Vanishing Programmable Resources: Design, Materials, and Characterization

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Abstract and Introduction:
Printed wiring boards (PWBs) act as the mechanical structure supporting the electronic connections between the different functional components in microelectronic devices. Stable materials are generally desired so that long mission life can be achieved, however, there is growing interest in self-decomposing materials because of environmental concerns. Sustainability requires an effective way to dispose of the multitude of PWBs currently in use. This has prompted the development of PWBs that can be triggered to disappear after a time-independent, fully-functional life span.

For this project, an optically-triggered disappearance mechanism was explored. UV-sensitive polymers, poly(phthalaldehyde-co-butyraldehyde) and poly(dihydroxy-tetrahydro naphthalene), Figure 1, were characterized using nanoindentation. Four-point probe analysis was used to analyze composite films that contained 3 µm dendritic copper nanoparticles; the addition of copper provided the conductive portion of the PWB. Composite films were also made using photo-acid generator (PAG), an iodonium salt, to improve the optical-trigger. Layered-films, comprised of stacked composite films, were analyzed using exposure techniques. This method of construction was used to test the permeability of the stacked films.

Experimental Procedure:
In order to test the different films, formulations were made following the same basic procedure: the polymer solids, solvent, and additional materials were combined in a vial and vortexed/sonicated. See Table A for the list of formulations made, including the use, basis, solvent, and soft-bake/cure procedure for each. The optimum loading for metal nanoparticles is 70-80 vol% [1], so 75 vol% was chosen as our loading. The copper used was cleaned in an acid bath and stored under PGMEA. All formulations containing PAG were made and worked with in the dark. Films were made using a doctor-blading technique.

Nanoindentation was done to find the reduced Young’s modulus and hardness of the polymers. A 10-second load, 10-second hold, 4-second unload function was used, and a 9-point matrix of decreasing force from 650 µN to 50 µN was used to collect data points. An area function was created using polycarbonate as a standard. Four-point probe analysis was done on the copper and polymer films to measure sheet resistance to be used to calculate conductivity.

The layered-films were exposed to a dose of UV-light that we knew would activate all of the PAG to determine if the copper/polymer film was permeable to the acid generated from the top film. The layered-films were exposed to a dosage of 10000 mJ/cm², and before, immediately after, and every hour after the exposure, the resistance of the copper/polymer film was tested using a multimeter.

<table>
<thead>
<tr>
<th>Solids</th>
<th>Solvent</th>
<th>Basis</th>
<th>Soft-Bake/Cure</th>
<th>Use</th>
</tr>
</thead>
<tbody>
<tr>
<td>p(PHA-co-BA)</td>
<td>GBL</td>
<td>30-40 wt% polymer</td>
<td>100°C for 5 min</td>
<td>nanoindentation</td>
</tr>
<tr>
<td>p(DHTN)</td>
<td>GBL</td>
<td>30-40 wt% polymer</td>
<td>100°C for 5 min</td>
<td>nanoindentation</td>
</tr>
<tr>
<td>Cu/polymer</td>
<td>PGMEA</td>
<td>75 vol% Cu</td>
<td>100°C for 5 min</td>
<td>four-point probe</td>
</tr>
<tr>
<td>Cu/polymer</td>
<td>THF</td>
<td>75 vol% Cu</td>
<td>air cure for 10 min</td>
<td>layered-films</td>
</tr>
<tr>
<td>PAG/polymer</td>
<td>THF</td>
<td>30 wt% polymer/10 pp phr PAG</td>
<td>air cure for 10 min</td>
<td>layered-films</td>
</tr>
</tbody>
</table>

Table A: Formulations.
**Results and Conclusions:**

Nanoindentation testing of p(PHA-co-BA) and p(DHTN) gave reduced Young's moduli of 4.56 GPA and 0.055 GPA, and hardness readings of 270 MPA and 3.1 MPA, respectively. We compared the polymers to ideal values represented by FR4: a reduced modulus of 24 GPA and a hardness of 200 MPA. FR4 is a fully cross-linked, epoxy board with fiberglass matrix and is meant to be rigid and long-lasting. The p(PHA-co-BA) values are promising, especially the hardness because it is above the ideal. The modulus and hardness of p(DHTN) are far enough below the ideal values. This polymer did display tacky qualities, both qualitatively through observation and quantitatively by the unloading function displayed in its indentation profile. The low values dismissed p(DHTN) as a possible bulk material for the PWB, but the adhesive quality it has made it potentially useful for areas like conductive contacts connecting devices to the board.

Four-point probe analysis resulted in a conductivity of $4.5 \times 10^3 \ \Omega^{-1}\cdot m^{-1}$ for a 75 vol% Cu film. This is several magnitudes below the bulk copper value of $4.9 \times 10^7 \ \Omega^{-1}\cdot m^{-1}$ due to the nature of nanoparticles and the resulting oxidation issues. These were combatted using cleaning methods on the copper and by using the layered-films as a construction technique. Copper nanoparticles are still effective for the conductive portions of the PWB even with a lower conductivity in the polymer matrix.

Initially, we attempted to create formulations that included the polymer, copper, and PAG in solvent. These formulations were not successful because the copper and PAG interacted in a way that depolymerized the matrix and oxidized the copper before being triggered. A new construction technique, layered-films, Figure 2, was considered to combat the oxidation/depolymerization issue. Layered-films showed an increase in the resistance of the copper/polymer film after exposure. The resistance increased several magnitudes over the course of three hours, from 2 MΩ to 200 MΩ. This showed that the acid was diffusing through the copper paste and depolymerizing the polymer matrix after triggering, and that layered-films would be an applicable construction technique.

**Future Work:**

In order to improve upon the material used in the transient PWBs, several areas may be investigated or expanded upon. An investigation of newly synthesized polymers with faster rates of depolymerization and vapor evolution will be helpful for improving the bulk and conductive matrices. Expanded testing of the adhesion strength of p(DHTN) should be done to determine the full extent of use for the material. The ultimate end goal of the future work is to fabricate a fully functional PWB using the explored methods and materials. This PWB will need conductivity testing to ensure electrical connections are functional before triggering and non-functional after. Devices can then be added to the PWB to create a multi-functioning sensor.

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**References:**