TECHNICAL PAPER

The State of UV-LED Curing: An Investigation of Chemistry and Applications

By Ed Kiyoi

Light-emitting diodes for ultraviolet-curing applications (UV-LEDs) have been commercially available for nearly 10 years. However, their unique output characteristics require newly formulated UV chemistries in order to take advantage of UV-LEDs' many benefits. This paper discusses the characteristics of UV-LED lamps; the importance of properly formulating chemistries; the benefits to end-users; commercial applications of UV-LEDs; and future expected developments.

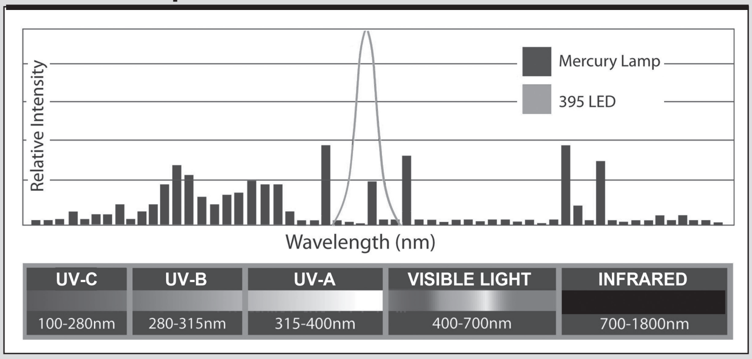
Characteristics of UV-LED lamps

Traditional UV arc lamps produce UV energy by generating an electric arc inside an ionized gas (typically mercury) chamber to excite atoms, which then decay and emit photons. The emitted photons cover a broad range of the electromagnetic spectrum, including some infrared and even visible light as shown in Figure 1. Only about 25% is in the safer UV-A range.

A UV-LED generates UV energy in an entirely different way. As an electric current (or electrons) move through a semiconductor device called a diode, it emits energy in the form of photons. The specific materials in the diode determine the wavelengths of these photons and, in the case of UV-LEDs, the output is typically in a very narrow band +/- 20 nm. The wavelength is dependent on the band gap between excited state and the ground state of the semiconductor material. The chart in Figure 1 compares the output of a 395 nm, UV-LED lamp with a typical mercury-arc lamp. It is important to note the difference in intensity and wavelength of the output as both are key to understanding a UV-curing process.

FIGURE 1

Wavelength output comparison of mercury-arc and UV-LED lamps



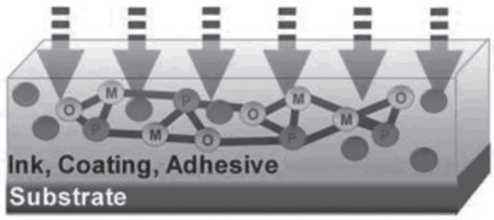
The UV-Curing Process

UV curing is a photopolymerization process that uses UV energy to change a liquid to a solid. Upon absorption of the UV energy (as shown in Figure 2), the photoinitiator (PI) produces free radicals that initiate crosslinking with binders (monomers and oligomers) in a polymerization reaction to cure or solidify the ink, coating or adhesive. UV formulations also incorporate various additives such as stabilizers, wetting agents, adhesion promoters, defoamers and pigments to provide desirable characteristics or color of the cured material.

UV

Figure 2

UV-curing photopolymerization process



Comparison of Solvent and Waterborne to UV Processes

Solvent and waterborne formulations change from a liquid to a solid ("dry") via evaporation of the solvent—typically volatile organic compounds (VOCs) or water. This drying process (often requiring an oven) takes time, generates VOCs and the dried film thickness is less than originally applied. UV curing happens much faster (typically less than a second), does not generate VOCs and the film thickness applied is what remains as a solid (critical for certain end-use applications). UV-curing processes are environmentally friendly, save energy costs and floor space, and typically increase production rates while reducing scrap or waste streams.

Formulating UV Chemistries for UV-LED Lamps

For efficient and effective UV curing of an ink, coating or adhesive, the formulator seeks to overlap the UV lamp output with the spectral absorption of the PI. The amount of PI in a typical UV formulation is usually very small, less than 5%. PIs typically absorb across a range of wavelengths, not a narrow band. For example, Figure 3 shows the spectral absorption for different PIs and the wavelength output for mercury-arc UV lamps. Many existing UV formulations developed for curing with a typical mercury-arc lamp (shown as H-bulb) use a broad spectrum PI. While there is often some absorption within the UV-LED output range, it is clear to see that much of the PI absorption range is wasted. A more efficient cure is possible with a formulation designed specifically for UV-LED curing using a PI with concentrated absorption in the UV-A range such as those shown in Figure 4.

The monomers in the formulation serve as the reactive diluent enabling the formulator to control viscosity for proper application (spraying, rolling, screen printing, etc.) of the uncured material. Rather than volatilizing, as is typical with conventional formulations, the monomer reacts and becomes part of the UV-cured material. The oligomers (and their backbone structure) determine the overall properties of the material. Monomers and oligomers are generally derivatives of acrylates or methacrylates containing polyurethanes, polyesters or polyethers.

The longer wavelength output—such as the UV-A range seen from UV-LEDs—penetrates through thick and pigmented systems producing through-cure of the material that ensures surface adhesion and the ability to cure thicker screen ink or pigmented wood coatings. Short wavelength output (200-280 nm) is unable to penetrate very far into a material, but provides surface curing which is important for surface properties such as scratch and chemical resistance.

Overcoming Surface Cure Issues

Surface curing due to oxygen inhibition was often an issue for UV-LED curing, but has largely been overcome by various means. Of course curing in an inert (nitrogen) atmosphere is one option, but it adds cost and complexity to the system. Another option is to add in oxygen-

Figure 3

Photoinitiator spectral absorbance compared to traditional UV lamp output

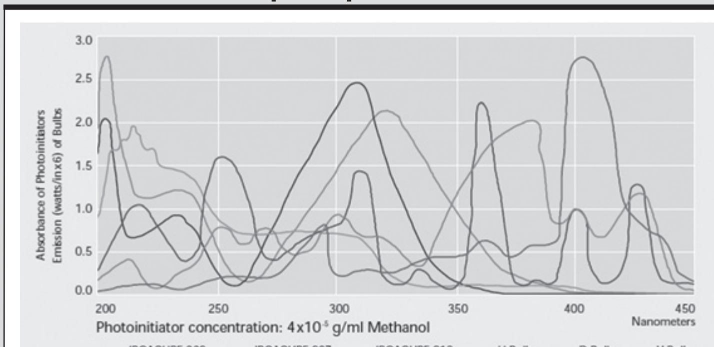
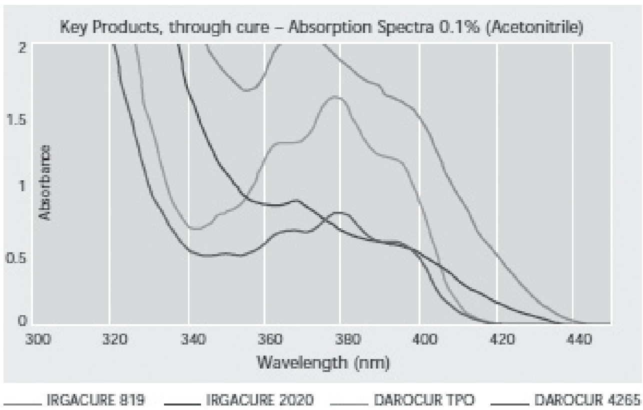


Figure 4

Examples of longer wavelength absorption photoinitiators



consuming or scavenging compounds such as amines or aminoacrylates to overcome oxygen inhibition.[1]

Research has indicated that peak irradiance (W/cm^2) and total UV-A energy (mJ/ cm^2) delivered are more important than a precise wavelength match on formulations developed to cure in the UV-A region. Peak irradiance is an important metric since intensity is required to initiate the polymerization. Higher peak irradiance (such as that found in UV-LEDs) results in a more aggressive polymerization mechanism helping to overcome oxygen inhibition at the surface and achieving the required cure rate.[2]

More recently, it has been shown that higher functional oligomers can also minimize the oxygen inhibition and improve surface curing. Commercially, Cytec offers a co-resin called ADDITOL® LED 01, a mercapto-modified, polyester-acrylate resin that replaces a portion of the oligomer in a UV formulation to improve surface curing under UV-LED lamps. This co-resin is compatible with urethane acrylates, some epoxy and polyester acrylates, and acidic adhesion promoters and typically accounts for 20-40% of the formulation by weight. Mono- (MAPO) and bisacylphospineoxides (BAPO) are recommended photoinitiator types for UV-LED curing. Some commercial examples are IRGACURE® 2100, LUCIRIN® TPO-L and ADDITOL® TPO.[3]

In September 2012, Eileen Jaranilla-Tran with the Rahn-Group reported on her investigation of overprint varnishes (OPV), flexographic inks and inkjet inks. She found that Norrish Type I PIs such as BAPO are effective to achieve good surface cure (and preferable to TPO and BDMM), especially when combined with highly reactive acrylate oligomers and it minimizes yellowing. ITX (Type II) was more reactive, but caused too much yellowing for OPV and white inks. She also noted that pigment selection is key because pigments compete with the PI for UV energy.[4]

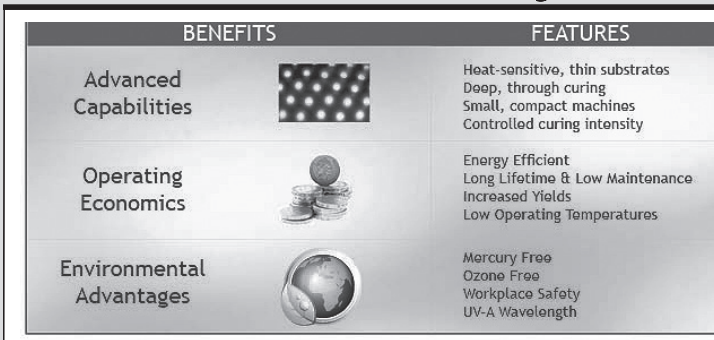
Many advances have been and are being made by raw material suppliers and, in turn, more UV-LED formulations are being commercialized that result in production speeds comparable to traditional mercury lamp processes. Formulators should work closely with their suppliers to develop new UV-LED cure chemistries which are non-yellowing, will overcome surface cure issues and meet the end-use production requirements.

Benefits UV-LED Curing Delivers to End-Users

The benefits of UV-LED as compared to traditional mercury-arc UV lamps are numerous and significant as shown in Figure 5. UV-LEDs are more environmentally friendly because they do not generate ozone and contain no mercury as arc lamps do. They are a cool source compared to arc lamps, largely due to no output in the infrared range. This reduced heat eliminates complicated cooling mechanisms such as chill rolls and external shutters, and

Figure 5

Benefits and features of UV-LED curing



enables applications on heat-sensitive substrates. The electrical-to-optical conversion efficiency of UV-LEDs is much better and the ability to instantly turn the unit off and on enables saving about 50-75% on electricity.

Table 1 shows a comparison of key characteristics of UV-LEDs versus traditional mercury-arc UV lamps. Compared to an arc lamp's 500-2,000-hour life, most UV-LEDs are specified for 10,000 hours, but can last more than 20,000 hours. It's also important to note that over this lifetime UV-LED output only drops about 5%, compared to arc lamps that can lose about 50% of their original output by the end of their life. In a production environment, UV-LEDs require significantly less space, monitoring, maintenance and downtime. That translates into higher productivity rates, less scrap and higher quality end products. Paybacks for retrofitting onto existing machines or replacing existing UV arc lamps can be as low as 12 months.

Commercial Applications of UV-LEDs

Some of the earliest UV-LED commercial applications were small area adhesive and bonding applications such as medical device assembly; low-end thermal inkjet printing applications such as marking, coding and variable printing; and field repair of fiberglass composites. These early applications took advantage of UV-LEDs' form factor (lightweight and small), through-cure capabilities and the increased safety inherent with longer wavelengths. In fact, many of the earliest applications were actually in the visible wavelength range. Today, as the energy density has increased and costs have decreased (especially for 395 nm output), UV-LED is commercial in the graphic arts market, wood coatings, electronics, composites and others.

Commercial UV-LED applications in the graphic arts market (especially digital inkjet applications) advanced first owing to their form factor, low heat and energy savings advantages. Commercial inkjet applications today include all inkjet segments, including wide-web printing on a variety of substrates for many end-use applications. There are many UV-LED-specific inkjet inks and most inkjet printing presses are available with UV-LEDs. For example, EFI Inkjet Solutions offers a 126-inch wide, UV-LED curing printer capable of 1,000 dpi and eight-color (plus white) with speeds of up to 1,200 ft^2/hr. End-users are able to print on thinner, more heat-sensitive materials reducing material costs in half without sacrificing any quality or speed.[5]

Table 1

Comparison of UV-LED to mercury-arc UV lamps

	UV-LED	Mercury Arc
Life	20,000+ hrs	500-2,000 hrs
On/Off	Instant	10 Minutes
Output Consistency	Very Good. 95%+	Drops up to 50%
Heat Generated	60°C	~350°C
Energy Efficiency	Saves 50-75%	
Environmental	Mercury Free, Ozone Free	Mercury Waste, Generates Ozone
Footprint	30-50% less	

Narrow Web Flexo Takes Off

More recently, UV-LED inks are being used for screen printing (rotary, flatbed and container) and narrow web flexographic printing. Flint Group introduced the first UV-LED combination print inks, flexographic four-color process and rotary screen white inks branded as EkoCure™ at Label Expo in September 2012. In October, they began working closely with a beta customer (a large label converter) to validate the inks and process in a commercial setting. The customer had a narrow web flexographic press running waterborne inks. They simply installed UV-LED lamps to run the new EkoCure™ inks. Since the UV-LED lamps run cool, there was no need to use chill rolls or other web cooling devices as would typically be required for mercury-arc lamps. They have seen no film distortion, even on heat-sensitive, low-gauge films such as shrink films.

"Our beta site customer runs a variety of different commercial products. So, as they needed something new, we formulated it for them," said Tom Hammer, product manager, Narrow Web North America, Flint Group. "We started with flexographic inks, but have also done clearcoats and adhesives, both PSAs and laminates. Nothing has been a problem and the customer is very impressed."

The beta customer has been running the 10-station, 17" press since October on a 24/7 schedule. No matter what they've been running—shrink films, four-color processes, pressure-sensitive labels, lamination and others—they are seeing faster line speeds than with traditional UV. They are currently on track to see a payback for the press retrofit in less than 12 months. The beta customer is also adding a rotary head to the press and will run the opaque white ink already developed for UV-LED curing. Flint Group plans to further develop rotary screen inks in a variety of colors for UV-LED cure.

"Formulating inks for UV-LED curing does not require starting from scratch, but it is also not as simple as just replacing the photoinitiator with one that has a longer wavelength absorption. The pigments used in the flexographic and rotary inks are similar to those used in traditional UV-cured inks as are some of the oligomers and monomers," added Hammer. "However, there are fewer choices of photoinitiators (longer wavelength) to use and it is more challenging to get cure performance (surface and through-cure) while still keeping costs for the end-user in mind."

Wood Coating Applications

Sherwin Williams introduced its Becker Acroma™ UV-LED coatings for wood in January 2012 and their customer BJS has been successfully using the UV-LED coatings since June 2012.

"The primary driver for developing these UV-LED coatings was to extend the use of UV curing to heat-sensitive wood substrates such as pine (< 45°C) and other resinous woods. Most end-users in Europe face strict limits on VOC emissions and traditional UV arc lamps cause problems on heat-sensitive wood material," said Lars Sandqvist, technical project manager at Sherwin-Williams Sweden. "With the UV-LED coatings, end-users have a choice of arc or LED, or even a combination. Customers who have a UV line, but have heat problems, can retrofit the line with LED in a couple of positions to get the temperature down and keep the rest of the arc lamps to minimize investment."

BJS (which runs both arc lamps and UV-LEDs on the same line) has seen a 60% energy savings with the UV-LED compared to the arc lamps. In addition to energy cost savings, the UV-LED lamps provide consistent output, require less maintenance and reduce the fire hazard. Gloss control has been an issue when applying thick, pigmented layers (>15g/m^2) via roll coating or with spray application (rarely used). When the customer needs to produce matte finishes they simply use a combination of arc lamps and the UV-LED. Gloss control is not an issue for thinner topcoats. There is also an EU framework project FP7 (*http://www.fp7-uvled.eu*) focused on researching UV-LED wood coatings. Findings were expected in early 2013.

Future UV-LED Applications

The future for UV-LEDs looks very bright given the progress made to date by raw material suppliers and formulators. And, if the trends for UV-LED development continue—namely increasing peak irradiance (77% compound annual improvement) and decreasing costs—we should see rapid adoption by end-users in the near future for many new applications.

According to Hammer, Flint Group is developing UV-LED inks for offset and letterpress applications and he fully expects this to translate to sheet-fed and wide-web applications as well. Hammer also sees food packaging as a growth area, once low migration inks are available. Right now, most of the photoinitiators approved for food packaging are not appropriate for UV-LED ink formulations.

Sherwin-Williams is developing UV-LED fillers for use by furniture manufacturers who want to use lower cost particle board, but need a smooth edge after cutting and shaping. The clear, thick fillers are an ideal application for UV-LEDs. According to Sandqvist, another application that will soon be available is UV-LED coatings on wood moldings. The coatings are ready and shown to cure at the required speeds of 40-100 m/min. All that is needed is an end customer willing to be first, as is so often the case with "new" technologies.

Richard Baird, a process engineer for Boeing, wrote in the fall 2011 issue of the *RadTech Report* that he expects UV-LED curing to become a viable option for large-scale aerospace paint curing in the very near future.[6] By all indications, this and many other UV-LED curing applications will indeed be taking off soon. ◗

References

1. *UV-LED Lamps: A Viable Alternative for UV Inkjet Applications*, by Michael Beck, *RadTech Report*, November/December 2009, p. 39, *http://www.phoseon.com/Documentation/UV-LED-Lamps-A-Viable-Alternative-for-UV-Inkjet.pdf*
2. *Characterizing the Efficiency of UV-LED Curing*, by Rob Karsten and Bonnie Larson, Phoseon Technology and Kent Miller, University of Akron, presented to Radtech Europe 2009.
3. UV-LED Curing ADDITOL® LED 01, CYTEC presentation, April 2011, *https://www.cytec.com/uv/Downloads/ProductPresentationADDITOLLED01.pdf*
4. *UV-LED Curing in Graphic Arts Applications*, by EileenJaranilla-Tran, RAHN-Group, presented at Chicago Printing Ink Production Club meeting, September 2012, *http://www.cpipc.org/downloads/cpipc%20led%20092012.pdf*
5. Maturing UV-Cure Technology, by Bill Schiffner, Sign & Digital Graphics, February 1, 2012, *http://sdgmag.com/article/printing-finishing/maturing-uv-cure-technology*
6. *UV-Curable Paints for Commercial Aircraft Exteriors*, by Richard W. Baird, *RadTech Report*, Fall 2011, p. 43, *http://radtechreport.com/pdfs/RT_fall11_baird.pdf*

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