● UV-curable adhesive that also cures in shadowed area

Kazuki Oofusa

Key Word : Shadow cure, UV-curable adhesive

1. Introduction

Since UV-curable adhesives are solvent-free and can be cured at room temperature in a short time, they have characteristics such as lower environmental impact and higher productivity compared to other adhesives.

In recent years, market needs for environmentally friendly adhesives have been increasing, and the market and application areas for UV-curable adhesives have been steadily expanding. Furthermore, with the recent spread of compact and power-saving UV-LEDs, UV-curable adhesives are now available at DIY stores, etc., and are becoming more familiar to general consumers.

We have been developing and marketing UV-curable adhesives for many years, and these products are used in a wide range of applications, including industrial materials such as paper, film, and molded plastic products, and high value-added products such as medical components, electronic materials, and optical components (Fig. 1).

This article introduces our new UV-curable adhesives with "shadow curability," which can cure even in shadowed areas that are not directly exposed to light during UV irradiation.

Figure 1: Application examples of UV-curable adhesives

2. Shadow curability

UV-curable adhesives tend to have adhesion defects or insulation defects due to insufficient curing in shadowed areas that are not directly exposed to UV light, and this has become a hindrance to the development of applications. Therefore, there is a strong need for UV-curable adhesives with shadow curability, in which even the shadowed areas can be cured. Fig. 2 shows a conceptual diagram of shadow curability.

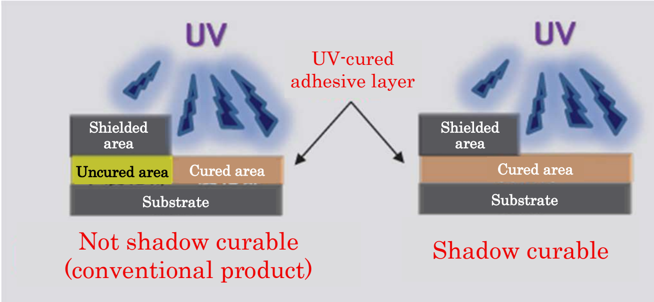

Figure 2: Conceptual diagram of shadow curability

As methods of imparting shadow curability to UV-curable adhesives, combination of light curing and moisture curing (isocyanate or silane compounds)[1),2)], combination of thermal radical polymerization by thermal decomposition of peroxides and photo-radical polymerization[3)], photocationic polymerization of epoxy[4)], and systems using redox decomposition of peroxides[5)] have been put to practical application (Table 1). These systems are used in a variety of applications, such as securing cameras, assembling speakers, and bonding steel plates together.

However, each of these methods requires a long time to fully cure, and the advantage of short curing time, which is a feature of UV-curable adhesives, is currently compromised. There are also various other problems such as poor workability, and the market is looking for a technology that enables shadow curing only by UV irradiation.

New Products Research Laboratory, Nagoya Criatio R&D Center, Toagosei Co., Ltd.

Source of curing	Chemical reactions used for shadow curing	Issues
Light + moisture	• Isocyanate crosslinking • Silane crosslinking	• Slow curing (several hours to several days) • Deterioration in workability (large effect of humidity)
Light + heat	• Radical polymerization by thermal decomposition of peroxides	• Slow curing, heating requirement • Two-component system is required for low temperature curing
	• Cationic polymerization of epoxy	• Slow curing, heating requirement • Possibility of metal corrosion due to strong acid
Light + catalyst	• Redox decomposition of peroxides	• Two-component system is required (primer, A/B liquid) • Deterioration of workability (two-component system, gelation in equipment, etc.)

Table 1: Method of imparting shadow curing

As a result of examining the construction of a new UV-curable system to solve the above issues, we have developed a technology that enables curing of the area around the irradiated area, including shadowed areas, using only a short UV exposure, without combining heat or moisture curing. Fig. 3 shows an image of this curing system.

This curing system mainly employs radical polymerization of special acrylates and does not use cationic or anionic polymerization. There is therefore no curing inhibition by moisture or acidic/basic components, which is a problem in cationic and anionic polymerization.

Since it also does not contain thermal radical initiators such as peroxides or azo compounds, it requires no primer or adoption of a two-component system, and rapid thickening or gelation due to contamination with metal content is unlikely to occur.

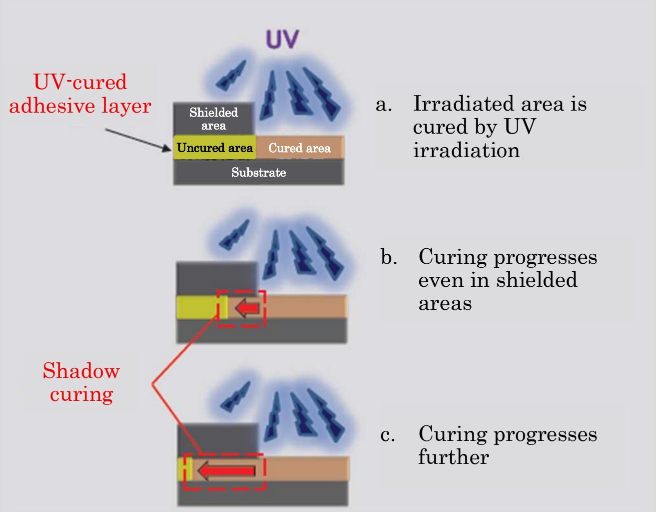

Figure 3: Image of the new shadow curing system

While the shadow curability expressed by this curing system varies depending on the type of adherend, film thickness of the adhesive, the amount of light exposure, etc., shadow curing of 5 to 20 mm is possible even in the shadowed area when the substrate is black PET, the adhesive film thickness is 0.5 mm, and a UV-LED light source is used at 15 J/cm^2 (illuminance: 0.5 W/cm^2). Fig. 4 shows the actual appearance of the shadow-cured product.

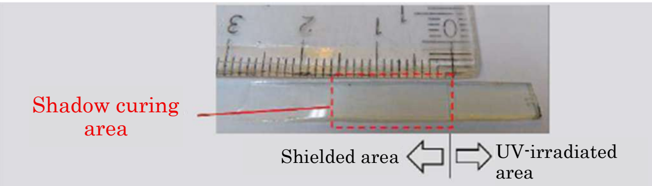

Figure 4: Appearance after shadow curing

3. ARONIX® UVX-8032 and 8037

3.1 Main physical properties

ARONIX UVX-8032 and 8037 are UV-curable adhesives in our development pipeline, imparted with shadow curability through our proprietary technology described above. Table 2 shows the main physical properties.

Table 2: Main physical properties of ARONIX UVX-8032 and 8037

Evaluation item		UVX-8032	UVX-8037
Viscosity (25ºC) mPa·s		660-1,500	3,800-8,400
Shadow curability (mm) *1		13	15
Storage modulus E' (MPa)*2	25ºC	32	133
	85ºC	18	18
Glass-transition temperature (°C) *3		16	27
Elongation (%) *4		53	60
Shore hardness		D54	D69
Shear strength (MPa) *5	Glass/glass	0.84	1.44
	PMMA/PMMA	0.62	0..94
	SUS/aluminum	0.70	1.37
Refractive index after curing n_D^{25}		1.52	1.51
Curing shrinkage (%) *6		5.3	4.5
Water absorption (%) *7		1.4	1.2

*1: UV-LED, 15 J/cm^2 (0.5 W/cm^2), film thickness 0.5 mm, black PET
*2: Dynamic viscoelasticity (tensile mode), frequency 1 Hz
*3: Dynamic viscoelasticity (tensile mode), frequency 1 Hz, tanδ maximum temperature
*4: Tensile speed 10 mm/min
*5: Tensile speed 10 mm/min
*6: Calculated based on the specific gravity before and after curing
*7: Immersion at 25°C x 24 h

A major difference between UVX-8032 and 8037 is viscosity. Since the appropriate viscosity grade must be selected based on the application method and substrate type, these products are offered in multiple grades.

UVX-8032 and 8037 have a tanδ maximum temperature (an indicator for glass transition temperature) near room temperature (16°C and 27°C, respectively), and their storage modulus at 25°C (32 MPa and 133 MPa, respectively) is below the typical glassy region, exhibiting elastomer-like hardness. The elongation is 53% and 60%, respectively, and they are flexible enough to resist damage under deformation such as being bent.

The shadow curability of UVX-8032 and 8037 is 13 mm and 15 mm, respectively (adherend: black PET, adhesive film thickness: 0.5 mm, UV-LED light source: 15 J/cm^2 (illuminance: 0.5 W/cm^2)). Below, we present an adhesion example utilizing this shadow curability.

3.2 Application example: bonding between wire and protective tubing

Wires such as electric cables and optical fibers are sometimes covered with plastic tubing for protection. However, when the tubing is colored and UV-impermeable, normal UV-curable adhesives could not cure the interior, sometimes causing poor adhesion.

We therefore conducted a study using UVX-8032 for bonding between a wire and a colored tube (Fig. 5). We used our conventional UV-curable adhesive as the comparison product.

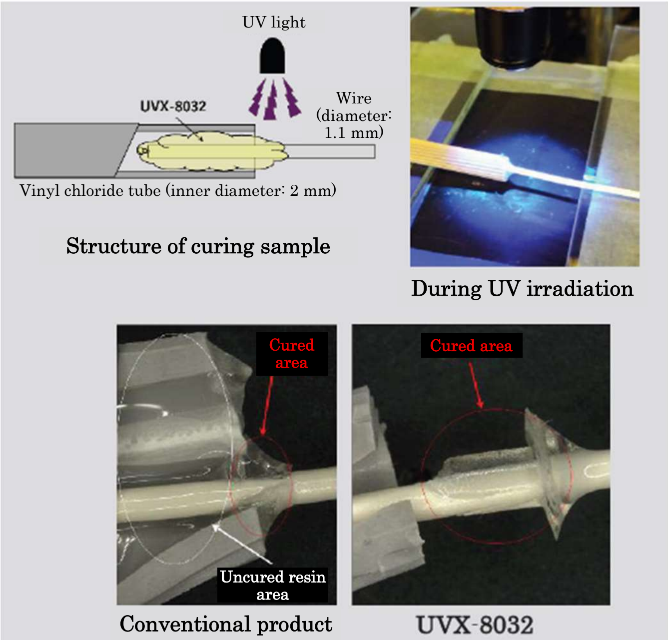

Fig. 5: Securing the wire to the protective tube (irradiation conditions: 365 nm UV-LED, illuminance 0.5 W/cm^2, irradiation time = 30 s)

Observation of the UV-cured and bonded samples after dismantling them revealed that the part inside the tube did not cure at all with our conventional UV-curable adhesive and remained in liquid form, whereas UVX-8032 cured to the inside of the tube and the wire was firmly fixed.

In the past, when attempting to cure such components to the inside of the tube with UV-curable adhesives, it was necessary to use UV-curable adhesives such as those listed in Table 1. However, there were disadvantages such as the time required for the shadowed area to cure and the need for a two-component system. UVX-8032 is ideal for this application because it can be applied as a one-component system without compromising the fast curing properties of UV-curable adhesives.

4. ARONIX® UVX-8092 and 8093

In response to requests for even higher shear strength than ARONIX UVX-8032 and 8037, we developed the new ARONIX UVX-8092 and 8093 (Table 3).

Table 3: Main physical properties of ARONIX UVX-8092 and 8093

Evaluation item		UVX-8092	UVX-8093
Viscosity (25ºC) mPa·s		8,000-12,000	8,000-12,000
Shadow curability (mm) *1		14	9
Storage modulus E' (MPa)*2	25ºC	1,125	928
	85ºC	5	9
Glass-transition temperature (°C) *3		52	97
Elongation (%) *4		75	320
Shear strength (MPa) *5	Glass/glass	2.63	3.93
	PMMA/PMMA	0.93	0.97
	PC/PC	2.39	2.63
	SUS/aluminum	3.31	5.38

*1: UV-LED, 15 J/cm^2 (0.5 W/cm^2), film thickness 0.5 mm, black PET
*2: Dynamic viscoelasticity (tensile mode), frequency 1 Hz
*3: Dynamic viscoelasticity (tensile mode), frequency 1 Hz, tanδ maximum temperature
*4: Tensile speed 10 mm/min
*5: Tensile speed 10 mm/min

UVX-8092 and 8093 are grades with improved shear strength on various substrates, achieved through composition adjustments such as increasing polar groups and tuning the molecular weight between crosslinks. Compared to UVX-8032 and 8037, the shear strength on inorganic materials such as glass and metal, as well as polycarbonate (PC), is greatly improved.

Since metals are completely opaque to UV, UV-curable adhesives have rarely been applied to bond metals together. In the future, we plan to develop applications in such unexplored fields.

5. Conclusion

Although UV-curable adhesives are expected to continue to expand in application and market in the future, due to their advantages such as low environmental impact and high productivity, they have a major disadvantage in that they do not cure in shadowed areas. Conventional technologies to impart shadow curability had problems such as long curing time and deteriorated workability due to the use of two-component systems, etc., and a technology that can express shadow curability only by UV irradiation has been desired.

We have developed a new shadow curing system that uses only photo-radical polymerization and successfully solved the conventional problems. As UV-curable adhesives applying this curing system, we have developed ARONIX UVX-8032 and 8037, as well as ARONIX UVX-8092 and 8093, which have improved shear strength.

We often receive high praise from our developer customers for the fact that our UV-curable adhesives maintain the inherent advantages of adhesion on demand despite their shadow curing properties, and we feel that there is a high potential need for these adhesives. We plan to continue to develop new applications for UV-curable adhesives, which were not possible with conventional UV-curable adhesives.

Reference

1) ThreeBond Technical News, vol. 44, p. 4-5 (1995)

2) For example, Patent No. 6510788.

3) K. Yamaguchi, Journal of the Adhesion Society of Japan, **Vol. 42**, No. 11, p. 18-27 (2006).

4) https://www.epotek.com/wp-content/uploads/2021/01/EPO-TEK%C2%AE-Specialty-UV-Curing-Adhesives.pdf.

5) ThreeBond Technical News, vol. 44, p. 9 (1995).