

# ThreeBond TECHNICAL NEWS

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## Visible-Light-Curing Resin

### Introduction

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Currently, light-curing resins are used in many forms: inks, paints, adhesives, sealants, sealing agents, printing plates, and various resist materials. Three Bond has made great contributions to the electric, electronic, automotive, and mechanical industries with its ultraviolet-curing adhesives, the ThreeBond 3000 and 3100 Series. The development of lasers, in particular visible lasers, has led to increasing demand for resin that is cured in visible light.

This issue introduces a technical approach to resin that is cured by visible light—that is, light with a longer wavelength than is used for conventional ultraviolet-based light-curing resin.

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## 1. Background of visible-light-curing resin

While the demand for light-curing resin has been expanding year after year, most products consist of ultraviolet-curing resin that uses ultraviolet rays as the curing energy. Added to this on the market is visible-light-curing resin, which cures in response to the radiation of visible light. When did such a resin that uses visible light as the curing energy come onto the market? Its history dates back to the late 1970s, when it was used as a dental resin. Therefore, visible-light-curing resin is not a very new development. When visible-light-curing resin came into being, light-curing technology was little used in industrial applications. Its history as an adhesive is just short. This can be attributed to the fact that the market share of light-curing resin itself was low in the adhesive industry.

In recent years, however, many resins that use light as the curing energy have been developed due to the need for a one-part, non-solvent, fast-curing configuration. Hence, so-called "ultraviolet-curing resin," which uses ultraviolet rays as the curing energy, has made a fabulous debut. Due to the fact that ultraviolet-curing resin has overcome the drawbacks of conventional resins, such as the long

curing time and two-part configuration, demand for it has grown each year.

Against such a background, ultraviolet-curing resin has found uses in inks, paints, adhesives, sealants, sealing agents, printing plates, and various resist materials, expanding its commercial use in a wide range of industries.

As the industry develops, however, industrial materials also develop rapidly and many new industrial materials appear. Among such materials are those that are vulnerable to ultraviolet rays or are hard to penetrate it. The material technology for optical materials in particular, including special prisms and plastic lenses, advances year after year. Materials of these types do not pose a significant problem for ordinary processing techniques; however, in the field of adhesive processing using ultraviolet-curing resin, utilizing this curing technique for such materials is expected to be difficult. In the bonding of these optical materials, ultraviolet-curing resin is inferior to the adhesives of a generation ago. Hence, curing techniques based on active energy beams other than ultraviolet rays have been attracting attention. The key factor in this trend is a curing technique based on visible light.

Table 1. Classification of Electromagnetic Waves

γ-ray	X-ray	Ultraviolet rays		Visible light	Infrared ray
		Far ultraviolet rays	Near ultraviolet rays		
$10^{-1}$	100	200	300	400	800 (nm)

## 2. What is visible light?

Next, let's look at visible light. Table 1 shows the classification of electromagnetic waves. These waves include  $\gamma$  and X-rays with short wavelengths, followed by ultraviolet rays, visible light, and infrared ray, in that order. The table shows that visible light has a wavelength of 400 nm to 800 nm, i.e., visible light has a distribution of longer wavelengths than does ultraviolet. Generally, a wider distribution of wavelengths broadens the effective range of the wavelengths necessary for curing, whereas visible light has only low energy, which makes it poorly suited for curing. Table 2 shows the energy levels of electromagnetic waves.

The one that has the highest energy level is the

electronic beam, followed by ultraviolet rays, visible light, and infrared rays, in that order. To allow light to cause a chemical reaction, the energy must be sufficiently high. From this standpoint, the electronic beam is the best light source, but is rarely used in industrial applications today. A comparison of energy levels between ultraviolet rays and visible light shows that that of visible light is approximately 1/2 that of ultraviolet rays, though it is subject to variation depending on the wavelength. Hence, it can be said that ultraviolet rays are useful as an energy source for curing, whereas it is not a very good light source in terms of safety. Moreover, as we will see later in this paper, visible light has advantages that ultraviolet cannot provide.

Table 2. Energy Levels and Frequencies of Electromagnetic Waves

	Energy (kJ/mol)	Frequency (1/s Hz)
Electronic beam	Up to $10^6$	Up to $2 \times 10^{16}$
Ultraviolet rays	300 to 600	$0.75$ to $1.5 \times 10^{15}$
Visible light	150 to 300	$0.40$ to $0.75 \times 10^{15}$
Infrared ray	8 to 60	$0.20$ to $1.50 \times 10^{14}$

### 3. Problems with ultraviolet-curing resin

Ultraviolet-curing resin is widely used in the fields of electric, electronic, automobiles, optics, communications, construction, and the like, due to its one-part, non-solvent, fast-curing configuration. This resin is cured using ultraviolet with a wavelength of 200 nm to 400 nm. As its applications expand, a number of problems with it have attracted attention, one of which is the emergence of materials through which ultraviolet is difficult to penetrate.

So-called "engineering plastics," when used outside, have an ultraviolet-absorbing agent added to prevent deterioration. Table 3 shows the light penetrativity of various materials. The wavelengths at which penetrativity was compared were 365 nm for ultraviolet and 400 nm and 435 nm for visible light. This table indicates that most of the materials collectively referred to as engineering plastics do not penetrate ultraviolet rays (or do absorb it). This makes it difficult to bond such materials by using ultraviolet-curing resin. In practice, however, curing speed is accelerated by increasing the output from the radiator, and therefore the apparent curing time is longer than that of the resin. While alumina used as a filling and soda glass found in ordinary windowpanes generally have low penetrativity, the penetrativity of visible light is higher than that of ultraviolet rays. The special applications of ultraviolet-curing resin include mixture with a filling. When ultraviolet rays are used for curing, however, not much filling can be used due to the short wavelength of irradiated ultraviolet rays.

Table 3. Light Penetrativity of Various Materials

Material	365nm	400nm	435nm
Hard PVC <sup>*1</sup>	0.07%	50%	80%
Soft PVC <sup>*2</sup>	0.3%	44%	77%
ABS <sup>*3</sup>	0.05%	5%	10%
PBT <sup>*4</sup>	0.1%	13%	17%
Polycarbonate <sup>*5</sup>	0.5%	50%	95%
Alumina <sup>*6</sup>	1.5%	5.2%	6.6%
Soda glass <sup>*7</sup>	48%	80%	85%

\*1: Mitsubishi 302 (2 mm)

\*2: Takato Kasei (2 mm)

\*3: Tsutsunaka Tough Ace EAR003 (2 mm)

\*4: Duranex 2002 (2 mm)

\*5: Teijin Panlite PC-111 (2 mm)

\*6: Showa Denko UA-5205 30 wt% cured with Ep-828/DYCY (2 mm)

\*7: Tempax (5 mm)

### 4. Advantages and disadvantages of visible light

A simple comparison of energy levels shows that the energy of visible light is lower than that of ultraviolet rays. The long wavelength, however, has certain advantages. Those of visible light are as follows.

- (1) High light penetrativity
- (2) Safe to the human body
- (3) Inexpensive radiation system

Advantage (1) permits the use of a filling mixed with an adhesive and a resin for semi- to non-transparent materials. The light penetrativity of the resin to be cured itself improves. The penetrativity of ultraviolet rays through a resin is only several millimeters from the surface, whereas visible light penetrates deeper into a material due to its long wavelength. Thus, better thick-film curing can be achieved (Fig. 1).

Advantage (2) is that the health of workers is not impaired. Ultraviolet rays affects the human body. The ultraviolet irradiator, therefore, must be designed in consideration of the safety of workers.

Advantage (3) will become a disadvantage if a high-pressure mercury lamp or similar irradiation system is used. The introduction of a system of this type is costly. Following its introduction, the running cost and lamp service life will pose problems. In contrast, the visible-light-curing resin can be cured well with a commercially available halogen lamp, and therefore the total cost will be lower than that of a mercury lamp.

Well, what are the disadvantages compared to ultraviolet rays?

- (1) Lower energy level than ultraviolet
- (2) Poor surface curing of resins

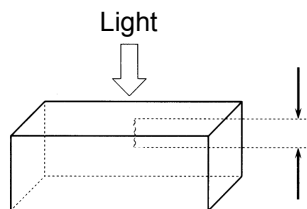
For (1), the energy level of the visible light is approximately 1/2 that of ultraviolet rays, and therefore the curing of visible-light-curing resin is slower than that of ultraviolet-curing resin. For applications that require a high line speed, efforts should be made to improve the performance of the resin or increase the output of the light source.

For (2), the low energy level of the visible-light-curing resin, as in (1), makes it difficult for radicals trapped by oxygen to become an active species again.

With these advantages and disadvantages, the curing energy of visible light has characteristics not found in ultraviolet rays, and thus visible light is worthwhile to study for use as a curing-energy medium.

### Ultraviolet-curing resin

As the entering light is not penetrated through well, only a layer several millimeters from the surface is cured.



### Visible-light-curing resin

As the entering light is penetrated through well, the resin cures to a greater depth.

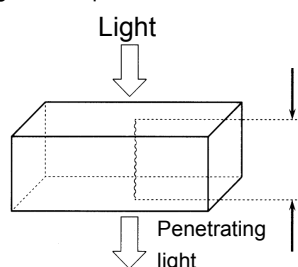


Fig. 1 Light Penetration through a Resin

## 5. Reactive mechanism of visible-light-curing resin

### 5-1. Radical-generating mechanism

The most familiar example of photoreaction with visible light is the photosynthesis of plants. Photosynthesis is a "photoreaction" using sunlight. It is a photo-oxidation-reduction reaction caused by chlorophyll and a reducer. Related technology is widely applied in the photochemical industry. Photo-reactive techniques using visible light range from the silver salt photographs of centuries ago to the high-sensitivity photopolymers of today. The performance of photosensitive resin as a polymer can be controlled using a blend of oligomers and monomers in most cases. The difference from the ultraviolet-curing resin lies in the type of photo-initiator contained. The curing mode is radical polymerization, as in the case of ultraviolet-curing resin. Fig. 2 summarizes the reactive mechanism of radical polymerization. The mechanisms of the generation of radicals can be classified as shown in Fig. 3. The only thing that is required of a technique for initiating curing (polymerization) using visible light is the development of a material that both absorbs visible light and serves as the generating source for curable (polymerizing) active species.

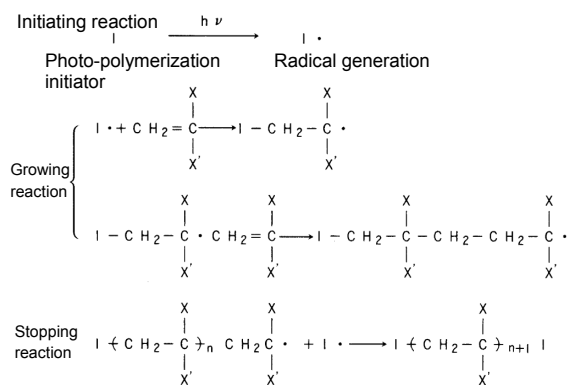


Fig. 2 Radical-Reactive Mechanism

### 5-2. PI-type initiator

The most popular ultraviolet-curing resin uses the PI-type photo-initiator. The reactive mechanism of radical generation is as follows: a single-molecule photo-initiator cleaves and then generates two radicals. Because little light is absorbed near the visible-light range, the visible-light-curing resin does not show an orthodox curing mechanism. Thus, very few visible-light-curing resins use a single-molecule photo-initiator such as the PI-type. Many photo-initiators in use are the two-molecule type, such as the PII-type.

### 5-3. PII-type initiator

The outstanding feature of the PII-type initiator is that radicals are generated mainly as a result of energy or hydrogen migration due to light between two molecules, which differs from the case of the PI type. As mentioned above in this issue, curing with visible light is applied to photopolymers in most cases, and thus many photo-initiators consist of combinations of dyes and radical generators (or hydrogen donors). Visible-light-curing resin, which was developed based on dental-material technology, normally uses  $\alpha$ -diketone derivatives as photo-initiators. The reactive system consists of a photo-initiator ("I" in Fig. 3) and a photo-initiation assist ("R-H" in Fig. 3). "I," excited by the radiation of visible light, removes hydrogen from "R-H," and results in generating radicals. Though hydrogen is thus removed directly, hydrogen transfer may also occur as a result of the generation of an excited compound between "I" and "R-H." The double-molecule type causes not only a single reaction, but also two or more reactions with sub-reactions. Unlike the single-molecule type, the reactive mechanism of the double-molecule type has not yet been revealed.

Shown below are the results of our investigation of the relationship between the photo-initiator and photo-initiation assist carried out by using the PII-type photo-initiator.

For the photo-initiator assist, most chemical compounds can be used, provided that they are hydrogen donors. As can be seen from feedback in the field of dental-material technology, most of such compounds are amine in general. The type, chemical structure, and amount of added amine vary with the type of  $\alpha$ -diketone derivative of the photo-initiator and the added amount of photo-initiator. Fig. 4 shows the effect of added amounts of amine. The diagrams show the relationship between the glass transition point and the added amount of amine. These diagrams indicate that, as the added amount of amine increases, the glass transition point lowers. From this, it can be seen that the photo-initiator assist acts as a curing accelerator, whereas the excessive addition of it may inhibit curing. Moreover, the added amount of amine significantly affects other physical properties of resin. Fig. 5 shows the relationship between the heated percent decrease in the resin after curing, and the added amount of amine. As is clear from the diagram, the excess portion of amine only evaporates during heating.

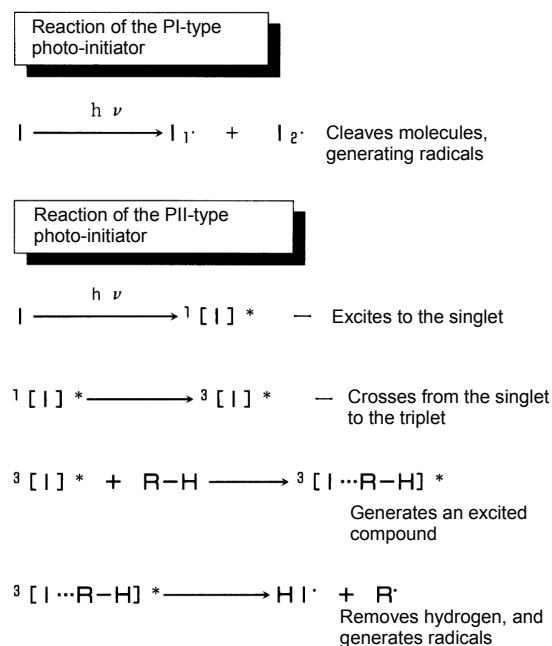


Fig. 3 Classification of Radical-Generation Mechanisms

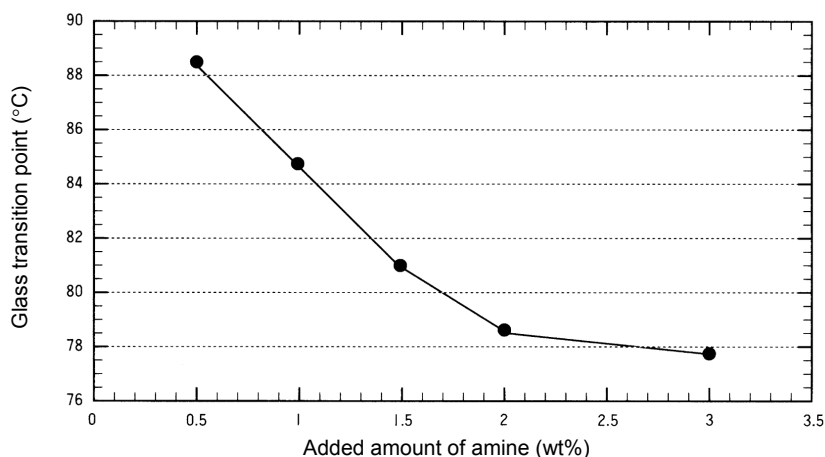


Fig. 4 Relationship between the Added Amount of Amine and the Glass Transition Point

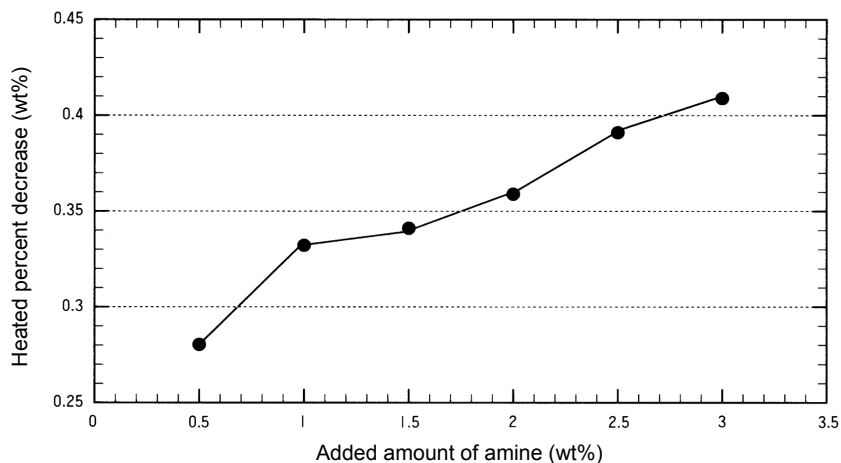


Fig. 5 Relationship between the Added Amount of Amine and the Heated Percent Decrease

## 6. Visible-light lamp

As the absorption wavelengths of photo-polymerization initiators range from 400 nm to 500 nm, any light source can be used for visible-light-curing resin. Though each lamp has its own advantages and disadvantages, the optimal one can be chosen in accordance with the applications. Table 4 lists the advantages and disadvantages of various light sources. Details are shown below.

### (1) Halogen lamp

This is the most commonly used light source, and is outstandingly low in price. As the light source for visible-light-curing resin, dental composite resin has shown proven results. Many irradiators for this application are on the market. This light source is not only inexpensive, but it is also readily available. The drawback is that the lamp cannot be produced in a large size. In addition, there are limitations on increasing the output. Thus, the halogen lamp is more suitable for handy- and spot-type irradiators than for large-area radiation.

### (2) Xenon lamp

The wavelength distribution of a xenon lamp is similar to that of sunlight, and it can produce a high output. Thus, the xenon lamp is considered best suited for industrial irradiators. The majority of the wavelengths are in the range of visible light, and

thus it is hoped that the lamp becomes increasingly used as a radiator in this field.

### (3) Metal halide lamp

Most metal halide lamps have been in use as a light source for ultraviolet-curing resin. With changes in the type and composition of metals sealed in a lamp, the lamp can easily be converted into a visible-light lamp by using current technology. Thus, for metal halide lamps, it is hoped that a radiator with a low price, high output, and long lamp service life will be developed.

### (4) Incandescent lamp

Though this is most inferior in performance as a light source, it is cheap and easy to obtain. These advantages allow this lamp to be included in the listings of light sources, along with the halogen lamp. As the output is low, however, it is difficult to introduce the lamp in industrial use. In addition, the service life is rather short.

### (5) Sunlight

This is a light source that exists in nature, and can therefore be used for adhesion outside. As the amount of irradiance cannot be controlled, the physical properties after curing vary.

Table 4. Comparison of Various Light Sources

Light source	Advantages	Disadvantages
Halogen lamp	Low cost; compact	Short life; intermediate output
Xenon lamp	High output; wavelengths primarily in the range of visible light	High cost
Metal halide lamp	Compact; long service life	High cost
Incandescent lamp	Low cost; compact	Short life; low output
Sunlight	No equipment required	Control impossible

## 7. Applying visible-light-curing resin

Visible-light-curing resin has characteristics that are not found in ultraviolet-curing resin, and such characteristics can be applied to various purposes of use. As described earlier in this issue, in addition to bonding and sealing materials that do not penetrate ultraviolet, visible-light-curing resin can be used as a resin for the pouring mold, sealing, and coating. Listed below are the major possible applications and applied fields.

### (1) Optical communications

Bonding couplers, optical splitter, optical couplers, light-emitting devices, photo-detectors, and the like for optical communications.

### (2) Optical pickups

Precision-bonding optical lenses, mirrors, prisms, photodiodes, and the like for optics.

### (3) Medical

Fastening and bonding injector needles in place.

### (4) Decoration

Bonding ultraviolet-cut glass, colored glass, and glass with a large surface area for interior decoration.

The curing system can use not only a generic irradiation lamp, but also a laser as the light source. Recently, 3D modeling by using a CAD-controlled laser beam has been attracting a great deal of attention. In the future, resins that cure by using a visible-light laser such as a relatively inexpensive semiconductor laser may be developed.

## 8. Problems with visible-light-curing resin

Though visible-light-curing resin is a new type of light-curing resin that compensates for the drawbacks of ultraviolet-curing resin, it poses a number of problems involving the use of visible light.

### (1) Need for shielding

As visible-light-curing resin cures under the radiation of visible light (including sunlight), it must be shielded from light as much as possible during handling. While curing using interior lights is slow, exposure to light for an prolonged period significantly reduces the storage stability of the resin.

### (2) Skin-irritation

As the main component of visible-light-curing resin is a special acrylic resin, it is lightly to intermediately skin-irritation, as in the case of generic ultraviolet-curing resin. While working, workers should wear protective gloves.

### (3) Low reactivity

As PII-type photo-initiator is used, polymerization is inhibited by oxygen during the generation of radicals, causing an inductive phase during the reaction. Currently, this problem is generally solved with the aid of an irradiator, but the inferior surface curing should be improved.

### (4) Resin coloration

As photo-initiator excited by visible light has an absorbing range in the visible-light range (a range of wavelengths that can be sensed by the human eye), the resin is colored in advance (some resins are colorless). In spite of this coloring, however, some resins discolor due to the conjugated bond within the molecule being cut after the photo-initiator generates radicals.

## Conclusion

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Thus far, I have described technical matters involving visible-light-curing resin. Compared with ultraviolet-curing resin, visible-light-curing resin has a short history and few results in the industry. However, this is simply due to the technology for visible-light-curing resin having not yet been as well established as that for ultraviolet-curing resin, despite the fact that the former is an extension of the latter.

With the development of the industry, the advantages of light-curing resin will be improved in terms of both productivity and ease of handling. Under such circumstances, I believe that we will be able to make visible-light-curing resin available to you in the not-so-distant future.

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