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Light-curing adhesives compatible with UV-LED light sources

Introduction

The proliferation of light-emitting diodes (LEDs) has brought the lighting industry to a major transition point. These devices have entered use not just for special lighting applications like those encountered for mobile phones, liquid crystals, or in the automotive industry, but for general-purpose domestic lighting. Driving this trend is light-emitting diode technology's potential for addressing recent global environmental concerns. In lighting devices, LEDs provide longer life, power savings, and lower heat emission. Today's eco-boom suggests these trends will gain strength. Light irradiation systems based on light-emitting diodes are rapidly gaining a wider share in the light-curing adhesive market and have already been introduced in various domains, including the pickup, HDD, and liquid crystal industries.

Since its founding, ThreeBond has widely marketed adhesives for various applications, including light-curing adhesives. Over twenty years have passed since ThreeBond marketed its first product. During this time, ThreeBond has continued to develop light-curing adhesives that offer diverse curing characteristics, including UV curing and visible-light curing.

This issue introduces three light sources based on light-emitting diodes and the products that can be used with these light sources: ThreeBond 3017D, ThreeBond 3017E, and ThreeBond 3017F.

(Note that ThreeBond is abbreviated "TB" in product names hereafter.)

Contents

1. Background

Light-curing resins cure instantly when exposed to light from a light source, a trait that has led to growing demand in the electric market, especially in applications involving inks, paints, adhesives, and optical materials. Curing requires a light source. Discharge lamps (e.g., high-pressure mercury lamps and metal halide lamps) are conventional and widely used light sources, but light-emitting diodes (light emission by electroluminescence and DC voltage; LED hereafter) and their advantages over discharge lamps have drawn attention. Since the commercialization of GaN-based blue LEDs by Nichia Corporation in 1993, use of LEDs as light sources for light curing has rapidly grown. Figures 1, 2, and 3 below show examples of applications in which LED light sources have been introduced.

In general, special light sources in the area of light-curing adhesives use LEDs that emit light at a wavelength of 365 nm. Hereafter, we will refer to LED light sources emitting light at a wavelength of 365 nm as UV-LED light sources.

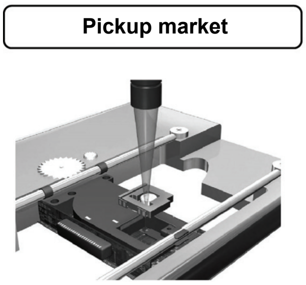


Figure 1: Adhesion of lens and holder

Figure 2: Adhesion of lens and tube

Figure 3: Temporary bonding of liquid crystal panel

2. Overview of UV-LED light sources

2-1 Principles of LEDs

The basic structure of an LED is a "PN junction," which consists of a p-type semiconductor (a semiconductor with holes as majority carriers) and an n-type semiconductor (a semiconductor with electrons as majority carriers). The junction is covered by transparent resin (generally, epoxy resin). When voltage is applied, the holes and electrons move and collide, emitting energy. An LED emits light when the emitted energy is converted to light energy. This is the principle of light emission (Figure 4). Here, the wavelength of the light emitted varies according to the type of component semiconductors.

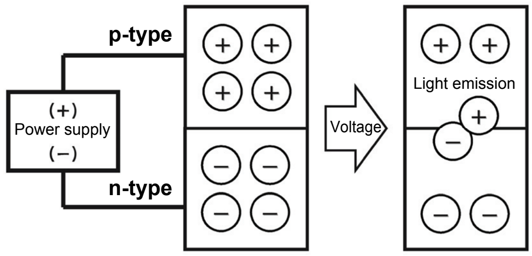


Figure 4: Principles of light emission

Most LED products have one of two types of structures. One is the bullet LED, in which the frame and the LED chip are integrated and encapsulated in epoxy resin (Figure 5).

The other is the surface-mounted (SMD) LED, which is encapsulated in silicone or epoxy resin (Figure 6). LEDs incorporate reflectors or lenses to improve the directionality of the emitted light. Since thermal degradation reduces an LED's output power, improvements in heat dissipation via heat sinks or other devices are essential to high output power.

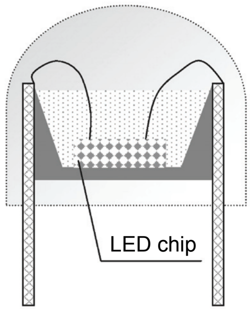


Figure 5: Bullet type

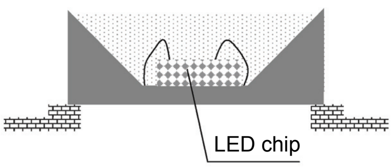


Figure 6: Surface-mounted (SMD) type

2-2 Comparison of wavelength of light emitted from UV-LED source and discharge lamp

Figures 7 and 8 below show the wavelength of a UV-LED light source and a discharge lamp, respectively. The UV-LED light source is characterized by its monochromatic nature.

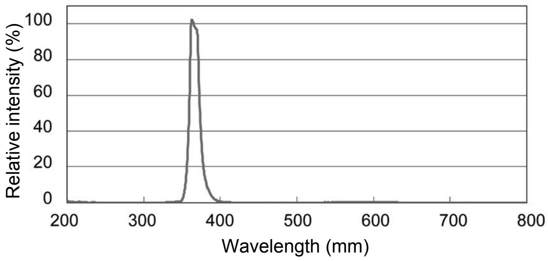


Figure 7: Wavelength of UV-LED light source

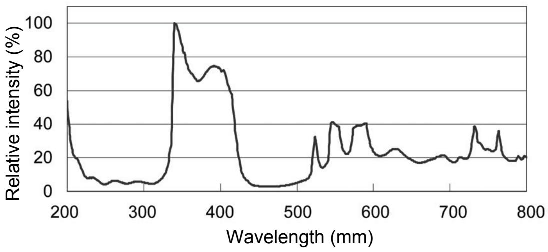


Figure 8: Wavelength of discharge lamp

The difference in wavelengths corresponds to the difference in energy. While discharge lamps have raised concerns regarding the effects on resin materials caused by high-intensity peaks in the visible and infrared region, UV-LED light sources are free of such concerns. Figure 9 illustrates the difference in the measured temperature increase.

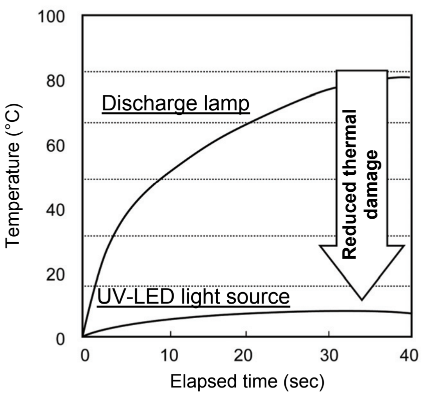


Figure 9: Comparison of temperature increase

The difference in the wavelength corresponds to the difference in energy, apparently demonstrating the clear advantage of a UV-LED light source. In fact, this trait raises concerns when UV-LED light sources are used for light curing. It also requires careful design in the corresponding light-curing adhesives. The reason is that the advantages in the device are not necessarily accompanied with advantages in the reaction. Table 1 below shows the wavelength dependence of energy. Energy is greater for shorter wavelengths. A light source with a wavelength of less than 365 nm—for example, in the range of 200 nm to 300 nm—provides several times more energy and is a better light source for inducing reactions. For this reason, particularly with relatively low energy at the 365 nm wavelength provided by a UV-LED light source, improvements in reactivity require simultaneous technical innovations in light-curing adhesives.

Table 1: Energies and frequencies of electromagnetic waves

	Energy (kJ/mol)	Frequency (1/s Hz)
Electron beam	to 10^6	to 2×10^{16}
Ultraviolet	300 to 600	0.75 to 2×10^{15}
Visible light	150 to 300	0.40 to 2×10^{15}
Infrared	8 to 60	0.20 to 2×10^{14}

Application also requires attention regarding the transparency of the material. Table 2 below shows the light transmission characteristics of typical materials. Light-curing adhesives are used not just in applications requiring direct light irradiation, but in applications requiring light irradiation through materials—for example, when bonding two materials. In such cases, we cannot ignore light absorption, even in transparent materials. A UV-LED light source is monochromatic at 365 nm, requiring even greater care.

Table 2: Light transmission of various materials

	365 nm	405 nm	435 nm	Remarks
Rigid PVC	0.1%	50%	80%	Mitsubishi 302 (2 mm thick)
Flexible PVC	0.3%	44%	77%	Takato Kasei (2 mm thick)
ABS	0.1%	5%	10%	Tsutsunaka Tough Ace (2 mm thick)
PBT	0.1%	13%	17%	Duranex 2002 (2 mm thick)
Polycarbonate	0.5%	50%	95%	Teijin Panlite PC-111 (2 mm thick)
Soda glass	48%	80%	85%	Tempax (5 mm thick)

Note: The above materials require care when used with a UV-LED light source.

As discussed above, using a UV-LED light source effectively requires new designs for light-curing adhesives based on the wavelength and energy of the light source and the material to be bonded. The next section discusses various aspects affected by differences in light sources, using radical reactions as an example.

3. Applying UV-LED light sources

3-1 Radical reactions

Radical reactions are the most common reactions used with light-curing adhesives. Equations 1, 2, and 3 below show typical reaction formulae. In general, we use backbones with acrylic (or methacrylic) groups. The main backbone structure varies widely and includes epoxy, silicone, urethane, and polyester. The reaction begins with light absorption by the photo-polymerization initiator, which generates the radical species (Equation 1). The reaction proceeds with the radical species initiating the polymerization reaction (Equations 2 and 3).

[Radical polymerization reaction]

Equation 1) $PI \xrightarrow{h\nu} PI^*$

Equation 2) $PI^* + M \rightarrow PIM^*$

Equation 3) $PIM^* + M \rightarrow PIMn^*$

Note:
PI: Photo-polymerization initiator
PI*: Photo-polymerization initiator radical species
M, Mn: Monomers

Equations 4, 5, and 6 show the polymerization termination reaction. Deactivation occurs when oxygen combines with the photo-polymerization initiator radical or the monomer radical and generates the termination reaction. Oxygen can react with the radical species, even if the oxygen itself is in the ground state.

[Radical termination reaction: oxygen inhibition]

Equation 4) $PI \rightarrow I^* + O_2 \rightarrow PI-OO^*$ (Termination)

$\downarrow$

Equation 5) $PI-M^* + O_2 \rightarrow PI-M-OO^*$ (Termination)

$\downarrow$

Equation 6) $PI-Mn-M^* + O_2 \rightarrow PI-Mn-OO^*$ (Termination)

Note:
PI: Photo-polymerization initiator
I*: Photo-polymerization initiator radical species
M, Mn: Monomers
O_2: Oxygen

3-2 Use of UV-LED light sources

As discussed above, a UV-LED light source is monochromatic. Its overall energy is relatively low. In terms of reaction formulae, this means that the termination reaction indicated by Equations 4, 5, and 6 occurs readily, because the termination reaction caused by oxygen inhibition and the polymerization reaction are competing reactions. Lower energy increases oxygen reactions. In other words, we must be aware that a UV-LED light source requires consideration of oxygen inhibition to an extent we might not expect with conventional light sources. To use a UV-LED light source effectively, we must design the light-curing adhesives with an eye to preventing the reaction termination and efficiently curing the resin.

Manufacturing problems stemming from the reaction termination include adhesion of foreign objects caused by lowered surface curing, increased outgassing, and increased water absorption. All these phenomena result in product defects and require care. Reaction terminations that generate the phenomena occur readily with flexible resins, since reactions in flexible resins tend to be slow, with poor surface curing even when using conventional light sources. Any change in light sources will degrade curing still further.

In sum, developing flexible light-curing resins compatible with UV-LED light sources poses numerous challenges for conventional technologies. Based on its early start, ThreeBond has already brought products to market. The next and subsequent pages introduce our product line of flexible light-curing adhesives compatible with UV-LED light sources.

4. Products (TB3017D, TB3017E, TB3017F)

ThreeBond has developed the TB3017D, TB3017E, and TB3017F mainly for bonding lenses and holders in the electronics market, including optical pickup and camera modules. The product features are listed to the right. The most prominent feature of these flexible light-curing acrylic adhesives, which tend to be sensitive to oxygen inhibition, is smooth curing with UV-LED light sources. Compared to conventional adhesives, the products offer improved bonding strength to cycloolefin polymers (COP), a difficult-to-bond material. They also meet halogen control requirements for today’s markets.

4-1 Product features

(1) Curable with a UV-LED light source.
(2) Flexible; excellent surface curing performance
(3) Excellent bonding strength to COP
(4) Excellent environmental durability
(5) Low halogen products with total chlorine and total bromine, each less than 900 ppm and together less than 1,500 ppm

Tables 3, 4, and 5 below give the physical properties.

Table 3: General properties

Test item	Unit	TB3017D	TB3017E	TB3017F	Test method	Remarks
Features	-	Low viscosity	High viscosity	High strength	-	
Appearance	-	White	White	White	3TS-201-1	
Viscosity	Pa•s	13	25	7.5	3TS-210-10	Shear velocity: $20s^{-1}$
Specific gravity	-	0.93	0.93	0.93	3TS-213-02	

Table 4: Characteristic values

Test item	Unit	TB3017D	TB3017E	TB3017F	Test method	Remarks
Hardness	Type-A	41/40	35/33	58/59	3TS-215-01	$30kJ/m^2$
Water absorption	%	0.2/0.3	0.4/0.6	0.3/0.4	3TS-233-03	$30kJ/m^2$
Cure shrinkage	%	6.4/6.0	6.5/6.2	6.6/6.3	3TS-228-01	$30kJ/m^2$
Thick film curing	mm	2.5/2.6	3.0/3.3	2.6/2.9	3TS-222-01	$30kJ/m^2$
DMA	Pa	$9.1 \times 10^6/7.1 \times 10^6$	$6.9 \times 10^6/5.9 \times 10^6$	$1.1 \times 10^7/1.2 \times 10^7$	3TS-501-04	E', 25°C, $30kJ/m^2$
	°C	-54/-52	-55/-52	2.0		E'' peak, $30kJ/m^2$
	°C	-18/-16	-26/-23	13/11		tan δ peak, $30kJ/m^2$

Note: A or B indicated identifies the curing conditions as below.
A: Discharge lamp (30 kJ/m^2, dominant wavelength 365 nm)
B: UV-LED light source (30 kJ/m^2)

Table 5: Tensile shear bonding strength

Test item	Adherend	Unit	TB3017D	TB3017E	TB3017F	Test method
Tensile shear bonding strength	ZnDc/glass	MPa	4.3/4.3	3.0/3.2	3.4/3.2	3TS-301-13
	COP/COP (Zeonex®)		2.6/2.7	2.8/3.0	2.8/3.0	
	COP/ZnDc		3.0/2.7	3.0/3.2	3.8/3.9	
	COP/LCP (Vectra® E130i)		1.0/0.9	1.0/1.1	2.0/1.9	
	COP/PPS (Tosoh Susteel® GS40)		1.2/1.2	1.2/1.2	2.4/2.2	

Note: A or B indicated identifies the curing conditions as below.
A: Discharge lamp (30 kJ/m^2, dominant wavelength 365 nm)
B: UV-LED light source (30 kJ/m^2)

4-2 Curing speed

Curing speed is generally measured by changes in the characteristic peaks of the functional groups observed in FT-IR. As shown in Figure 10, the peak shapes differ before and after the reaction. Here, changes appear in the double-bond peaks of the vinyl group near 1610 cm^{-1} to 1630 cm^{-1}. The peaks decrease as the reaction progresses. This decrease is used to check the reaction percentage.

By monitoring changes in reaction percentage over time, we can also measure reaction percentage per unit time, or the reaction rate. As shown in Figure 11, the product line is also compatible with UV-LED light sources with respect to curing speed; these products provide even faster curing.

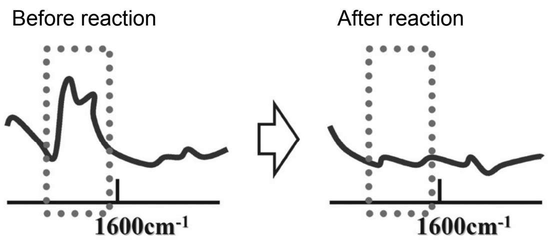


Figure 10: Decrease in peaks associated with reaction

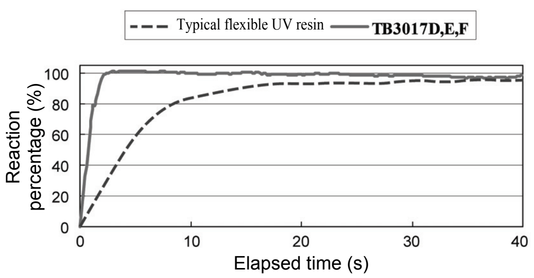


Figure 11: Reaction rate measurement by FT-IR

Note: The resin is cured with a UV-LED light source (200 mW × 15 sec.)

4-3 Reliability data

This product line not only offers sufficient curing speed with UV-LED light sources; they offer better performance than conventional adhesives with respect to durability under various environmental conditions.

Figures 12 and 13 below show the results of durability tests.

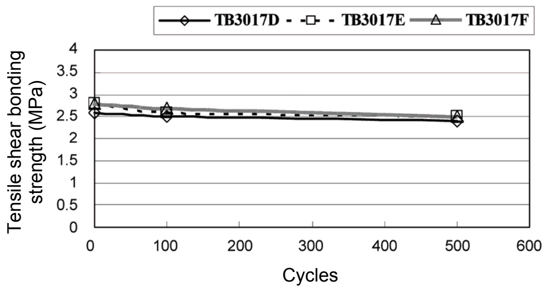


Figure 12: Heat cycles (−40°C to 80°C, 30 min. each)
Tensile shear bonding strength after predetermined duration
(Adherend: COP/COP)

Note: The resin is cured with a UV-LED light source (200 mW × 15 sec.)

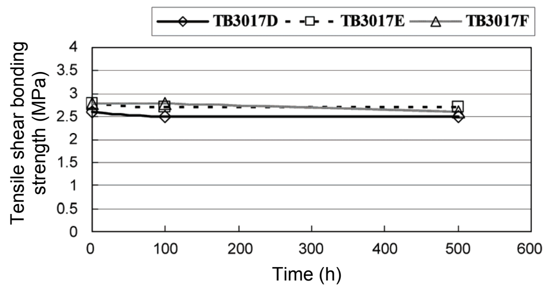


Figure 13: Humidity (60°C × 95% RH)
Tensile shear bonding strength after predetermined duration
(Adherend: COP/COP)

Note: The resin is cured with a UV-LED light source (200 mW × 15 sec.)

Table 6: Tensile shear bonding strength for different UV-LED illuminance

Test item	Adherend	Unit	TB3017D	TB3017E	TB3017F	Test method
Tensile shear bonding strength	COP/COP (Zeonex®)	MPa	2.6	2.9	2.9	3TS-301-13
			2.7	3.0	2.9	
			2.7	3.0	3.0	

Note: The resin is cured with a UV-LED light source (200 mW × 15 sec.)

5. Overview of UV-LED system

This section discusses overall differences in system configuration, beyond the difference in the light sources discussed above. (Data provided by Omron Corporation)

Table 7 below compares the two light source systems. The table shows that there are many differences among light source systems. We will discuss the details of major items later. UV-LED light source systems also have other advantages with respect to the environment, such as mercury-free construction and reduced power consumption.

Table 7: Comparison of light sources

	UV-LED light source	Discharge lamp
Illuminance	94kW/m^2	Approx.40kW/m^2
Life	40,000 hours	Approx. 3,000 hours
Space saving	Yes	No
Light source response	ON/OFF control possible	Continuous lighting
Stress to adherend	Small	Large
Environmental concerns	No mercury	Contains mercury
Power consumption	Approx. 53 W	Approx. 250 W

[Space savings and branching efficiency]

The two light source systems differ significantly in one particular respect: whether the light-emitting section is inside or outside the system main body. With discharge lamp systems, the light-emitting section is positioned within the main body, requiring a relatively large space. With UV-LED light source systems, the light-emitting section is at the cable end, outside the main body. The latter configuration allows space-saving designs.

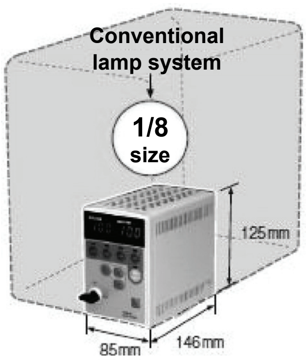
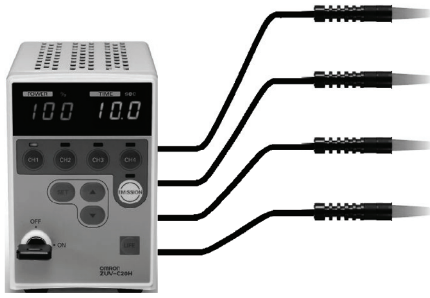


Figure 14: Volume of light source

Further, branching in UV-LED light source systems does not reduce output, for the same reason: the light source section is not inside the main body. With discharge lamp systems, which have the light source inside the main body, output falls at every branching, and final illuminance also falls due to use of long fiber. UV-LED light source systems improve productivity by allowing control of large-scale branching.



	1 branch	2 branches	3 branches	4 branches
UV-LED light source system	100%	100%	100%	100%
Discharge lamp system	100%	85%	66%	57%

Figure 15:Comparison of output after branching

[Proposal for reducing damage to adherends]

A UV-LED light source can reduce the heat generated during extended uses. This feature resolves problems with targets potentially subject to deformation or shrinkage caused by heat.

(See Figure 9.)

[Proposal for reducing operating costs]

The higher stability of the light source output eliminates the need for continuous lighting. The system provides longer life and can significantly cut operating costs. Products with considerably reduced initial operating cost are also available.

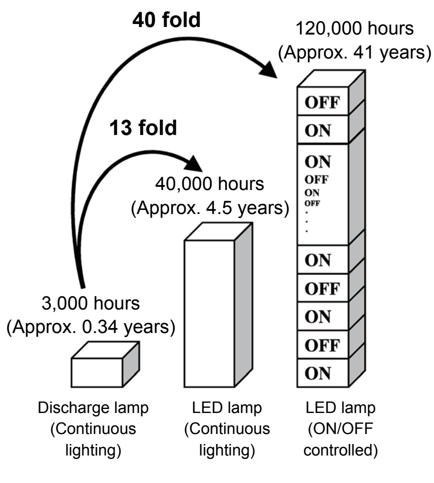


Figure 16: Comparison of operation life

Note: Omron ZUV Series

Conclusion

The demand for spot curing systems based on UV-LED light sources is growing annually in the areas of camera modules, HDDs, and pickup systems. Area curing systems are also scheduled for marketing in liquid crystal-related applications.

ThreeBond has continued to provide adhesives suitable for customer systems, and it will continue to strive to serve as an effective partner by developing light-curing adhesives that meet changing needs.

<References>

Omron Corporation

- Catalog: Introduction to UV Curing
- Catalog: UV Curing System ZUV Series
- Catalog: Applications

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