

Composite materials fabricated by dispersing a discrete conducting filler powder in an insulating matrix are widely used in applications such as antistatic surfaces, electromagnetic interference (EMI) shielding, resistors, conductors, conducting adhesives, and resettable fuses [1-9]. In contrast to materials with an intrinsically conducting matrix, electrical transport occurs through percolative conductive / resistive paths through the material, depending on the matrix and filler composition and morphology, with interparticle charge transfer possibly occurring through various mechanisms [2-4, 10-13]. Insulating matrices may be both mineral (glass) for high-reliability devices [4,5,10], or organic (thermoplastics or thermosets) [2,3,6] for versatility, low cost and compatibility with a wide range of substrates.

In the latter case, the electrical behaviour will be strongly dependent on the evolution of the relatively unstable matrix. For instance, using a crystalline thermoplastic polymer [9] or wax [14] matrix, with a quite definite melting point T_m , yields abrupt positive temperature coefficient (PTC) effects at T_m , attributed to the volume expansion due to melting. More

progressive PTC behaviour may be obtained with an elastomer silicone matrix [15] having a high coefficient of thermal expansion (CTE)

Recently, it has been shown that dispersing a conductive filler with magnetic properties in an organic resin and hardening this matrix in the presence of a magnetic field allowed creation of anisotropic conduction paths stemming from the formation of filaments of particle agglomerates (needles) aligned to the direction of the field. Several systems, such as Ag-coated superparamagnetic magnetite ($\text{Fe}_3\text{O}_4@\text{Ag}$) nanoparticles in a silicone matrix [16], or nickel powder in epoxy resin [17,18] have been investigated. However, the overall arrangement of conductive magnetic particles may not be reconfigured after polymerisation, as silicone and epoxy resins are thermoset materials.

For another application (3D structuration of ceramic circuits), we have developed "hot-melt" organic mixtures [19], where an amorphous thermoplastic polymer such as ethylcellulose (EC) is formulated together with a wax such as cetanol (hexadecanol, $T_m \approx 49^\circ\text{C}$). This wax appears as a crystalline filler at low temperature, but acts as an efficient solvent for EC above its melting point, this transformation being reversible upon cooling. By varying the cetanol:EC ratio and EC molecular weight, as well as incorporating other additives, the properties of the system (melting point, expansion on melting, hardness and viscosity in the liquid state, ...) may be tuned to a considerable extent.

Therefore, we explore in this work the formulation of resistive composites made of such hot-melt mixtures as organic matrices, together with Ag-coated conductive magnetic fillers, with the aim to achieve reconfigurable materials and study the interplay of the thermal behaviour of the thermoplastic matrix and the magnetic response of the filler. Such materials may either directly be shaped in bulk form by melting and casting in a mould, or, if dissolved in an appropriate solvent, be applied as a thick-film material by screen printing.

Here, the composites are dispensed as thick films onto ceramic bars that comprise an integrated heater on the bottom side, and a three-resistor layout on the top side (Figure 1), with possibility of applying external magnetic fields. Preliminary results show that reconfiguration of the magnetic filler particles into long chains can be achieved, by melting the matrix and applying a magnetic field (Figure 2). We intend to further study the effect of magnetic reconfiguration on the electric properties, the thermal response, as well as the degree of retention of both configuration and resistance in the frozen state.

2 EXPERIMENTAL

2.1 Organic matrix vehicle

The organic matrix system was chosen with the following properties in mind:

- Sharp melting behaviour, i.e. based on a solid-liquid transition, rather than going through a glass transition (progressive lowering of viscosity)
- Moderate melting temperature, to avoid oxidative degradation during melting cycles
- Low affinity for water / water solubility, to avoid effects of humidity
- Processable both in the melt, for bulk sample, or dissolved in solvents, for thick-film deposition on substrates
- Not too low viscosity in the molten state, to avoid sedimentation

Based on previous experiments [19], it was decided to use a combination of EC ("N" type, 48% ethyl grade), a standard amorphous polymeric binder (glass temperature $T_g \sim 150^\circ\text{C}$) used in thick-film screen printing, and a crystalline wax that acts as a latent solvent (similar to some "hot-melt" glues):

- At low temperature, the wax precipitates out of the polymer.

- At high temperature, the wax melts and then dissolves the polymer.

The investigated wax compounds are given in Tab. 1. They are commonly-used emollients and surfactants in the cosmetics industry, i.e. they are easily-obtained common products, and have low toxicity. To assess their suitability for our purposes, the solubility of the waxy compounds was tested in common solvents (Tab. 2) compatible with EC "N" and with boiling points / evaporation rates in the usable range for screen printing.

Vehicles were prepared by dissolving EC and the waxes in the selected solvent, and their stability against wax precipitation over time was checked.

Tab. 1: Investigated waxy materials

Wax	Melting point [°C]	Boiling point [°C]
Tetradecanol / 1-tetradecanol / myristyl alcohol	38	290
Cetanol / 1-hexadecanol	49	344
Octadecanol / 1-octadecanol / stearyl alcohol	58	-
Steareth-2 / PEG-2 stearyl ether (PEG = polyethylene glycol)	44	-
Sorbitan monopalmitate	48	-

Tab. 2: Investigated solvents (evaporation rate relative to n-butyl acetate at room temperature)

Solvent	Evaporation rate [°C]	Boiling point [°C]
Hexanol / 1-hexanol	0.05	157
Butyl lactate	0.04	187
Texanol / 2,2,4-triméthyl-1,3-pentenediol monoisobutyrate	0.00	257

2.2 Conducting fillers and composite materials

Fe_3O_4 and Fe_2CoO_4 particles covered with Ag ($\text{Fe}_3\text{O}_4@\text{Ag}$ & $\text{Fe}_2\text{CoO}_4@\text{Ag}$) were manufactured according to the procedure defined previously, by chemical techniques [16, 20]. Although the primary particles are nano-sized, there is some agglomeration during the Ag coating step, resulting in powders of agglomerates sized around 1 μm .

Composite materials were fabricated using standard thick-film techniques, i.e. mixing the powders into the vehicles, deposition by screen printing onto heating platforms with electrodes (Fig. 1), and drying by evaporation of the solvent. The binder and the wax remain behind, acting as the matrix of the composite.

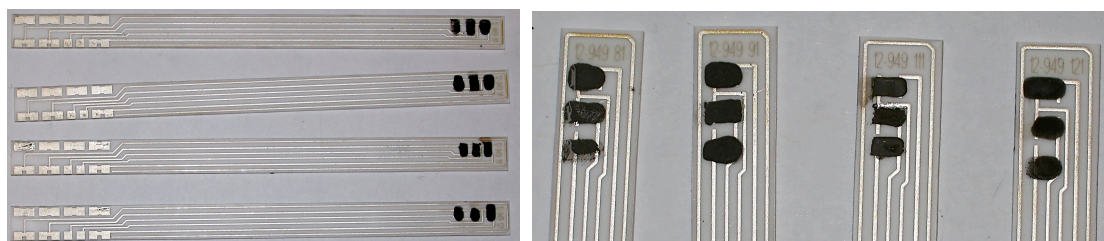


Fig. 1: Composite materials (black zones) deposited on heating platforms with electrodes

2.4 Measurements

The samples were measured before, during and after melting (60-100°C). As the vehicle is thermoplastic, it may be re-melted at will, and a magnetic field applied to reorient the particles. Heating was carried out using a screen-printed heater placed behind the ceramic bars, and resistance was measured between the sample electrodes.

To enhance conductivity, a magnetic field is applied in parallel with the current flow, as in previous experiments with a silicone matrix [16, 20].

3 RESULTS AND DISCUSSIONS

3.1 Solubility of the waxes and properties

Tab. 3 gives some results of room-temperature solubility of the investigated waxes. Expectedly, fatty alcohol waxes are best dissolved by (similar) hexanol, in accordance with literature data for tetradecanol and cetanol [21-23]. However, in a viscous solvent + binder solution, it was discovered that, under fast cooling and stirring, these waxes could precipitate as very fine suspensions at high loadings. Therefore, there are two possibilities:

- 1) Soluble wax type, with wax remaining in solution in the vehicle
- 2) Suspension wax type, with wax forming a fine precipitate in the vehicle

Both types allow the manufacture of thick-film pastes, but the 2nd method restricts the subsequent filler loading, as the precipitate already acts as a filler. The main restriction we found is that the wax content should be either reliably in the solubility limit (1) or well above (2), so a fine precipitate may be formed on cooling. If the wax content lies somewhat in between, the paste will have unstable rheological properties, and its formulation must therefore be adjusted.

After drying of the solvent, tetradecanol, steareth-2 and sorbitan monopalmitate tend to yield soft layers, while cetanol and octadecanol are harder.

Tab. 3: Room-temperature solubility of investigated waxy materials, in % of overall weight (solvent + wax)
 † Precipitates as fine suspension up to 30-40%; "low": <5%

Wax	Solvent = hexanol	Solvent = butyl lactate	Solvent = texanol
Tetradecanol	50%		
Cetanol	25%	8%	"low"
Octadecanol		"low"	"low"
Steareth-2	50%		25%
Sorbitan monopalmitate	6%†		4%

3.2 Processing

The evolution of a paste (EC-cetanol-hexanol with ~20% weight $\text{Fe}_2\text{CoO}_4@Ag$ in EC-cetanol) was monitored throughout a basic drying and re-melting sequence, and is shown in Fig. 2.

Upon application of a strong magnetic field (0.3 T during 1 h in the molten state), the particles visibly orient, as shown in Fig. 3.

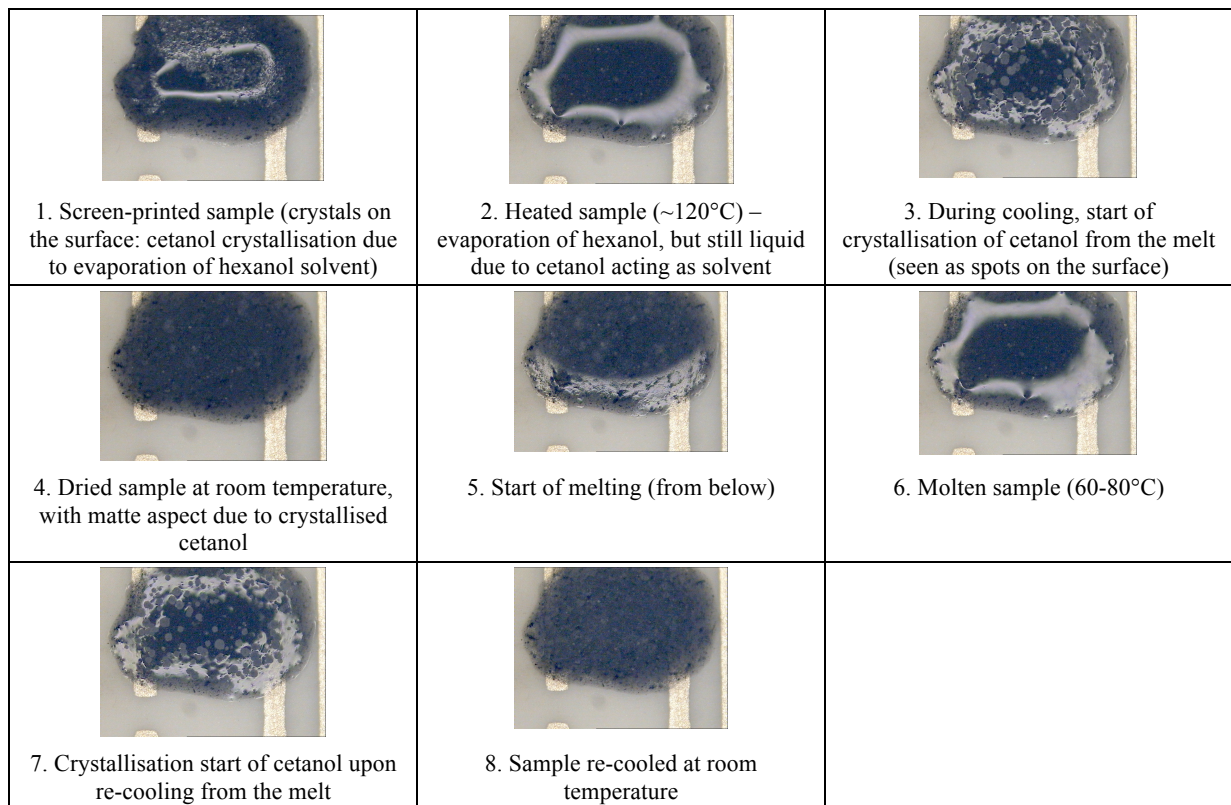


Fig. 2: Illustrated processing sequence of a thermoplastic composite thick-film composition

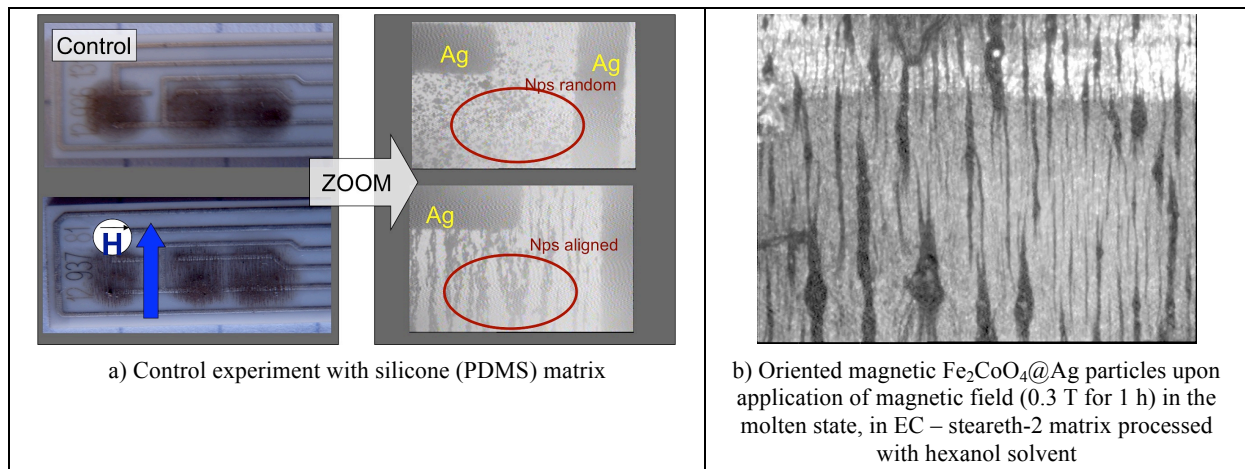


Fig. 3: Result of hardening (PDMS, a) or melting (thermoplastic compositions, b) under magnetic field, showing strong alignment of magnetic particles in field, vs. random arrangement in zero field.

3.3 Electrical measurements

Although strong alignment could be established, the samples shown in Fig. 2 and 3 did not exhibit in-plane electrical conduction. Complementary tests showed that conduction may be established by loading with ca. $\geq 20\%$ vol. particles, but the dependency on magnetic field is no longer very clear. As difficulty was encountered establishing conductivity, some measurements were performed vertically (Fig. 4), by printing onto a planar electrode and setting a metal sheet above the layer as a top electrode. This yields a small interelectrode distance ($\sim 100 \mu\text{m}$) and large cross section ($2\text{-}3 \text{ mm}^2$). Conductivity could be established, but only by applying some pressure after cooling, with the material expectedly responding sluggishly to pressure (relaxation time $\sim 20 \text{ min}$), due to its thermoplastic nature. This contrasts with the fast response of composites with elastomeric matrixes to applied mechanical or magnetic stimuli [16].

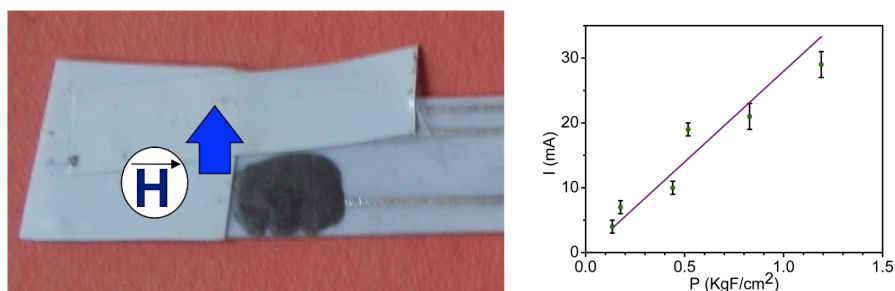


Fig. 2: Vertical conductivity measurement: setup (left) and current measured vs. pressure (right)

4 CONCLUSIONS

In addition to the previously-investigated compositions with a silicone matrix, "hot-melt" thermoplastic matrices based on EC and suitable waxes were developed, with the waxes acting as latent solvents for this binder above their melting point, but crystallising out upon cooling. Corresponding thick-film compositions loaded with magnetic particles coated with Ag were successfully formulated.

However, although formation of oriented filaments was clearly established under melting in a magnetic field, this was not sufficient to create conductivity. This was only possible with a vertical arrangement, with much shorter interelectrode distances and large cross sections, together with application of some vertical compressive pressure.

Therefore, future tests will concentrate on optimising materials formulation and other aspects such as physical interactions at the electrode materials.

5 ACKNOWLEDGMENTS

The authors acknowledge assistance of the of the EPFL (*École Polytechnique Fédérale de Lausanne*) International Cooperation Programme.

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