Introduzione

I pasti di inchiostro conduttivi sono usualmente formulati con sistemi polimerici complessi e riempiti con particelle di argento altamente ingegneggiate. Tipicamente schermati su film polyester o polimide flessibili, vengono utilizzati per creare circuiti conduttivi flessibili come switch membrane.

Questi sistemi polimerici di inchiostro devono avere le seguenti proprietà:

- Adesione forte alla substrato
- Flessibilità e elasticità simili alla gomma
- Alto carico di particelle d'argento per formare pattern conduttivi
- Capacità di dispergere i riempitivi di argento
- Resistenza alle esigenze di elaborazione

Sono stati sviluppati vari sistemi polimerici con tecniche uniche di ingegneggimento particelle per soddisfare queste varie proprietà di uso finale. Particolare attenzione è stata data a migliorare la flessibilità della pellicola conduttiva fissata al test ASTM F1683 stress test (Crease Test/ processo di piegatura con peso di rotolamento).

Un'inchiostro conduttivo commercialmente disponibile ha dimostrato di essere nettamente superiore alla concorrenza dimostrando la sua capacità di resistere a 20 cicli di piegatura, che è cinque volte meglio di altri marchi di portata. La superiorità può solo essere attribuita a un sistema polimerico unico combinato con un pacchetto particolare di additivi.

Decomporre il sistema polimerico a livello di formulazione fornisce accesso alla formulazione design e conferma la presenza di un particolare pacchetto di additivi. Normalmente, strumenti di decomposizione, come FTIR, GPC, e DSC, forniscono solo accesso limitato informazioni a causa della complessità del sistema polimerico.

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EXPERIMENTAL

Materials

A silver-filled ink paste sample was obtained from Foxconn’s electronics processing line and an analytical procedure was developed in Spectra Analysis’ analytical lab using the DiscovIR-LC GPC-IR hyphenated technology.

Ink Sample Preparation

The ink paste was dissolved in THF and the silver fillers were allowed to settle overnight. The top layer was collected and then filtered through 0.45 µm PTFE disk filter into a standard LC vial before GPC injection. The polymer concentration was ~ 5 mg/ml (~0.5%).

GPC Conditions

LC system: Agilent 1200
Column: 2 x Jordigel DVB Mixed Bed, 25 cm x 1 cm I.D.
Mobile phase: THF at 1.0 ml/min flow rate
Injection volume: 60 µl

FTIR Detection

DiscovIR-LC solvent-removing direct-deposition solid phase FTIR
Nebulizer power: 7 W
Cyclone temperature: 130ºC
Carrier gas: 250 cc/min
Condenser temperature: 15ºC
Disk temperature: -10ºC
Disk speed: 12 mm/min
IR detector resolution: 8 cm⁻¹
Results

Figure 1 (below) shows infrared chromatogram of the polymer solution from the silver ink paste generated by the GPC-IR detector. The trace is a display of maximum band absorbance over the whole mid-IR range showing three components A, B and C from high MW to low MW corresponding to GPC elution times.
Figure 2 (below) is the stacked IR spectra of each component at its MWD peak maximum. The three snapshot IR spectra were compared against a commercially available IR database to identify Components A, B and C.

The commercial IR libraries used in the ink deformation were from Thermo Fisher Scientific, Inc. (81 Wyman Street, Waltham, MA 02454) and Fiveash Data Management, Inc. (211 Vista Road, Madison, WI 53726) and enabled the identification of polymers, copolymers, additives, impurities, degradants and many organic compounds.
Figure 3 (below) shows the IR spectrum (red) of Polymer A and its top match (purple) with 96.6% match rate (100% indicating a perfect match). The IR database search identified Polymer A (red) as aliphatic polyester (purple) with the specific supplier information (Amoco Resin PE-350) available from the Coatings Technology Library.

The next two matches with 95.6-96.0% high match rates also led to the same identification - aliphatic polyester, but from different manufacturers.

<table>
<thead>
<tr>
<th>Match Order</th>
<th>Index</th>
<th>%Match</th>
<th>Compound Name</th>
<th>Library</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>434</td>
<td>96.63</td>
<td>Amoco Resin PE-350</td>
<td>Coatings Technology</td>
</tr>
<tr>
<td>2</td>
<td>450</td>
<td>95.96</td>
<td>Dynapol LH-812</td>
<td>Coatings Technology</td>
</tr>
<tr>
<td>3</td>
<td>467</td>
<td>95.65</td>
<td>Vitel VPE-222F</td>
<td>Coatings Technology</td>
</tr>
<tr>
<td>4</td>
<td>443</td>
<td>95.06</td>
<td>Dynapol L-411</td>
<td>Coatings Technology</td>
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<tr>
<td>5</td>
<td>466</td>
<td>94.45</td>
<td>Vitel PE-200</td>
<td>Coatings Technology</td>
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</tbody>
</table>
Figure 4 (below) shows the IR spectrum (blue) of Polymer B and its three top matches (purple, red and aqua) from the IR libraries. The IR database search identified Polymer B (blue) as aliphatic polyurethane (purple) with the specific supplier information (product brand and number) available from the Coatings Technology Library. The next two matches (87.3-87.5% match rates) led to different polymers: polyester polyol (red) and polycaprolactone (aqua) with broad IR absorbance across 3000-3600 cm\(^{-1}\) range from their OH functional groups.

The relatively narrow IR bands around 3300-3500 cm\(^{-1}\) from both Polymer B (blue) and the top match (purple) confirmed the NH functional group from their polyurethane nature, excluding the second and third match. Polymer B was identified as Spensol L-53, now called UROTUF L-53, manufactured by Reichhold Chemicals, Inc.

![Figure 4. The Commercial IR Database Search Identified Polymer B (Blue) as Aliphatic Polyurethane (Purple) with the Supplier Information Available from Coating Technology Library](image_url)
Figure 5 (below) shows the IR spectrum (red) of Component C and its top match (purple) with 92.7% match rate from the IR libraries. The next four matches can be easily excluded due to their low match rates (62.0-65.3%). The IR database search clearly identified Component C (red) as Desmodur LS-2800, a cross-linking agent manufactured by Bayer Material Science.

<table>
<thead>
<tr>
<th>Match Order</th>
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<th>Library</th>
</tr>
</thead>
<tbody>
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<td>Coatings Technology</td>
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<td>65.30</td>
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<td>9302</td>
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<td>Monophenylbutazone</td>
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<tr>
<td>4</td>
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<td>62.15</td>
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<td>Coatings Technology</td>
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<td>5</td>
<td>860</td>
<td>62.05</td>
<td>Spenlite M-27</td>
<td>Coatings Technology</td>
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</table>
Figure 6 (below) displays the chemical structure of the identified additive: ketoxime blocked HDI trimer with CAS #93919-05-2 and low molar mass at 766 g/mol.

Component C is a latent cross-linker which is stable at ambient temperature during the ink manufacturing, ink storage and screenprinting operation but will de-block at >130°C during the thermal curing to generate tri-functional isocyanate for cross-linking with NH or OH functional groups from other components in the ink formulation.

![Chemical Structure of Additive C Identified by GPC-IR as Latent Cross-Linking Agent: Ketoxime Blocked HDI Trimer (CAS# 93919-05-2) Manufactured by Bayer Material Science](image)

GPC-IR hyphenated technology separated the complex polymer mixture from the silver ink paste and identified three components and their specific suppliers by IR database search.

**Polymer A** was identified as an aliphatic polyester resin from Amoco (there are similar products from Evonik Degussa and Bostik) with high MW and broad MW distribution. This polymer is very flexible with very strong adhesion to flexible polyester or polyimide films.

**Polymer B** was identified as an aliphatic polyurethane Spensol L-53 (now UROTUF L-53) from Reichhold Chemicals, Inc. with medium MW and narrow MW distribution. This polymer is very elastomeric and highly flexible, and can be cross-linked with tri-functional isocyanate additives.

**The Component C** was identified as the latent cross-linking agent Desmodur LS-2800 manufactured by Bayer Material Science.

**Additive C** (blocked HDI trimer) is stable at room temperature but will de-block during the curing at 150°C to generate triisocyanate which will then cross-link with polyurethane (Polymer B) to form strong, flexible and elastomeric 3D network. The latter may form a unique interpenetrating polymer network (IPN) with the flexible Polymer A that holds all the silver particles in place to form conductive circuitry paths, even under many cycles of harsh folding.

This rapid deformation was made possible because of GPC-IR ability to capture infrared spectral information (full FTIR range) for GPC separated components. By comparison against references, the characteristic IR bands serve to indicate the chemical structure of the monomers and small molecules (additives) present. A GPC-IR instrument, such as the DiscovIR-LC, enables formulators to gain an insight on the intellectual property and marketing competitiveness of rival companies.