Light-Emitting Diodes Generate Sufficient Intensity to Cure Visible Light Adhesives

By Edwin R. Perez

UV and/or visible light-absorbing urethane acrylate-based adhesives are typically cured with high-intensity light sources, such as metal halide, electrodeless and/or wand systems. Such systems are costly to maintain as they require ongoing lamp maintenance, substantial dedicated floor space and health- and safety-related equipment expenditures.

To minimize costs and improve safety, adhesive manufacturers have developed light-emitting diode (LED) cure equipment for processing radiation-cure adhesives. These fully visible radiation-curing systems are safer and longer lasting than high-intensity light sources.

This article illustrates the performance of three recently developed radiation-cure adhesives when cured by 460nm LED and visible light-emitting flood systems. A variety of adhesive properties will be reviewed, including curing and physical data.

Background

Light-curing acrylic adhesives (LCAA) have been available for more than 30 years. They are widely used in markets (such as medical, automotive and electronic assembly) to bond glass, plastics and metals.

Modified (meth)acrylate oligomer/monomer mixtures combined with an ultraviolet absorbing photoinitiator pioneered the LCAA market. Typically, derivatives of acetophenone were used as initiating compounds in the ultraviolet range of the electromagnetic spectrum (Figure 1).

Initiating species are formed from a unimolecular hemolytic cleavage upon exposure to radiation of specific

FIGURE 1

2,2 diethoxy acetophenone is an example of a type 1 photoinitiator.

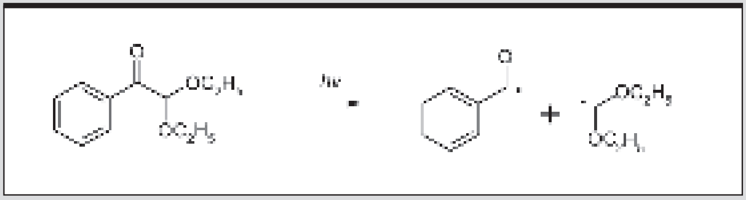
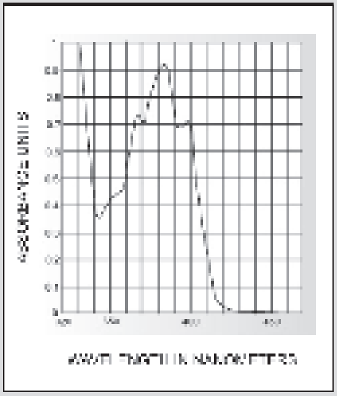


FIGURE 2

Absorption spectrum of monoacyl phosphine oxide-type photoinitiator



wavelengths, typically between 300-400 nm.

For outdoor light protection, ultraviolet absorbers that absorb light wavelengths below 400nm were incorporated into thermoplastics, such as polycarbonate. This would interfere with curing of the adhesive through the thermoplastic sheet. This change in plastic formulating created demand for radiation-cure systems that cure with visible light.

During the 1990s, monoacyl phosphine oxide-type initiators capable of initiating polymerization in the UV/visible light range became available. These initiators are also Type I. They undergo photocleavage of the bond linking the carbonyl and the phosphine oxide upon exposure to light, ranging from 340 to 420 nm. The radiation-curing industry classifies these systems in the UV-Visible category (Figure 2).

Ideally, a LCAA formulator will try to best match the spectral output of the light source to the absorption characteristics of the photoinitiator in the liquid adhesive formulation. Upon exposure to light of the appropriate wavelength, radiation-curable adhesives polymerize by a free-radical mechanism to form clear, colorless thermoset polymers. Immediately after the formulated adhesive is irradiated, the photoinitiator breaks apart, forming free radicals. These radicals attack the C=C bonds of the acrylate portion of the mixture of monomer(s) and oligomer(s), initiating a crosslinking photopolymerization.

As the growing polymer radicals become attached to the network under formation, they lose their reptation mobility. Polymerization and crosslinking will continue until vitrification and decreasing monomer diffusion occludes the propagating radical, and they eventually terminate with other radicals or with oxygen.[1] If the correct adhesive is selected for a particular application, upon cure it forms a thermoset polymer with suitable adhesion to the selected substrates.

Although medium- and high-pressure mercury lamps, metal halide and wand lights were available to process UV and UV-visible light absorbing systems, electrodeless Fusion radiation-curing systems became the curing workhorse of the industry (Figure 3). Spectral outputs of these bulbs are ideal for processing UV and UV-visible radiation curing urethane acrylate adhesives because the wavelengths can be tailored to meet the needs of the adhesive's photoinitiators.

Electrodeless bulbs consist of a quartz tube filled with gases that are excited to a plasma state using focused microwave energy from a magnetron.[2] The output of these bulbs remains fairly consistent for about 5,000 hours. Their maximum length is 10 inches. When large parts need irradiation, several power supplies and magnetrons must be used, resulting in increased energy consumption and added operating costs.

Because of the UV light emitted, chambers and shutters protect operators from exposure to damaging UV irradiation. These chambers may occupy between 10 and 15 linear feet, increasing the manufacturer's overall process cost. To control ozone emissions from UV light, special venting and expensive protective equipment for operators are required in most manufacturing plants.

Many high-performing UV and UV-visible urethane LCAA processed with electrodeless bulb systems were developed to meet industrial demands. However, early in this century, customer feedback showed increasing demand for lower total system costs and increased operator health and

FIGURE 3

Spectral outputs of electrodeless Fusion H and V bulbs.

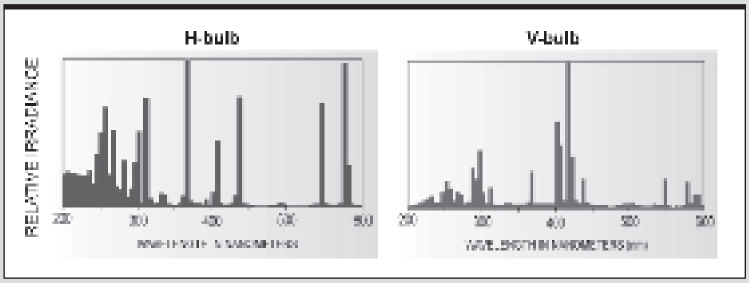
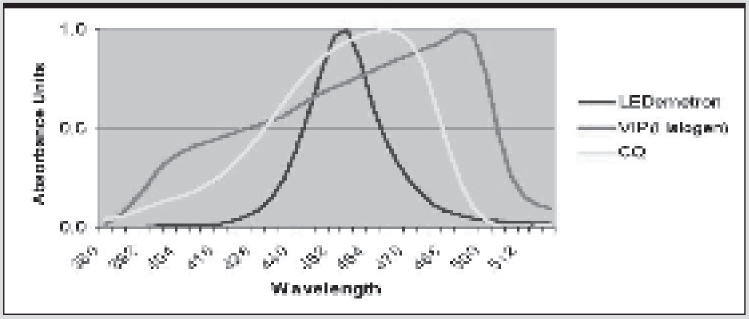


FIGURE 4

Emission and Absorption Spectrum



Spectral output of LED matches absorption characteristics of photoinitiator d,l camphorquinone(CQ). Halogen lamps may also work, but are not as effective.

FIGURE 5

UV

1. PI + UV or Visible radiation →P• + I•
2. P• + O2→P-O-O•
3. R• + R→RR•→RRR• etc.
4. R• + O2→R-O-O•
5. . R• + R•→R-R

Free radicals form upon absorption of suitable light by the photoinitiator (PI), Step 1. These initiator fragments could react with oxygen as in Step 2, become part of the growing polymer chains (R) as in Step 3, or terminate through radical coupling as in Step 5. When these radicals react with oxygen, they yield peroxy radicals, Steps 2 and 4.

safety. To fulfill these demands while maintaining the performance properties of the UV-visible LCAA, adhesive formulators had to develop total visible radiation-curing systems.

Visible Light-Emitting Diodes (LED)

Instead of using electricity to energize magnetron and excite gas mixtures into a plasma state, LEDs emit light by moving electrons in a semiconductor material. These systems require less energy to generate light outputs equivalent to conventional UV and visible light sources. LEDs turn on and off instantly without warm-up or cooling periods, further increasing efficiency.

Visible LED has been used for years in the dental industry, where resins are cured with LEDs that emit mostly blue light within the 450-470nm range. Relative to the spectral output of electrodeless systems, visible LEDs typically have a narrow emission distribution. Since the components are typically a mixture of monomer, 2-hydroxyethyl methacrylate, photoinitiator d,l camphorquinone (CQ) and a filler, an LED with most of its output between 450-470 nm is ideal for processing (Figure 4).

Demetron LED, which emits visible light with a peak irradiance of 1 W/cm^2, is ideal for the dental industry where 60-plus seconds processing time is acceptable. However, manufacturers joining parts with urethane-based LCAA systems expect full strength and adhesive properties inside and outside a bond within 10 seconds—a challenge for a fully visible light system where high-energy/short-wavelength UV light is excluded. The greatest challenge is in generating a dry surface outside the bond area when curing for only 10 seconds, as oxygen scavenges free radicals from initiator fragments by reacting with the formed free radicals. This prevents effective growth of polymer chains resulting in tacky surfaces (Figure 5).

It is extremely challenging to formulate adhesives that overcome oxygen inhibition without using high-energy UV radiation. As the absorption characteristics of photoinitiators shift toward the IR wavelength range, color of the adhesive becomes an issue. Increasing the levels of blue light-absorbing initiators causes adhesives to become more yellow. In many cases, this is an undesirable aesthetic concern for the end-user. The formulator will use the maximum level of blue light-absorbing photoinitiators to generate more free radicals faster, while maintaining an acceptable liquid appearance to the customer.

Another approach to overcoming oxygen inhibition is adding acrylic functionality and selecting fast-reacting/high-performing urethane acrylate oligomers. Also, by incorporating oxygen-scavenging groups into the oligomer's backbone, tack-free surfaces are possible when processing solely with low-energy visible light. Lastly, the higher the irradiance of the visible light source, the better the chance that adhesives will perform at least as well as conventional UV-visible curing systems.

Fully visible light curing systems are now available. Adhesives that respond to blue light can be processed like conventional UV-visible light systems. Besides being able to process UV-inhibited devices, these novel systems allow for the assembly of semi-transparent blue, gray and purple parts.

High-Power Visible LED

Visible LED systems emitting light in excess of 4W/cm^2 for ~ 0.4 inches diameter offer irradiance high enough to consistently cure tack-free adhesives that respond to visible light. Such high intensities can overcome oxygen inhibition of urethane-based LCAA. To reduce processing costs, LED light sources offer instant on/off performance, consistent light output and useful life of up to five times that of a typical UV-visible bulb system.

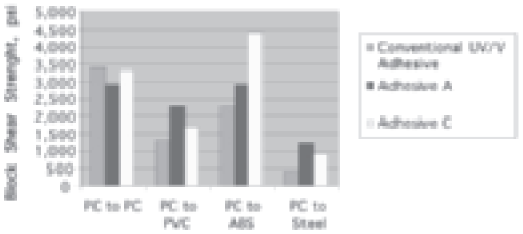
Many bonding applications involve curing large bond areas. Stacking LEDs can effectively do this. Visible light-emitting flood lamps that irradiate high-intensity light over a significant bond area are also accessible.

Flood-visible Light

Visible flood systems offer light output rich in light wavelengths close to 400 nm. High-intensity, bench-modular light cure systems are equipped with four-inch/400W visible arc lamps with expected bulb life of about 2,000 hours. With a typical cure area of approximately 2x4 inches, their emission area is much larger than that of the visible LED, but their irradiance is lower. At a 2-inch distance, their average irradiance is 225mW/cm^2. For applications that require light emission areas larger than eight square inches, multiple units can be mounted side by side.

FIGURE 6

Substrate Versatility



PC = UV absorbing polycarbonate, PVC= polyvinyl chloride, ABS = acrylonitrile butadiene styrene.

Solely visible light systems can now be used to process urethane LCAAs. The high irradiance of the visible LED, in combination with strategically formulated urethane-based LCAAs, allow for the assembly of visible light transmitting devices.

Visible light cure systems provide similar performance as—and in some cases better performance than— UV-visible systems without the environmental concerns of UV light. Lower processing costs are also attainable.

Recently Developed Visible Light-Curable Adhesives

UV-visible light-curable adhesives can withstand sterilization and have excellent environmental resistance properties. However, new generation visible light-cure adhesives cure quickly on exposure to visible light and adhere well to thermoplastics, metals and glass. Three visible light-curable adhesives offer solutions to many current device assembly challenges.

Table 1 compares the viscosities and bulk properties of a conventional UV-visible light curing adhesive and new visible light cure products.

Visible Light-Curable Adhesives A and C

Adhesives A and C are one-part visible light-curable adhesives primarily

TABLE 1

Viscosity & Bulk Properties

Adhesive	*Viscosity, cP	Modulus of Elasticity, PSI	Elongation @ Break, %	Tensile Strength @ Break, PSI	Hardness Shore D-2
Conventional UV/Vis	200-10,000	87,000	100	2,900	73
Visible A	5,000	114,000	30	4,100	70
Visible B	1,000	167,000	10	5,400	76
Visible C	300	175,000	10	5,450	77

TABLE 2

Comparison of the adhesion needle assemblies

Substrate	Conventional UV-visible Adhesive	Adhesive A	Adhesive C
PC hubs to SS needle, lbf (pounds of force)	25	31	29

PC = UV absorbing polycarbonate
SS (below needle assembly) = stainless steel.

designed for bonding polycarbonate substrates. Good adhesion to other thermoplastics, metals and glass may also be attained. For simplicity, technical information is reported only for adhesives A and C, as adhesive B is simply a higher viscosity version of adhesive C. Figure 6 illustrates the substrate versatility of these adhesives.

While the conventional adhesive was cured with an electrodeless V bulb, adhesives A and C were processed with metal halide visible light for 10 seconds at 225mW/cm^2. Results indicate that substrate versatile visible light-curing adhesives A and C generate equivalent or better block shear strengths than conventional UV-visible processed adhesive. Their superior ability to bond can be attributed to the unique combination of acrylic oligomers, monomers and photoinitiator contained in their respective compositions.

Evaluation of a typical needle assembly (Table 2) using the same curing conditions as in the block shear study further confirms the substrate versatility of these adhesives.

The relative high viscosity of adhesive A makes it suitable for applications where gap filling is required, as in blood oxygenators and blood heat exchangers. As adhesive C is lubricious and has low viscosity, it enables easy assembly of components with close fitting tolerances, such as PVC. Both adhesives are suitable for bonding semi-transparent materials. Typical properties for both adhesives in the uncured state are shown in Table 3.

Both adhesives have been formulated to cure rapidly upon exposure to visible light. There are two ideal sources for processing Adhesives A and C:

1) Flood systems containing a 400W/4-inch visible arc bulb with a typical curing area of 8 in^2 (a 2 x 4-inch curing area) at a distance of 2 inches.
2) High-power visible LED sources with a typical cure area of 0.4-inch diameter at 0.5 inch.

Upon exposure to suitable radiation, adhesives A *and* C cure very rapidly to form transparent, durable and sterilizable bonds. In addition to being *ISO 10993-certified*, adhesives A *and* C pass Minimum Essential Medium (MEM) elution and agarose overlay cytotoxicity testing. These characteristics make the adhesives suitable for use in the medical industry. Table 5 illustrates the block shear strength in a bonded specimen after exposure to several environments.

STM Method 726 was used for block shear strength determinations on medical-grade UV-absorbing polycarbonate. Gaps were not induced. Both adhesives were exposed to 225 mW/cm^2 for 30 seconds under a Loctite® Indigo™ 7418™ Visible Flood System followed by 24 hours post cure at room temperature prior to testing.

TABLE 3

Uncured Properties

Property	Adhesive A	Adhesive C
Chemical Type	Modified acrylate oligomer/monomer	Modified acrylate oligomer/monomer
Appearance	Clear liquid	Clear liquid
Specific Gravity, g/mL @ 25˚C (77˚F)	1.0856	1.0934
Refractive Index, N_D	1.4800	1.4820
*Viscosity @ 25˚C (77˚ F), cP	5,000	300
Flash Point (TCC)	89.5˚C (192.2˚F)	91.5˚C (196.7˚F)
Stress Cracking, ASTM D-3929, minutes to stress crack medical-grade polycarbonate.		
Induced stress to polycarbonate 2,000 psi	> 15	>15

(Viscosities were determined using Physica Viscometer, 50 s-1 with spindle MK22, 25(C +/- 0.5)*

Conclusion

Lower processing costs and environmental health and safety concerns are motivating manufacturers of disposable medical devices to implement "Total Visible Light Curing Systems" in their plants for assembling thermoplastics, such as polycarbonate, acrylic, ABS, polycarbonate/polyester blends and PVC. A number of UV-visible processing limitations (such as protective equipment, IR generation, ozone removal, bulb life, equipment maintenance, floor space and power consumption) have incentivized equipment manufacturers to develop one-part visible light-curable acrylic technology. Furthermore, processing and producing dependable medical devices that consist of selected semi-transparent materials is now possible. ◗

References

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2. Noonan, Brian and Courtney, Patrick J., "Applying Advances in LED Technology to the Use of Light-Curing Adhesives," *RadTech Report*, Jan/Feb 2005, pp 53-57.
3. Hanrahan, Michael J., "Oxygen Inhibition: Causes and Solutions," *RadTech Report*, March/April 1990, pp.14-19.

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TABLE 4

Curing Properties

Cure Through Depth Inches	Adhesive A	Adhesive C
Flood Visible Light, Irradiance = 0.280 W/cm^2	>0.5	>0.5
LED Cure Jet, Irradiance = 4.0 W/cm^2	>0.5	>0.5
Tack Free Time, seconds		
Flood Visible Light, Irradiance = 0.280 W/cm^2	< 5	< 5
LED Cure Jet, Irradiance = 4.0 W/cm^2	< 5	< 5

(Note: Test intensities were measured with Zeta 7011-V Dosimeter-Radiometer for UV-V.)

TABLE 5

Environmental Exposure

Condition	Adhesive A	Adhesive C
PC to itself Block Shear Strength, psi	2,900	3,350
% Strength Retained after environmental exposure		
Heat Aging		
1 week @70˚C	100	100
1 week @93˚C	100	100
Heat and Humidity		
1 week @100˚F/95% RH	100	100
***Autoclave**		
30 min. @ 250-259˚F	100	100
Solvent Immersion		
Boiling Water, 2 hours	52	25
90% Isopropanol 1 week @ RT	75	82