

# Performance of the Light Emitting Diodes Versus Conventional Light Sources in the UV Light Cured Formulations

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**ABSTRACT:** UV light emitting diodes (LED) are compared with conventional light sources for curing acrylate formulations. Both polymerization rates and the properties of the resulting coatings were examined. UV LEDs are acceptable alternatives to conventional light sources for a va-

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**Key words:** photopolymerization; curing of polymers; light-emitting diodes; coatings

## INTRODUCTION

The power output and commercial availability of UV and visible light emitting diodes (LEDs) has increased noticeably over the last few years.<sup>1</sup> Because LEDs are narrow band inexpensive, efficient, long lasting, safe, portable light sources that generate almost no heat and require little power, we thought they might provide advantages as light sources for photopolymerization. Photopolymerizations are mostly generated by either photodecompositions or electron transfer events inducing free radical chain reactions in acrylate monomers.<sup>2,3</sup> Cationic photopolymerization of vinyl ethers or epoxides initiated by super acids constitutes a smaller segment of the commercial market for photopolymers. Multiple line, broad spectrum UV sources such as the Fusion H-bulb or the Xenon Xe-500B lamp have high power requirements and give off a lot of heat. Though they emit over a wide spectral range, the light emitted by the bulbs is mostly wasted. These bulbs operate very hot and can cause overheating of samples leading to poor control of polymerization

processes in the developing polymer. The output of UV lamps can be filtered, but this wastes energy, and requires additional components in any experimental setup.

LEDs, in contrast, emit over narrow wavelength ranges, and in theory one can choose an LED source whose narrow emission spectrum fits well the absorption profile of the photoinitiator (PI) (Fig. 1). Since there are few reports in which the efficacy of LEDs is compared with conventional light sources in photocuring processes,<sup>4–7</sup> the purpose of the work reported is to evaluate the curing performance of certain commercial UV LEDs using model formulations.

## EXPERIMENTAL

The output power of the Xe-500B (Xenon, Inc.) and the H-bulb setup (Fusion UV Systems, Inc.; <http://www.fusionuv.com>) was measured with an IL-1700 radiometer and confirmed with an IL-390 dosimeter both from International Light, Inc. The output power of target UV LEDs was similarly evaluated. Cure performance was estimated for various model formulations and compared using a Cure Monitor (Spectra Group Limited, Inc.) to measure rates of polymerization. Macroscopic characteristics of the coatings were evaluated on the basis of standard ASTM procedures.

Measuring the apparent microviscosity changes induced in the environment of a small molecule probe in a polymerizing resin was termed “cure monitoring” by the inventors of the technology.<sup>8–10</sup>

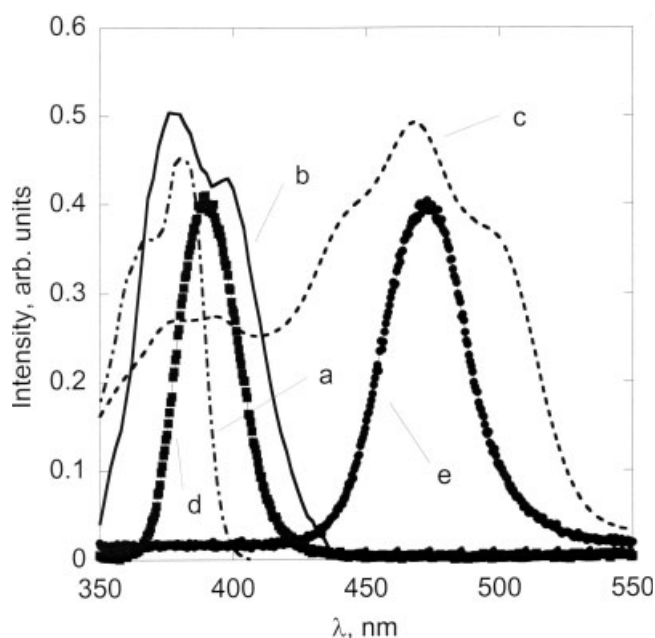
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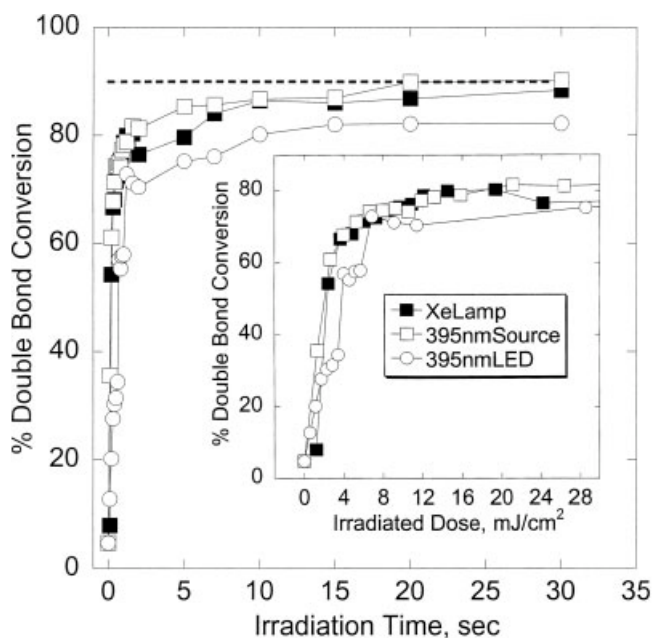
**Figure 1** Examples of the efficient spectral overlap between the absorption spectra of commercial photoinitiators: (a) ITX (isopropylthioxanthone), (b) Irgacure 819, (c) hv 470 (5,7-diiodo-3-butoxy-6-fluorone (DIBF); Spectra Group Limited, Inc.), and the output of (d) 395 nm UV and (e) 470 nm blue LEDs.

Fluorescence change in certain molecular probes has been shown a sensitive measure of molecular chain growth in a photopolymerizing system and is particularly useful for measuring cure rates in real time. In it, one eliminates artifacts by measuring a ratio of fluorescence intensities over a series of wavelengths from a single fluorophore. The obtained ratios linearly correlate with the changes in the degree of double bond (%DB) conversion measured by traditional methods such as infrared spectroscopy.<sup>11,12</sup> The latter directly relates to the concentration of monomer in the matrix while the former is an analytical tool that can be applied on line to relate, at any time, to the degree of polymerization in the matrix. The linear correlations are different for different formulations. In the specific cases tested here, 1-dimethylaminonaphthalene-5-sulfonyl-*n*-butylamide (DASB) was used as the fluorescent probe and fluorescence intensities of its emissions were measured at 456 and 558 nm as a function of molecular change. Each point on the polymerization profile (Figs. 2 and 3) derives from an average of 10 ratios obtained using a CM-1000 Cure Monitor. An acquisition time of 25 ms was used for each point and control experiments confirmed this was fast enough so that there was no interference from the 350 nm excitation light.

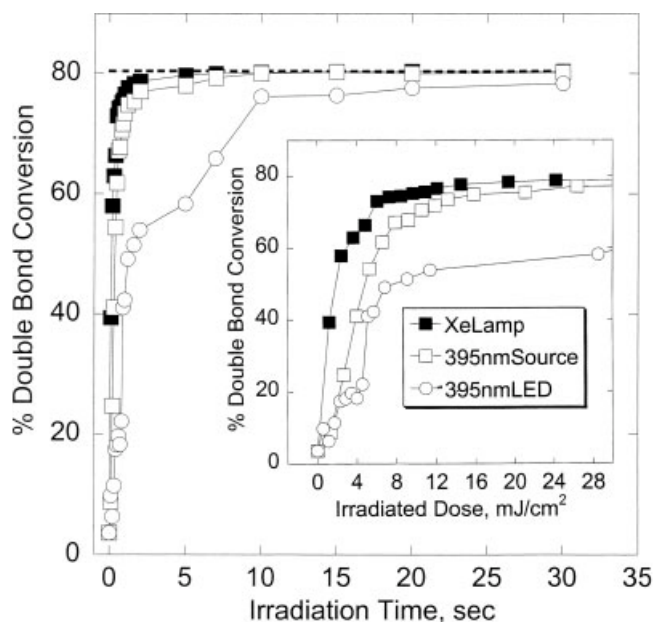
We tested model wood and poly(carbonate) coating formulations. (Selected model coatings represent relatively rapidly-cured formulations. Results may

vary for formulations which differ in composition.) Wood formulations contained 54% urethane acrylate oligomers and 46% acrylic monomers. The poly(carbonate) coating included 15% urethane acrylate oligomers in a mixture of multifunctional acrylates. The monomers and oligomers used were obtained either from Sartomer or UCB. Formulation compositions are given in Table I.

Irgacure 819 (2%; CIBA) and DASB (0.1%; Spectra Group Ltd.) were thoroughly blended into the formulation by mechanical and ultrasonic mixing. A portion of the formulation was placed on a glass slide for cure measurements and covered with second glass slide. A marked area on the slide containing the sample was irradiated with the appropriate light source, and the degree of cure monitored. Polymerization results using a single 5-mm 395-nm LED (LS Diodes Optoelectronics, Inc.) and CON-TROL-CURE 395-nm LED (UV Process Supplies, Inc) were compared with those obtained using Fusion H-bulb and Xenon Xe-500B sources. Results using a UV LED (Clearstone Tech. CF-1000) have been reported previously.<sup>6</sup> Samples were irradiated for designated times under controlled conditions. Each point on the cure profile (Figs. 2 and 3) corresponds to a single measurement. Irradiation times when the LEDs were used were established using a time delay relay unit



**Figure 2** Cure profile comparison for the wood coating formulation irradiated by a Xe-lamp (black squares), 395 nm UV LED light source (hollow squares), and single 5-mm 395-nm UV LED (hollow circles). Dashed line represents the H-bulb sextuple pass limit (dose of 720 mJ/cm<sup>2</sup>). Inset depicts the expanded initial regions of the profiles with the double bond conversion plotted as a function of the irradiated dose.



**Figure 3** Cure profile comparison for the polycarbonate coating formulation irradiated by a Xe-lamp (black squares), 395 nm UV LED light source (hollow squares), and single 5-mm 395-nm UV LED (hollow circles). Dashed line represents the H-bulb sextuple pass limit (dose of 720 mJ/cm<sup>2</sup>). Inset depicts the expanded initial regions of the profiles with the double bond conversion plotted as a function of the irradiated dose.

obtained from Grainger, Inc. This unit was capable of controlling times in the 0.01–999 s interval. For the Xe-500B source, an internal timer with a 0.1 s minimum time increment was used. Six conveyor belt passes under the Fusion H-bulb system (total dose of 135 mW/cm<sup>2</sup>) was considered sufficient to produce maximum DB conversion.

**TABLE I**  
Compositions of Tested Model Wood and (Poly)carbonate Formulations

Coating	Component	Percent
Wood	Urethane acrylate (blended with ethoxylated <sub>3</sub> trimethylolpropane triacrylate)	54.3
	Tripropylene glycol diacrylate	13.0
	Polyethyleneglycol (400) diacrylate	7.6
	Ethoxylated <sub>3</sub> trimethylolpropane triacrylate	9.8
	Propoxylated <sub>2</sub> neopentyl glycol diacrylate	12.0
	Dipentaerythritol pentaacrylate	3.3
(Poly)carbonate	Tris(2-hydroxyethyl) isocyanurate triacrylate	30.2
	Urethane acrylate	15.0
	1,6-Hexanedione diacrylate	22.7
	Pentaerythritol tetraacrylate	20.0
	Tetrahydrofurfuryl acrylate	10.1
	Silicone surface additive	2.0

Surface testing was carried out using three formulations including model wood and poly(carbonate) coatings and a proprietary anticorrosive metal paint (corrosion resistant energy cured paint (product number 459) available from Spectra Group Limited Inc., Millbury, OH).<sup>13</sup> Wooden tiles (pine, 1 in. × 3 in.), stainless steel panels (3 in. × 6 in.) and poly(carbonate) films were used as substrates. Coating thicknesses were 100 μm (4 mil) for wood and 150 μm (6 mil) for the steel and (poly)carbonate substrates. Coated substrates were irradiated for designated times (Table II).

The properties of the surfaces were tested as follows:

*Cure grade* is a measure of the tackiness of the surface and determined by touch. The assessment of cured surface was based on the following categories: 0 – wet surface; 1 – surface sticks to finger; 2 – surface slightly sticks to finger (slightly tacky); 3 – dry, tack-free surface.

*Cross-hatch adhesion* (ASTM D 2359) was tested via the creation of a lattice pattern with six cuts made in each direction. A pressure-sensitive tape was applied over the lattice, removed after 1 min, and adhesion assessed qualitatively on a 0B–5B scale. The 0B scale indicates more than 65% loss of the coating. 5B shows strong adhesion with very little or no peeling of the coating. 3B and 4B are the normal values accepted industrially.

*Methyl ethyl ketone (MEK) double rub* is a measure of a coating's resistance to solvent. Soft foam was wetted slightly with MEK and rubbed (~100 rubs) on the surface. Surfaces were then evaluated based on the following: 0 – complete loss of coating; 1 – partial loss of coating; 2 – no loss of coating, some loss of gloss (hazy); 3 – coating remains with no loss of gloss.

*Scratch adhesion* employs a scratching of the polycarbonate coating with a hard, pointed material. The degree of adhesion is classified: 0 – coating completely peels off; 1 – numerous cracks on the coated surface; 2 – few cracks on coated surface; 3 – no cracks on coated surface.

*Gloss* was evaluated qualitatively using the Horiba Handy Gloss Checker 1G-330. The device uses two optical systems to measure gloss at different measurement angles of 60° and 20°. The 20° meter has higher sensitivity and is better for high gloss levels.

**TABLE II**  
Minimum Irradiation Times to Achieve Cured Surfaces for Different Light Sources and Coating Formulations

Light source	Wood coating	Polycarbonate coating	Corrosion resistant metal paint
UV LED	15 min	5 min	1 min
Xe-lamp	5 min	2 min	1 min
H-bulb	Single pass	Single pass	Single pass

**TABLE III**  
**Output Comparison for Different Tested Light Sources**

Light source	Power (mW/cm <sup>2</sup> )	Working distance (cm)	Description
395 nm UV LED			
5 mm	5.31	2	Standard 5 mm LED
Control cure	29.6	2	Commercial LED source from UV Process Supplies, Inc. with 0.5 in. × 2 in. microarray
	10.3	4	
CF-1000	4.2	6	Commercial LED source from Clearstone Tech., Inc. with 4 in. × 4 in. array
	1.7	10	
	53.2	2	
	32.5	4	
	16.2	6	
	6.1	10	
Standard light sources			
Xe-500B	12.0	4	Industrial Xe lamp from Xe Corp.
H-bulb	134.6	10	Fusion UV Systems, Inc. industrial curing system
250 PMP	90.2	6	Pro Motocar Products, Inc. UV curing lamp
Ultracure	30.6	10	EFOS (currently EXFO) UV/visible light source
3M 910	10.0	10	3M overhead projector

As the reference plate for calibration the Gloss Checker is used to measure the gloss of a black glass plate that has a gloss level of 90 on the 60° meter and 84 on the 20° meter. The 20° meter was used for gloss evaluation of wood and polycarbonate surface coatings.

*Surface hardness (ASTM D 2134)* was tested using Gardner Sward Hardness Rocker model GSI. It evaluates surface hardness relative to glass which registers a value of 41. Rocker cycles are electronically determined and registered on a display.

*Abrasion resistance* is a measure of the surface resistance to abrasion. Rhodes American steel wool #0000 (super fine) was used to rub the surface (~ 100 rubs). Assessment of the abrasion resistance of the surfaces was based on the same categories as outlined for the MEK test.

*180° fold-bend test* involved folding the coated polycarbonate film twice in opposite directions to evaluate brittleness of the coating. The categories are as follows: 0 – bends with complete delamination of the coating; 1 – bends with some creasing (few cracks); 2 – bends with no creasing.

## RESULTS AND DISCUSSION

### Comparison of light sources

Power outputs for the sources are shown in Table III. The Xe-lamp yields pulsed output with high peak powers that represent different irradiative dynamics relative to steady mercury lamp radiation of the H-bulb system with intense emission lines centered at 302, 313, 334, 365, 391, 405, 436, 546, and 578 nm (Fusion UV Systems Inc.).

Solid-state LED emitters with single narrow emissions of appropriate wavelength having full width at

the half-maximum (FWHM) of 30–40 nm (Fig. 1) behave dramatically differently from the reference sources. The output of the 395-nm UV LEDs tested is comparable to the power characteristics of the Xe-lamp (Table III). The H-bulb system yields much higher power but this advantage is compromised by multiple drawbacks. The lower power from the LED output is compensated by precise overlap between the absorption spectrum of the PI and emission spectrum of the LED (Fig. 1). For example, the emission spectrum of the 395 nm UV LED overlaps well with the absorptions of Irgacure 819 (Ciba Inc.). A variety of other commercial visible light photoinitiators (hv 470, Irgacure 784, camphor quinone) are matched well by the blue light emitting LEDs. While Xe and mercury lamps require bulky and complex power supplies, a single 395-nm UV LED can be operated for extensive periods of time using a 6 V battery and arrays of these LEDs require simple 16–24 V power supply, which drives the LEDs without generating excessive heat. UV LEDs were selected for initial studies because many more commercial initiator systems use UV light, than visible light. The performance of the visible light LEDs is currently under investigation and results will be reported in the near future.

### Cure rate experiments

Cure rate measures for the wood and polycarbonate formulations are presented in Figures 2 and 3, respectively. Because monomer samples were placed between two glass slides, oxygen inhibition was minimized. Because the polymerization rate curves required point-by-point acquisition, a high concentration of photoinitiator was chosen thus reducing the length of the experiment. The thin sample allowed light to be efficiently absorbed throughout

**TABLE IV**  
**Properties of Model Wood Coating Cured by Different Light Sources**

Light source	Coating properties					
	Cure grade	Cross-hatch adhesion	Solvent resistance <sup>a</sup>	Gloss (max. 84)	Surface hardness (glass 41)	Abrasion resistance <sup>a</sup>
H-bulb <sup>b</sup>	3	4B	2 (2)	48	12	2 (2)
H-bulb <sup>c</sup>	3	>4B	2 (2)	35	9	2 (2)
Xe-500B <sup>c</sup>	2	>4B	2 (2)	26	3	2 (2)
UV LED <sup>c</sup>	2	4B	2 (3)	39	3	2 (2)

<sup>a</sup> X(Y): X, surface coating category; Y, gloss value after testing.

<sup>b</sup> Photoinitiator package: SR 1129, 5%; SR 1137, 3%.

<sup>c</sup> Photoinitiator package: proprietary blend.

the entire layer despite the high PI concentration. As can be seen from Figures 2 and 3, the double bond conversion curves generated by optimized UV LED output compare favorably to the results from both the high peak power pulsed Xe source and that of the H-bulb system. For a given formulation we assume that six passes under the H-bulb with exposure to a very large dose of 135 mW/cm<sup>2</sup> results in complete cure with the highest possible degree of the double bond conversion. These H-bulb limits are shown as a dashed line on Figures 2 and 3.

Wood coatings (Fig. 2) are cured rapidly by both the 395 nm LED and the Xe-lamp and greater than 90% of the maximum double bond (DB) conversion (marked by the dashed line of H-bulb limit) is achieved within the first 2 s. It is clear from the experiment that the 395-nm UV LED source matches the Xe-lamp in performance. The DB conversion limit of an H-bulb source is achieved in 20 s by both light sources tested representing an acceptable time for the industrial applications. A single 395-nm 5-mm LED slightly underperforms compared to the other light sources tested owing to its lower output power. However, the final DB conversion after 30 s irradiation is also close to the H-bulb limit.

Consistent with the lower content of acrylic urethane oligomers in the polycarbonate coating, these formulations cure more slowly (Fig. 3) and maximum possible DB conversion (90%) is exceeded after

~10 s of irradiation. The performance of the 395-nm UV LED is similar to that of the Xe source with both reaching the H-bulb limit after 20-s irradiation. The difference between cure achieved with the LED array and a single 5-mm 395-nm LED is more pronounced for the polycarbonate formulation.

#### Properties of cured coatings

The properties of the coatings are summarized in Tables IV–VI. A critical issue effecting the polymerization of coated surfaces is that the coating must be fully dried at the surface to be useful. Since oxygen inhibition and undercure result in a tacky feel of the top of the coating, tackiness is most often countered through the use of a N<sub>2</sub> blanket and/or high intensity light sources.<sup>14–16</sup> Since the high power requirement of a light source is always a problem, particularly if portable sources are needed, the impact of the use of low-power LEDs on these markets could be significant. If the LED emission output and PI absorption are well matched, efficient use of the emitted 395-nm UV light in producing reactive intermediates from the photoinitiator may also prevent surface tackiness.

With wood coating formulations (Table IV) a tack-free coat resulted only when an H-bulb was used. A slightly tacky surface was obtained with the 395-nm UV LED cure and this matches the performance of

**TABLE V**  
**Properties of Model (Poly)carbonate Coating Cured by Different Light Sources**

Light source	Coating properties					
	Cure grade (Tackiness)	Cross-hatch adhesion	Solvent resistance <sup>a</sup>	Gloss (max. 84)	Scratch test	180° fold-bend test
H-bulb <sup>b</sup>	3	5B	2 (8)	93	3	2
H-bulb <sup>c</sup>	3	5B	2 (2)	85	3	1
Xe-500B <sup>c</sup>	2	5B	2 (2)	83	2	1
UV LED <sup>c</sup>	2	5B	2 (2)	81	2	1

<sup>a</sup> X(Y): X, surface coating category; Y, gloss value after testing.

<sup>b</sup> Photoinitiator package: Darocure 1173, 3.8%, Irgacure 184, 1%.

<sup>c</sup> Photoinitiator package: proprietary blend.



**TABLE VI**  
**Properties of Anticorrosive Metal Paint Cured by Different Light Sources**

Light source	Coating properties				
	Cure grade (tackiness)	Cross-hatch adhesion	Solvent resistance	Surface hardness (glass 41)	Abrasion resistance
H-bulb <sup>a</sup>	3	>4B	0	7	2
H-bulb <sup>b</sup>	3	>4B	0	7	2
Xe-500B <sup>b</sup>	3	>4B	1	7	2
UV LED <sup>b</sup>	3	>4B	0	7	2

<sup>a</sup> Photoinitiator package: SR 1129, 5%; SR 1137, 3%.

<sup>b</sup> Photoinitiator package: proprietary blend.

the Xe-lamp. Diminished surface hardness of 3, which directly relates to the cure grade (tackiness), was also observed for the LED and Xe sources compared to the H-bulb results (surface hardness in the 9–12 range). Acceptable performance in resisting solvents and gloss was achieved with each of the light sources. The LED-cured formulation show good adhesion of 4B and this is similar to the adhesion obtained for the surfaces cured with the Xe-lamp and the H-bulb (both >4B). Overall, both the LED source and the Xe-lamp slightly under perform when compared to the H-bulb in two (cure grade and surface hardness) of six properties tested.

Table V summarizes the results for poly(carbonate) coatings. The differences observed in cure grade between cure by H-bulb and the other sources tested were similar to those obtained for wood coatings (3 versus 2, respectively). Scratch tests also indicated that there were differences between the coatings cured by H-bulb and other sources. Adhesion, solvent resistance and gloss were excellent and similar for each light source. A passing mark for the 180° bend test indicates that the cure by each of the light sources tested results in a nonbrittle coating. A complete match to the performance of the H-bulb in cure was displayed in four tested categories (adhesion, solvent resistance, gloss, and fold-bend properties), while a slight mismatch was observed in two tests.

Tack-free cure was afforded by each of the light sources with the pigmented corrosion resistant metal paint (Table VI). The abrasion resistance and surface hardness was also acceptable yielding the values of 2 and 7, respectively, for all light sources tested. The most significant result is that good cross-hatch adhesion of >4B, a critical parameter for the metal paints, was achieved for each light source. The coatings were poorly resistant to solvent in every case since this coating is designed to perform in an aqueous environment. Overall, coating properties were not compromised if a UV LED source, rather than the H-bulb and Xe-lamp, was used.

In summary, the results indicate that a UV LED source in many cases successfully matched the performance of the conventional light sources in both

the polymerization dynamics occurring within a cured layer and the final properties of the coatings. UV LEDs can be used as acceptable alternatives to conventional light sources with a variety of formulations used in many different applications.

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