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Rapid curing system with near-infrared laser with CLS system.

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Introduction

Epoxy resins are a generic term for thermosetting resins with two or more epoxy groups per molecule, which exhibit excellent adhesive properties, mechanical strength, electrical insulation, heat resistance, chemical resistance, water resistance and low shrinkage. Taking advantage of these characteristics, they are applied in a wide range of fields such as coatings, electrical and electronics materials and adhesives.

On the other hand, in recent years, there are trends towards higher density, further micro-scaling and more diversification in the fields related to information and electronics application. In the field of renewable energy such as photovoltaic and wind power generation, and of environmental / energy-saving such as SiC power semiconductors, high-power LEDs and electric vehicles, further strengthening and durability of components are required. In particular, remarkable progress has been made in the development of information and electronic equipment for in-vehicle applications.

In these new fields, there is an abundance of demand for materials that can be adapted to different materials, environments, and production processes. In response to these demands, we are focusing on product development that takes advantage of our strengths. In terms of technology, the research and development is focused on improving the molecular structure of resin materials and proposing new applications for bring out various physical properties. And in terms of fields, research and development is being conducted with "adhesion," the most outstanding property of epoxy resins, as the keyword.

Adhesive technology trends

For example, in the automobile industry, technological innovations are being promoted in order to improve fuel efficiency by reducing the weight of the vehicle and to electrify the powertrain from the perspective of preventing global warming, as well as by utilising electronic devices in the vehicle to ensure safe and accident-free driving and to improve the interior space. For vehicle weight reduction, the use of lighter and stronger aluminum and magnesium alloys and CFRP, which is a composite material of carbon fiber and resin, is being considered. Therefore, joining technology for these different materials is being studied as an alternative to welding. In addition, in order to improve the reliability of electronic equipment, new packaging materials that can provide sufficient durability for automobile durability tests are being developed.

For adhesives that meet these market requirements, epoxy resins with excellent shear bond strength, creep behavior, heat resistance and chemical resistance are expected to exhibit suitable properties [1,2]. In addition to basic performance requirements, there are also high productivity requirements in the manufacturing field, such as low-temperature curing and short-time curing. These requirements are aimed not only at productivity (time) = cost, but also at reducing the environmental load by saving energy through the reduction of the heating process.

1. New curing systems for epoxy resins

In general, curing of epoxy resins by amines, which are typical thermosetting resins, takes time. This is due to the reaction mechanism and reaction rate between the epoxide and curing agent [3]. Epoxy resins and curing agents are often used as one-component types for curing at high temperature and as two-component types mixed just before use for curing at low/ambient temperature, mainly from the viewpoint of storage stability. In order to achieve rapid curing with one -component type, the control of the stability control is most important technology.

We call the epoxy resin adhesives used in our laser ultra-rapid curing system the "CLS system" (Curing system of Latent hardener and Specialty epoxy resin). The CLS system enables thermoset ultra-rapid curing adhesives using a new compounding technology that combines original epoxy resins and latent hardeners with a highly reactive cyanate ester resins. These formulations provide suitable stability for one-component types and rapid-cure properties can be cured by near-infrared laser to make the curing reaction even faster.

2. Near infrared laser curing system

We have proposed a new thermal curing system that takes advantage of various excellent characteristics of the CLS system, which is composed of epoxy resin, cyanate ester resin, and latent hardener, such as ultra- fast curing, high heat resistance, and high adhesion. In particular, the near-infrared laser curing system makes maximum use of the ultra-fast curing property and enables thermal curing in a short time and with low energy consumption [4]. The near-infrared laser has recently come to be utilized to its fullest extent due to the low cost of semiconductor lasers, and is used in many fields, mainly in resin welding and bonding. In laser welding, thermoplastic resin such as PBT (Poly Butylene Terephthalate) is used as the welding material, the material on the laser irradiated side is light transmissive grade and the opposite side is light absorbing grade, and the welding interface is pressurized under load and adhered to the welding surface. The welding interface is heated to above the melting point of the material under load and pressurized to adhere to the welding interface. In such a system, the materials are limited to the same type of thermoplastic resin that easily melts, and the processing accuracy of the bonding interface is required.

At the same time, in the joining field, there is a growing demand for joining technology for dissimilar materials. For joining dissimilar materials, intermediate materials play a major role, and various developments have been made [5]. In order to meet these requirements, we have developed an adhesive system that can be cured by near-infrared lasers.

Near-infrared laser heating can heat materials instantaneously. To take advantage of this and make the process more productive, it is necessary to cure the adhesive in a shorter time. On the other hand, with conventional epoxy adhesives, although the curing reaction starts upon heating, a long period of heating (=laser irradiation) is required to obtain sufficient performance. Therefore, even when general thermosetting adhesives are heated with a laser, a long period of laser irradiation is required to complete the curing process. With long time near-infrared laser irradiation, the advantage of short curing times is lost. Furthermore, due to thermal damage around the irradiated area, the advantage of using the near-infrared laser is lost. Therefore, we designed a special adhesive that applies the ultra-fast curing property of the CLS system to shorten the curing process using the near-infrared laser (Figure 1).

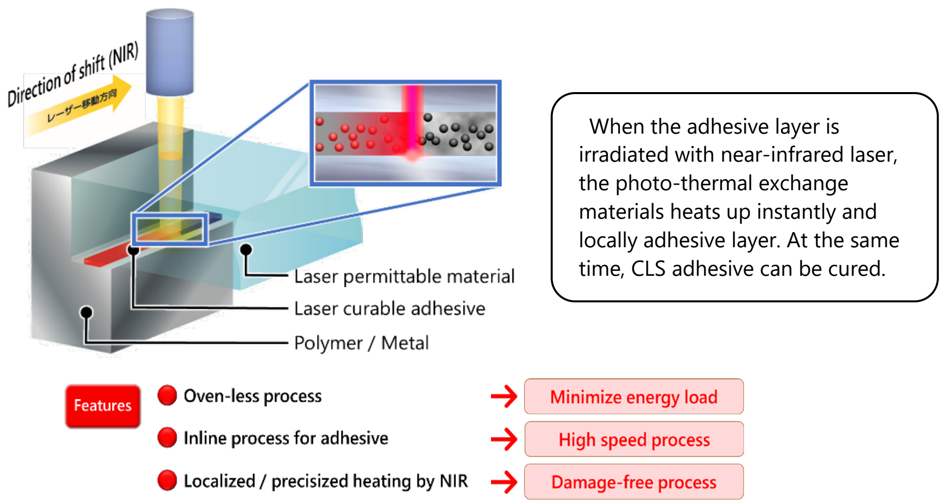


Figure 1 Laser Adhesive System.

The features of this system are "low energy load", "high-speed processing" and "minimization of thermal damage" (Figure 12). Compared to the conventional heating method using a furnace, the heating method using a near-infrared laser beam requires power only when necessary, thus reducing energy consumption. In addition, the time required in the curing oven, which was about one hour in the past, is no longer necessary because the adhesive can be cured by laser irradiation in a few seconds. Furthermore, since only the irradiated area of the near-infrared laser can be efficiently heated, the entire part can be cured without heating, thereby minimizing thermal damage to the part.

We are currently developing the practical application of the near-infrared laser adhesive system. In addition to adhesion of electronic components and protection of terminals, we are proposing the possibility of application to assembly such as casing and hole filling (Figure 2). In addition to ADEKA REMYLOP CLS-1132 (described below), we are also developing other adhesives for use in this system by adjusting the curing start temperature and various properties to suit the application. In the curing process, we have proposed various innovations in the irradiation of near-infrared laser light. For example, in addition to bonding using near-infrared laser- transparent materials such as plastic and glass, direct irradiation to adhesives and/or heating of the substrate surface by irradiation to the base material are proposed as heating methods. In addition to spot irradiation, the use of a near-infrared laser with a micro-diameter of several hundred μm enables rearrangement irradiation using diffractive optical elements and remote high-speed irradiation using galvanometer lenses, which are proposed as new heating methods.

The important points in realizing a laser curing system are as follows [6].

(1) Adhesives for laser curing systems
(2) Laser irradiation process

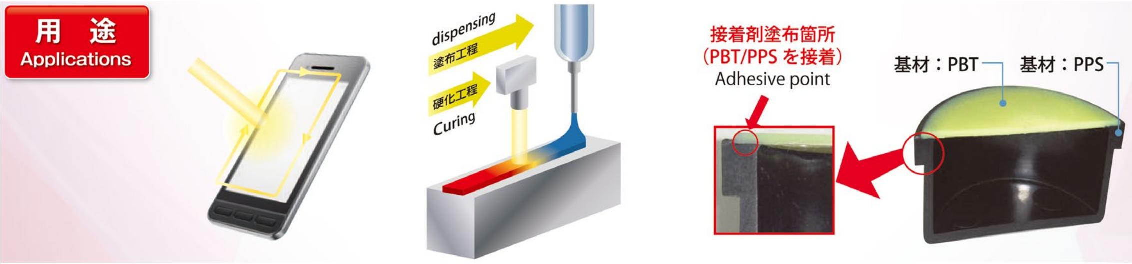


Figure 2 Laser gluing system application examples.

The fast curing adhesive process using a laser curing system not only enables reduced time for the adhesive process, but also offers new possibilities for the adhesive process itself (Figure 3). For example, the in-line process using laser/short-time curing enables shorter production times, a smaller facility area and a higher level of quality control compared to the conventional thermal curing process using batch-type ovens. In addition, as local heating is applied only to the necessary areas and no standby heating power is required, as in conventional ovens, a significant reduction in energy consumption is possible.

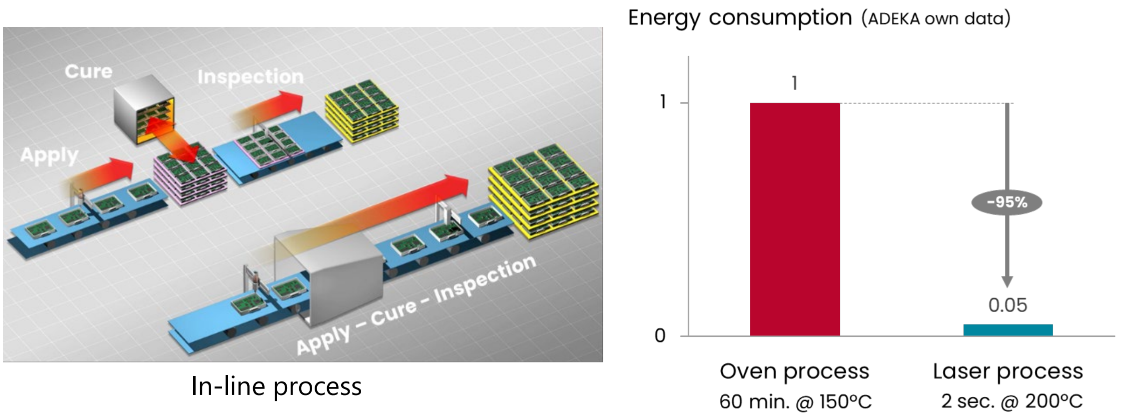


Figure 3 Benefits of laser and/or fast curing system

2.1 Adhesives for Near-Infrared Laser Curing System

In the development of fast curing adhesives by laser irradiation, several issues had to be overcome. The largest challenge of these was the solution to the internal shrinkage stresses associated with the cross-linking reaction that occurs instantly in the adhesive during short-time curing.

Internal shrinkage stress occurs when the distance between monomer molecules shrinks due to the bonds formed by the cross-linking reaction. If this internal shrinkage stress remains inside the adhesive or at the adhesive interface, it can lead to material cracking and a loss of interface adhesive strength. For excellent adhesive properties, it is important to release the internal shrinkage stresses generated by the curing reaction.

Generally, a flexible component such as rubber filler is added to add toughness, but this does not provide good relaxation of stress that occurs in a few seconds, as is the case with laser curing systems, because of the long time required for stress relaxation. To solve this problem, we thoroughly reviewed the chemical structure of the adhesive components. As a result, we had succeeded in instantaneously relaxing the stress generated by instantaneous curing by adding a stress relaxation function to the chemical structure of the adhesive's curing component itself.

This paper introduces the adhesives that have achieved physical properties suitable for various joints for the practical application of laser curing systems. Typical properties of ADEKA REMYLOP CLS-1132, the standard, are shown in Table 1. The cured material has a linear expansion coefficient of 25ppm (<Tg), which is close to that of various engineering plastics and solders, contributing to durability. In terms of adhesion, excellent adhesion can be obtained specially to engineering plastic substrates such as PBT and PPS, which have been considered difficult to bond (Figure 4). In addition, a lineup of adhesives with various properties is currently available for various applications, such as bonding materials with large differences in linear expansion coefficients and bonding brittle materials such as glass (Table 1).

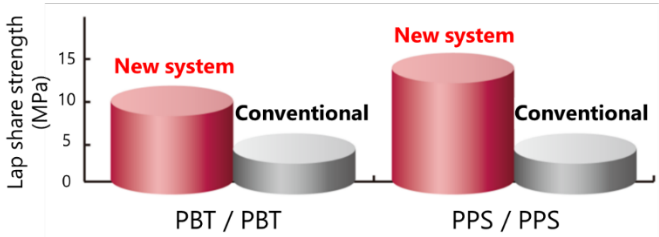


Figure 4 ADEKA REMYLOP CLS-1132: Adhesion test results.

Table 1 Typical properties of adhesives for laser adhesive systems

Grade	CLS-1132	High Tg & Low CTE	Low elasticity	Ultra-low modulus
Viscosity / 25 °C Pa･s / 20rpm	30	30	20	7
Filler Content wt%	55	70	–	–
Halogen free	Possible	Possible	Possible	Possible
Storage modulus (<Tg) GPa	6	14	1	0.1
Glass transition temperature (DMA) °C	120	140	50	30
Coefficient of linear expansion (<Tg) ppm	25	17	63	75

2.2 Curing by laser irradiation

In the laser irradiation curing process, the light-thermal conversion component of the adhesive rapidly heats the adhesive layer by near-infrared laser irradiation. When the heating temperature rises to the reaction-active temperature of the adhesive, the adhesive layer is heated and cured together with the curing reaction heat of the adhesive itself.

If the laser irradiation energy is not sufficient, the material cannot reach the reaction-active temperature and the curing reaction does not proceed. On the other hand, if the laser irradiation energy is too strong, the material becomes overheated, resulting in partial thermal decomposition of the material and failure to achieve the desired physical properties. Due to this points, the correct parameter setup is important for and homogenous curing result. For laser adhesive systems utilizing the CLS system, the following points are used as the standard conditions for laser curing.

a) Laser shape: Top-hat laser 3 to 15 W/4 φ
b) Energy required for curing: 0.24 W/mm2 × 3 to 10 sec.

These conditions are examples of the energy required for curing adhesives, so various adjustments will be necessary when applying the laser to actual parts. Furthermore, the laser irradiation equipment is not limited to mechanical irradiation position adjustment using an X-Y stage, robot arm, etc., as used in laser soldering, etc., but also includes irradiation using galvanometer lenses, which are often used in laser marking, etc., and various jigs introduced in laser resin welding, etc. Various jigs can also be applied, and it is important to select the equipment that best suits the purpose.

In combination with a system that can measure the temperature of the irradiated area simultaneously with laser irradiation, it would be possible to track the irradiation profile and control the bonding quality with high accuracy.

2.3 Bonding and curing methods

As a general joining method, an adhesive is applied between the adherends, the adherends are irradiated with a laser from the near-infrared laser-transparent side, and the adhesive layer is cured. It is also possible to cure the adhesive by direct laser irradiation of the adhesive, rather than by laser irradiation through a laser-transparent material. This laser adhesive system has the following features: it can be applied to joining dissimilar materials, which is difficult with conventional laser welding; it can be applied to joining materials that do not thermally melt; and it does not require precised surface treatment or pressurized adhesion of the joining interface.

It is also possible to cure the adhesive by direct laser irradiation of the adhesive, rather than by laser irradiation through a laser-transparent material. By optimizing the laser irradiation conditions, direct irradiation to the adhesive can be performed, enabling a wide range of applications such as temporary fixing where only the adhesive fillet is cured and processes where coating and curing are performed at the same time.

Furthermore, by applying the curing process by direct irradiation, it is also possible to propose bonding by curing in the depth direction. As an example, Figure 5 shows depth curing of an adhesive by laser irradiation. Although a thickness of several tens of micrometers is sufficient for the adhesive to function as an adhesive, it can be cured to a depth of 5 mm or more by continuous laser irradiation. This application of the new adhesive shows the possibility of bonding.

For example, by using a laser adhesive system instead of screws, not only the number of screw parts can be reduced, but it is also possible to bond shapes that were not possible with conventional materials, such as an octopus shape for more secure bonding.

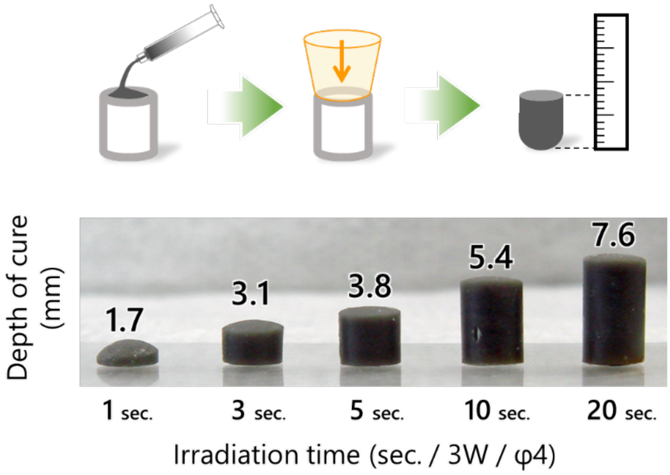


Figure 5 Results of deep curing test by laser irradiation.

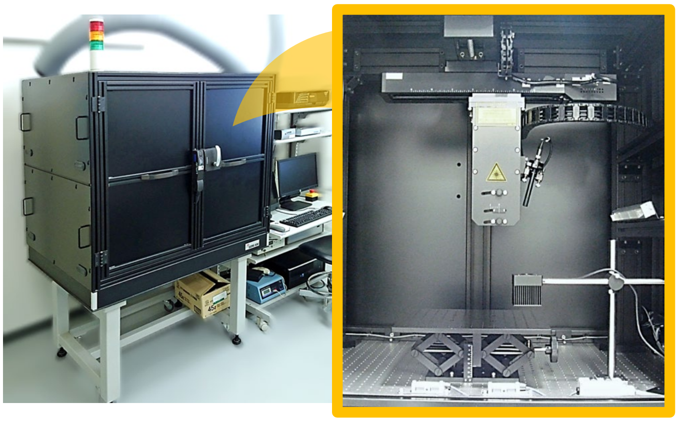
2.4 Approaches to Practical Application

ADEKA has opened an in-house open laboratory for the practical application of laser adhesive systems. The lab is equipped with various laser irradiation devices and a range of evaluation and analysis equipment, enabling curing tests to be carried out on test substrates and actual components.

An example of the experimental apparatus for the near-infrared laser adhesion system is shown below (Figure 6). This apparatus is equipped with a LED laser irradiator capable of irradiating lasers of 3 to 75 W/φ4, a camera for observing the irradiated area, and thermography for measuring the amount of heat, as equipment for examining the laser adhesive system. In addition, the equipment is equipped with interlocks and other devices to provide a safe working environment for handling near-infrared lasers. The irradiation lens installed in the equipment has a work distance of 200 mm to the focusing area, and all of the irradiation areas on the large 200 mm × 200 mm stage are equipped with arms that can move the irradiation areas, making it possible to perform laser irradiation tests using parts of various shapes. Furthermore, space is secured to install various devices, making it possible to conduct various evaluations of laser curing behavior at the same time.

The experimental equipment area is also equipped with evaluation testing equipment that is important when conducting experiments. These include surface treatment equipment for adherends such as UV treatment and plasma treatment for pretreatment processes, automatic dispensers and jet dispensers for adhesive application processes, thermal analyzers for curing evaluation, various thermal analyzers for evaluation after adhesive curing, adhesive strength measurement equipment such as die bond testers, and other equipment for post- curing and post-adhesive evaluation. In addition, we are equipped with various observation microscopes to observe the state of the adhesive after curing and after adhesive strength evaluation.

We have prepared an environment that allows us to carry out everything from pretreatment and curing to evaluation and examination, and we are verifying the practical application of the laser adhesive system.



Laser irradiation conditions	
Wavelength	940 nm
Diameter	φ4 mm
Laser power	3 to 75 W
Scanning speed	1 to 10 mm/sec.

Figure 6 Example of experimental setup for laser adhesive system.

Conclusion

As an example of application of the CLS system, which has a new and unconventional curing behavior, we have succeeded in establishing a rapid curing system using a near-infrared laser. We expect that this laser curing system, a curing technology that reduces the energy required for curing, will contribute to manufacturing as a curing process with overwhelmingly low CO_2 emissions. In addition, with the increasing demand for quality-critical manufacturing, it will be possible to apply the process as an adhesive curing process that enables new quality control different from the conventional one.

We expect that various joining technologies utilizing the CLS system will create new value and contribute to the development of society.

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