Critical photoinitiators for UV-LED Curing: Enabling 3D Printing, Inks and Coatings

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LED (395 nm) curing - Attractiveness

What are some key benefits with UV-LED lamps?

- Allows low temp curing, since it has no IR output
- Potentially more reliable & No Hg!
- Potentially less damaging to substrate/colorants
- Economically attractive compared to laser light sources for 3D imaging
## Application / process selection for UV-LED curing

<table>
<thead>
<tr>
<th>Application</th>
<th>Drop in replacement?</th>
<th>Comments / Qualifiers</th>
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</thead>
<tbody>
<tr>
<td>Composites</td>
<td>Yes</td>
<td>• Often better!</td>
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</table>
| 3D Printing | Yes (mostly)         | • Slightly longer wavelength compared to UV lasers, and affects PI choices  
                  |                      | • More prone to ambient light “poisoning”  
                  |                      | • May require better stabilizer packages or better shielding |
| Coatings    | Yes (mostly)         | • Hg lamps use short wavelength type PI for surface curing  
                  |                      | • Need to readjust PI for LED |
| Inks        | Yes                  | • Harder to get speed without inerting  
                  |                      | • Color matching might be more challenging  
                  |                      | • Need some reformulation of resin  
                  |                      | • May need LED + Hg lamp combo’s |
Dissecting the reasons why LED (395 nm) curing can (or doesn’t) work

What are the challenge(s) for developing UV chemistries for curing with UV-LED lamps?

- **direct replacement of LED arrays for Hg lamps (or lasers) may work only for certain applications**
- PI selection (for optical overlap with $\lambda_{ex}$) is even more critical for LED curing
- **$O_2$ effects & low color after curing** is a challenge (especially for UV inks) with LED curing
LED (395 nm) curing - Challenges

Other challenge(s) for developing UV chemistries for curing with UV-LED lamps?

- Traditional paradigm of PI blends targeting surface & thru-cure needs realignment (traditional PI combinations usually do not work)
- LED light flux is typically lower
- Resin & Modifiers reformulation may be needed
- Pigments (interference with optical overlap) might have surprising effects on curing of coatings
Spectral matching of the PI to the UV-LED
Spectral matching of the PI to the UV-LED

- DBA is a photosensitizer for cationic PI’s
- ITX is used “as is” or as sensitizer for AAK’s
- BAPO & MAPO photo-bleach for low final color
BAPO as a two-photon photobleachable photoinitiator

Great overlap with LED light, photobleaching enhances optical penetration, and lowers final color
Acyl phosphine oxides: a good fit for LED-395 nm curing for thick section curing

White UPES Gel Coat (resin: 1718-20-2, 15 wt% TiO2 in XR 1535 + 0.3 pph Irg 819 + 1 pph Irg 184) NB 1718-31

Exponential Fit:
Max cure depth = 23.3 mil,
1/e time = 3.6 min.
Pigment selection – cure window

- Pigments have greater effect on through-cure (Dp) vs. Hg lamps
- Ease of cure expected to follow %T
- White > Red ≈ Blue > Yellow > Black

LED Light
ITX + AAK’s – especially useful for inks

ITX can be Type II (H-abstractor), Electron Donor & Energy Transfer Donor
Photosensitizing cationic photoinitiator (CatS-1)

- Cationic curing is not affected by O2 quenching, compared to acrylates.
- Photocuring with LED array (395 nm) is possible using DBA as photosensitizer.
Resin selection - Managing O₂ inhibition

- Water-borne >> low viscosity (monomer rich) acrylates
- UPES > Methacrylate > Acrylate
- Amino acrylate > Ethoxylated multifunctional > Epoxy acrylate
- Diluent modifiers: DVE-3 (vinyl ether) at 10% improves photospeed of acrylated systems when photocuring in air
- Thiol terminated oligomeric chain transfer agents – need high purity (to control odor)
- Other additives – certain reactable siloxanes
- Cationic/hybrid
Conclusions

- UV-LED curing applications for industrial inks and coating are growing

- The “best” photoinitiator for UV LED curing depends on the application (in some cases it is a drop in replacement to conventional UV lamps, in other cases more work is required)

- For 390 – 405 nm LED, a good fit is with photobleachable photoinitiators, like BAPO

- Combinations of Type I and Type II photoinitiators or cationic photoinitiators can help manage oxygen inhibition effects
References


E.V. Sitzmann, K. Davidson, A. Bendo and P. Vanvolsum, “Photoinitiator selection strategies for thick section curing of composites and adhesives”, Radtech UVEB West 2007, Los Angeles, CA

E. V. Sitzmann, W. Brunsvold, J. Kazcun “New cationic photoinitiators for electronic, printing and coating applications “, Radtech UVEB West 2011, Santa Clara, CA

R. Balmer, T. Newsom, G. Shouldice, “Advances in Printing Inks for Alternative UV Sources”, NPIRI Technical Conference 2013

B. Rundlett, “Developing UV LED Curable Coatings“, Radtech UV.EB East 2013, Syracuse, NY

T. Mawby, “UV LED is Shining New Light on an Old Subject”, NPIRI Technical Conference 2014

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