LED Curing Versus Conventional UV Curing Systems: Property Comparisons of Acrylates and Epoxies

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Abstract:

The development of high power short wavelength light emitting diodes (LED) in the late 90s created the potential of a solid state ultraviolet/visible curing source. The benefits of LEDs are low heat, portability and low power consumption. These advantages are particularly attractive for the curing of various adhesives, inks, and coatings in applications where dimensional stability of the substrates is required. The properties of urethane acrylate adhesives are compared when cured with an LED light vs. a multiple wavelength mercury arc lamps. The UV sources at higher intensity settings may cause full cure in less than a second. Some surface tack may be present, but it is due to surface oxygen inhibition and not the UV source. Curing studies with epoxies, on the other hand, illustrate that curing with LED systems is limited by the absorption of common cationic photoinitiator systems. Current high power LEDs are commercially available at wavelengths of 400 nm or higher. In order to match the spectral emission of the LED light, epoxies may have to be modified. An example of a modified epoxy that can be cured with a longer wavelength LED is demonstrated.

1. Introduction and Background

A major advancement in solid state devices has been the development of high power UV LEDs. This has created the possibility of using light emitting diodes (LED) in curing systems rather than traditional UV lamps. The benefits of LEDs are low heat, targeted wavelength, low power consumption and portability. However, current LED devices are limited in wavelength (normally, > 380 nm) and power in the UV region. This leads to difficulty in the curing of some materials, particularly epoxy based materials, which normally utilize cationic photoinitiators (PI) with absorption in the short wavelength region of UVB (e.g. 250 nm). This work compared curing of acrylate and epoxy adhesives using traditional mercury lamps with an LED based curing system. It is shown that with epoxies a modification of formulation may be necessary to utilize high power LEDs to achieve the desired properties.

The benefits of UV curing materials are fast cure times, low temperature requirements, and low outgassing compared to solvent based thermal cure materials. UV cure materials are especially useful for the assembly of heat sensitive devices. The majority of UV cure materials are acrylate or epoxy based. Acrylate based materials exhibit fast curing characteristics with a radical photopolymerization mechanism (ref.1); epoxy based materials normally exhibit prolonged photopolymerization reactions after exposure to UV light.

The efficiency of the photopolymerization process is strongly dependent upon the overlap of the spectral power density of the curing system and the photoinitiator's absorption spectrum. The standard HBO or mercury lamp offers multiple wavelengths with peak emissions which may be of benefit for curing numerous materials using a single type of lamp system. For example, the standard UV curing system offers versatile curing for both UV acrylate and epoxy materials. However, the broad range of wavelengths may also cause excessive heating, uncontrolled reaction rates and shrinkage. In some special cases, photon bleaching may also occur, such as in the case of ink or DVD writable organic dye. Filters may have to be used to eliminate the IR and/or UVB and UVC spectral components to prevent the detrimental effects of the multi-wavelength curing. Figure 1 shows the standard wavelength output for a typical mercury lamp.

Short Wavelength LEDs, due to their solid state nature, exhibits a narrow emission band of 15-20 nm. Therefore, a die must be selected with an emission wavelength that matches the photoinitiator absorption peak of the UV curable materials. Such a device can be used to provide rapid curing of the adhesives with little or no heat/UV damage, but the range of commercially available LEDs with emissions in the UV are limited. Work is in progress to produce high power devices with lower wavelength emissions. Figure 2 illustrates the type of semiconductor material classes, their emission wavelengths and luminous intensity currently available or under investigation. Some applications require multiple curing processes, such as DVD manufacturing. LED systems provide wavelength targeted curing and potentially can be used for multi-layer processing. The other potential applications of LED curable materials include bio-compatible material for bio-medical usage (ref 2), ink curing (multi color application), and sensor applications (sealing of the samples).

Our studies have shown that acrylate materials can be efficiently cured using an LED array with emission in either the 400 nm or 450-470 nm range. Epoxy materials, on the other hand, required modified chemistry to enhance the absorption at the LED light emitting wavelengths to allow the energy transfer to activate the shorter wavelength PIs.

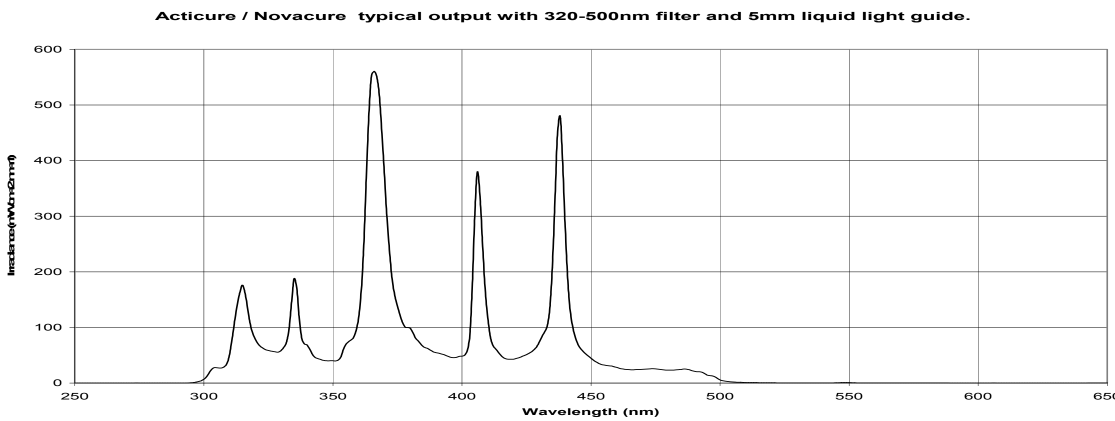

Figure 1. Typical output of HBO lamp with IR/UV filters (EXFO Novacure/Acticure output profile)

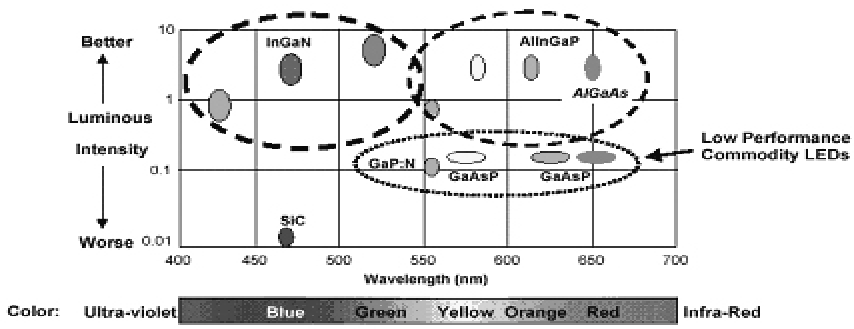

Figure 2. LED - Material Systems, Wavelengths and Brightness. The output power of the LED is device and material dependent. (From GECore- LED 101) Ref.3

2. Experimental Methodology

Curing of both urethane acrylate and epoxy materials was compared using a mercury lamp and a UV LED curing system. The mercury lamp systems used include a handheld UV BondWand from ElectroLite, and an EXFO Novacure. The BondWand has low intensity output of 4 mW at UVB of 280-320 nm. The Novacure provided irradiance values from 1,000 to 23,000 mW/cm^2 in two wavelength ranges (250-450 nm or 320-500 nm) selected using an optical filter. The LED curing system used was based on a proprietary EXFO 396 nm array which provided an irradiance of > 1,000 mW/cm^2. The LED array consists of 100 LEDs on a 5X5 mm substrate. The spectral output of the LED array is indicated in Figure 3.

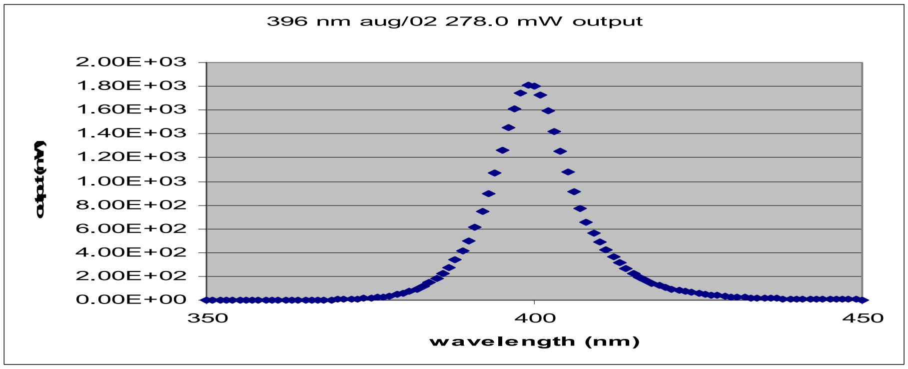

Figure 3. Typical output of 5x5 mm LED array with peak wavelength of 396 nm.

The properties of the cured materials were evaluated using the following methods:

(1) Photo DSC and FTIR analysis determine degree of cure.
(2) Hardness test for various curing conditions
(3) Adhesion test was performed based on standard lap shear test on microscope slides, fiber pull test were also used for the photonic application.
(4) Water absorption tests were performed using 85% RH/85 °C condition for 336 hr.

It was noted that the measured cure depth and uniformity were largely dependent upon the photoinitiator concentration. High concentrations of PI prohibit the penetration of UV radiation and limit the cure depth. The PI concentration must be optimized to achieve thick film applications. Table I lists the materials and summary of the results of this study.

3. Results and Discussion

The following materials (Table I) were evaluated using both the Novacure, and the LED curing systems. The optimized cure conditions and results are also listed. We limited the maximum cure time to 60 sec. to comply with the required industry throughput (cycle time).

Table I. List of UV materials and summary of results of this study

Material	**Curing light source**	**Curing Condition**	**Results**
Urethane Acrylate	UV systems and LED	>750 mW/cm^2 1 cm working distance	Both cured with LED cured material exhibit better properties?
Epoxy with sulfonium PI	UV systems only	1,000-14,000 mW/cm^2 1 cm working distance	%Cure varies with intensity. High intensity will achieve the full cure with Step cure profile
Epoxy with iodonium PI	UV systems only	1,000-14,000 mW/cm^2 1 cm working distance	% Cure varies with intensity Post thermal cure required
Epoxy with sensitizer modification	UV systems	1,000 mWcm^2 1 cm working distance	50% cure can be achieved. Post thermal cure required
	and LED	750 mW/cm^2 for LED for 30 sec 2 mm working distance	45% cure can be achieved with Post thermal cure required
Epoxy with sensitizer and PI concentration modification	UV lamp and LED	Reduced PI concentration using LED	Post thermal cure required

Urethane acrylate material normally exhibits high reaction rates due to its free radical photopolymerization characteristics. An exposure 1 sec at 750 mW/cm^2 with the LED system or 1000 mW/cm^2 with the arc lamp system can achieve >90% of cured structure. The PI absorption peak for the material matches well with the LED peak wavelength of 396 nm. The degree of cure of the acrylate material was determined by monitoring the FTIR peak at 1410 cm^{-1} (Figure 4). Most of cure occurs during the first second. The slow build up of reacted acrylate unsaturation (RAU) after the first second is due to the heat generated in the reaction (diffusion driven process). Similar results for degree of cure was obtained using photo-DSC.

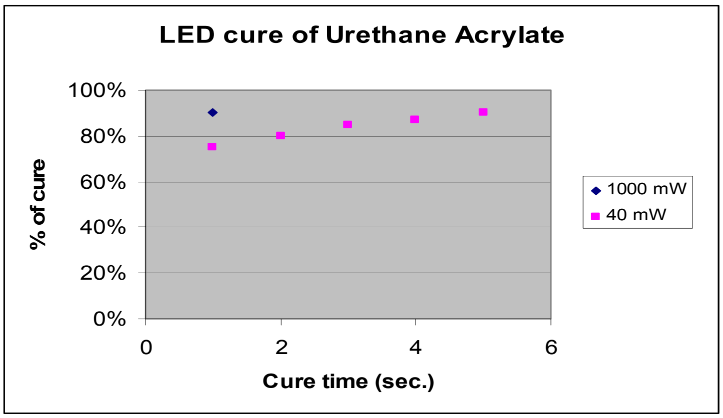

Figure 4. Degree of cure of Urethane Acrylate material determined from the evolution of the 1410 cm^{-1} peak in the FTIR spectrum. The material was cured using a 396 nm LED array.

A much slower reaction rate was observed for both sulfonium and iodonium PI epoxy materials. Both materials utilize PI absorption at the lower wavelengths of 250 to 350 nm. The degree of cure of the cationic PI epoxy material was measured using the FTIR oxirane peak around 800 cm^{-1} (Figure 6). Similar results were obtained using photo-DSC. With the arc lamp systems the epoxy materials were,effectively cured but with a much slower reaction rate. These are effective curing sources for this type of material due to their broad spectra. It was noticed that the percent of cure varied strongly with the intensity of the UV irradiance and exposure time. Little or no curing reaction was observed with the LED array. It is believed this is due to the lack of LED emissions in the PI absorption range of 250 to 350 nm(Figure 5). .

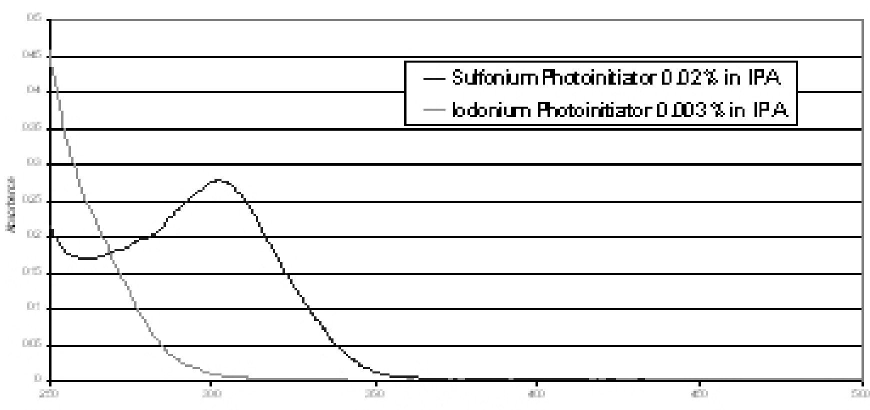

Figure 5. Cationic Photoinitiator Absorption spectrum

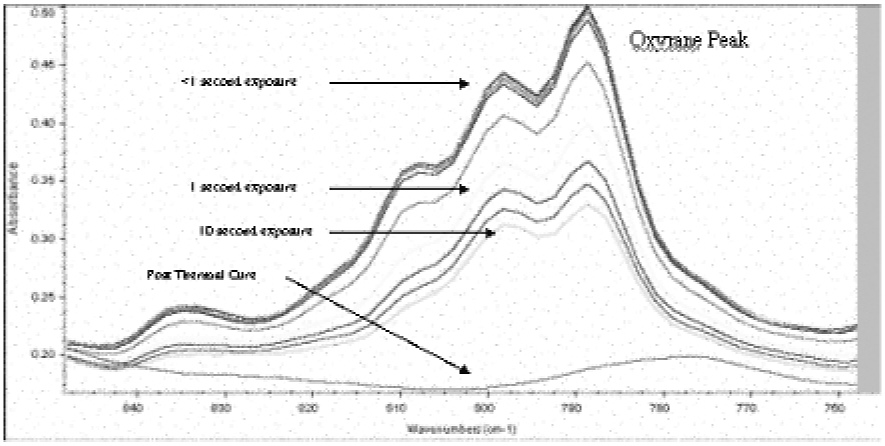

Figure 6. Oxirane peak is used to monitoring the degree of cure in the epoxy material studies.

Table II summarizes the measurement conditions and results obtained for the UV cured epoxy materials outlined in Table I. Hardness and adhesion were used to assess the properties of the cured epoxy material. It was found that with a low intensity exposure, such as large distance at low intensity setting of 3,000 mW/cm^2 (table II), the hardness was limited to Shore D 65 and poor adhesion resulted. Prolonged curing using low intensities did not improve the hardness value. Post thermal cure was required for the epoxy material to achieve a high degree of cure. High intensity curing was performed using the EXFO Novacure with a standard light guide delivery system. At the high intensity of 12,000 mW/cm^2, it was found that the large exotherm generated by the photoinitiated curing process was sufficient to complete the cure of the epoxy material without post thermal treatment. However, care had to be taken to prevent "thermal over run". The maximum hardness achieved for properly cured material (either use thermal post cure or high intensity cure) was Shore D 85.

Table II. Cure Condition and Data for UV cure Epoxy Adhesive

Cure system	Setting (mW/cm2)	Distance (inches)	Cure time (seconds)	lapShear Test* (pass/fail)	Shore D Hardness Test	Oxyrane peak (FTIR)	Adhesion Test ** (pass/fail)
BondWand	On (no setting)	2	240-300	pass	65	35%	fail
BondWand	On (no setting)	2	>600	pass	65	50%	pass
Novacure	3,000	5	20	pass	65	50%	fail
Novacure	3,000	2	5	pass	65	50%	fail
Novacure	3,000	0.5	<5	pass	65	50%	fail
Novacure	3,000	0.5	15	pass	65	50%	pass
Novacure	12,000	12	45	pass	65	40%	fail
Novacure	12,000	5	15	pass	65	50%	fail
Novacure	12,000	2	<5	pass	70	60%	pass
Novacure	12,000	0.5	<5	pass	85	100%	pass
LED	1,000	2mm	60	Not cured			
Post thermal***			>900	pass	85	100%	pass

*as per ASTM standard with glass substrates; ** fiber pull adhesion test at 8000 psi;
*** post thermal cure was 125 °C, 30 min.

A sensitizer (preparatory) was used to increase the absorption peak of the epoxy material in order to match it with the LED emission wavelength. Our tests show that a 45% degree of cure of the modified epoxy can be achieved using the LED array. Complete cure can be achieved using a secondary thermal cure at 125 C for 30 min. It was also find that excessive PI may result in the formation of a skin. A reduction of both sensitizer and PI concentration to their optimum will enhance the thorough cure of the material.

Four samples of the LED plus thermal cured material were also tested for moisture absorption characteristics under 85% RH/85 C for 2 weeks. The average water absorption was 0.55% with standard deviation of 0.16%.

4. Guidelines of Selection of UV Curable Materials and Curing Sources

Based on the test results presented, the following are the key criteria when selecting UV curable materials and curing sources:

(a) The epoxy material exhibited a slower cure than the acrylate materials and required thermal cure in order achieve its designed characteristics.

(b) Matching of the PI in the UV material and spectral profile of the curing system is the most important factor to achieve thorough cure of the material. For example, urethane acrylate can be cured within a few seconds using currently available LED or arc lamp technology. Delivering excessive power, however, may result in "thermal over run" and cause shrinkage, melt back, and photo bleaching of the material. This is typically only possible with the mercury arc lamp sources. Insufficient power may result in poor adhesion and inferior material characteristics. Selection of LED's with appropriate wavelength emissions can minimize heat affects and prevent both UV/IR damage to the material.

(c) Epoxy, in general, has the following benefits over acrylate materials: low shrinkage, low outgassing, low moisture absorption, and normally more mechanically stable over a wider temperature range. Therefore, it is more suitable for high reliability applications, such as optoelectronic packaging. With the presently available LED wavelengths it is necessary to modify either the PI or add a photosensitizer matched to the LED wavelength to initiate curing. It is recommended that this be followed by a thermal post cure step.

5. Conclusion

Urethane acrylate materials can be cured using both mercury lamp and LED based curing systems in less than 1 sec. The fast curing rate for both light sources is due to wavelength matching of the source to the absorption peak of the material and the reaction kinetics. The epoxy materials studied can be cured effectively using mercury lamp based systems. However, slow reaction rates and diffusion dominated processes necessitated additional thermal curing of the epoxy material to achieve the fully cured properties except when high powered lamp systems are used. For the studied epoxy materials, the absorption wavelengths of the cationic PI did not match with emission wavelengths of the LED system. A sensitizer was required to increase the absorption of the LED system emissions centered at 396nm to achieve a partial cure of 45%, similar to the low intensity cure achieved by the arc lamp system on same material without sensitizer. Excessive PI and sensitizer resulted in a skin effect and limited the depth of cure. It would be necessary to optimize the concentration of both to enhance the depth of the cure for the adhesives.

6. References

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