

Experiments with conductor-filled polymers

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Introduction and Summary

This work was largely inspired by the previous work of Leigh *et al.*: *A Simple, Low-Cost Conductive Composite Material for 3D Printing of Electronic Sensors* available at:

<http://www.plosone.org/article/info%3Adoi%2F10.1371%2Fjournal.pone.0049365>

I started by mixing graphite (C.K. Dry Powder Graphite) and silver (Johnson Matthey Silver Flake FS2) with both PCL and PLA, which didn't work - the result was always an insulator.

I then replaced the graphite with the carbon actually used by Leigh *et al.* (Cabot Black Pearls 2000). This was more successful, giving a material with a resistivity of (at best...) $1.7 \times 10^{-3} \Omega\text{m}$.

A PCL filament with a mixture of carbon and silver could be extruded in our extruders, giving an 0.5mm diameter filament that did conduct. Its resistivity was $0.5 \Omega\text{m}$, though this may improve if the material were actually used to print with, as opposed to just being extruded to form a narrow filament.

Method

For each of my experiments I used 3g of the plastic (either Polymorph brand PCL, or Faberdashery Arctic White PLA - note that the latter already has a TiO_2 filler).

For a carbon experiment I used 0.45g of carbon in each case, which is 15% by weight of the polymer - the proportion used by Leigh *et al.* For silver experiments I used 1.9g of silver, which (given the respective densities of graphite and silver: 2.1 g/cm^3 and 10.5 g/cm^3) should give roughly the same volume of silver as carbon. For mixtures, I mixed by volume, so a 50/50 mixture would be 0.225g C plus 0.95g Ag.

I put 40ml of dichloromethane in a conical flask with a PTFE magnetic stirrer flea and added the carbon or silver powder with the stirrer motor on.

I then added the polymer, which was granules in the case of PCL, and filament chopped into about 3mm lengths in the case of PLA.

I stoppered the flask and left it stirring for an hour, after which time all the polymer had dissolved, giving a solution with a slightly syrupy viscosity.

I then poured the results into petri dishes to a depth of one millimeter or so and left them under shelter outdoors to evaporate.

The result was a film of polymer with the conducting filler in the base of each petri dish. The thickness went from tissue paper thin to about 0.7mm, depending on the pattern of evaporation.

Results

Graphite and Silver

I did three initial graphite and silver experiments: all graphite; all silver; and a 50/50 mix. The pure graphite result did not conduct at all. The silver and the 50/50 both conducted on the bottom when removed from the petri dish, but not the top.

I conclude from this that the filler was sinking as the solvent evaporated, giving a concentration at the bottom.

When melted and reformed, none of the composites conducted at all. I rolled the silver PCL into a (roughly) 1.75mm filament and extruded some of it by pushing it by hand through a standard RepRapPro hot end. It extruded, but again the result did not conduct.

Conclusion:

- With conductor grains that are dense and solid conductivity is not possible.

Hypothesis:

- Sinking of the grains combined with the ease with which a solid grain can be completely covered with polymer isolating it from its neighbours is the problem. Melting and rolling to form filament exacerbates this.

Open Carbon and Silver in PLA

The Cabot Black Pearls 2000 carbon is nothing like graphite in appearance. It is an open light fluffy powder that hardly reflects any light at all.

I did two PLA experiments with this carbon: 100% carbon, and 50/50 carbon and silver.

Both the top and the bottom of the evaporated film for the 100% carbon experiment conducted. I cut a rectangle of dimensions 9.14mmx15.3mmx0.6mm from the film and measured its resistance by pushing the probes hard into it (for good contact). On top this gave 55K Ω , on the bottom 550 Ω , so it looks as if the carbon is still sinking.

A same-sized rectangle of the 50/50 material 0.4mm thick gave an infinite resistance on its top surface, though when the probes were laid flat to increase their contact area this dropped to $4K\Omega$. On the bottom surface the figures were 14Ω (probe points) and 7Ω (probes flat).

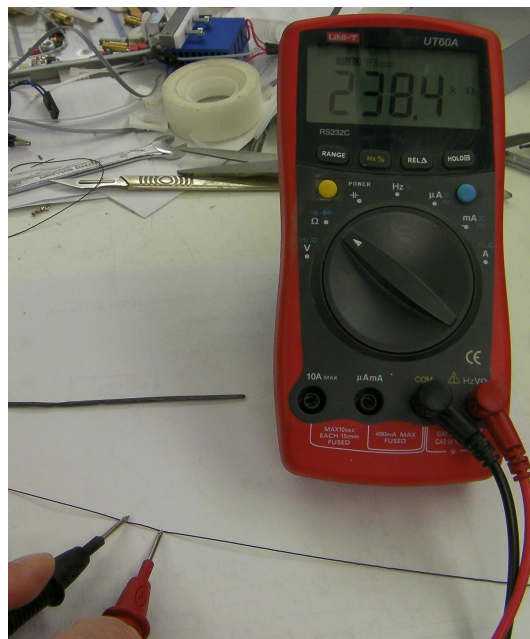
I then melted and reformed both materials on microscope slides on a hot plate. A rough lump of the 100% carbon material about 1mm thick and 1cm square had a resistance of $1K\Omega$. A similar sized lump of the 50/50 material wouldn't conduct at all. But when two dabs of silver paint were put on its surface and dried, the resistance was 600Ω .

Conclusions:

- Sinking is still a problem
- The silver helps reduce the resistivity, but
- The carbon is needed to make contact at the surface
- Surface contact is a big problem; once in the material the resistance is probably quite low
- Silver paint reduces the surface resistance
- The best resistivity (50/50 rectangle measured on the bottom with flat probes) was $1.7 \times 10^{-3} \Omega m$ (copper is $1.7 \times 10^{-8} \Omega m$, for comparison).

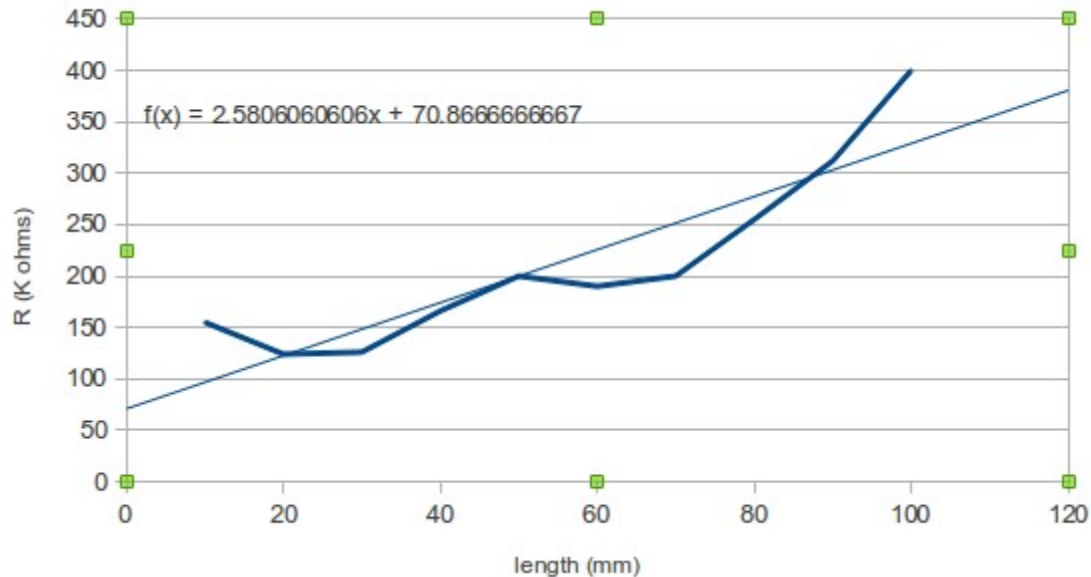
Open Carbon and Silver in PCL

I did these experiments with 70/30 carbon/silver in PCL. I melted the result together in boiling water and rolled it into (roughly...) 1.75mm filament. I then fed that through a standard RepRapPro Ltd hot end by hand, extruding 0.5mm diameter filament.



Measuring 0.5mm filament resistance

The graph below shows the result of measuring the resistance of the 0.5mm filament over various lengths. The gradient is $2.6 \text{ K}\Omega/\text{mm}$, implying a resistivity of $0.5 \text{ }\Omega\text{m}$, which is rather poor compared to the values in the previous section.



Resistance against length for 0.5mm filament

The intercept is at $71 \text{ K}\Omega$. I think that it is probably taking things too far to say that this is the contact resistance, but that is the implication.

Putting dabs of silver paint on the 0.5mm filament didn't seem to reduce its resistance. I tried removing some of the surface of the composite in a 2mm diameter length of the 70/30 material by rubbing it with dichloromethane on a cloth. This didn't seem to affect its resistance either.

Conclusions:

- It is possible to extrude this material
- The action of melting and refreezing it seems to increase its resistance
- Again, contact resistance is a big problem
- Exposing new surface with solvent had little effect
- Combinations of different filler materials (carbon and silver in these experiments) work better than just one.

Hypotheses:

- Poor resistivity of the extruded filament relative to the bulk material may be a statistical effect - there is not a lot of chance for conducting particles to touch if the cross sectional area is small. If this is so, things will improve if it is printed with.
- Many of the observed phenomena may be caused by quantum tunneling through very thin films between particles, rather than contacts between the particles, especially at the surface.
- The improvements obtained by using mixtures of conductors rather than just one may be a result of the low resistivity of some components (silver flake) and the high connectivity of the others (rather fluffy carbon). Thus by mixing different (or the same) conductors as fillers with differing particle geometries one may be able to get better results than by just using one material or one geometry on its own.