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New Light-Curing Instant Adhesives (ThreeBond 1771E, 1773E, and 1776E)

Introduction

As the name suggests, instant adhesives are bonding agents that instantly fix adherends of mutual bonding objects in several tens of seconds to several seconds. Properties such as quick curing, versatility, and ease of use have led to widespread use in home and industry. In recent years, deflation has lowered product prices and exacerbated price competition in many product areas. Such market conditions increase demands for cost reduction while maintaining product quality and functions with enhancing efficiency and streamlining production line. The instant bonding provided by instant adhesives is being recognized once again as a way to reduce labor requirements and improve production speed. Light-curing technologies have advanced rapidly, too, with emerging applications in electronics and other fields. Light-curing adhesives offer ease of use (requiring only irradiation to cure), versatility, and selective curing properties.

This issue introduces new light-curing instant adhesives that combine the advantages of the two types of adhesives: the instant adhesion of instant adhesives and the ease of use of light-curing adhesives.

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1-1. Curing mechanism

The main component of instant adhesives is 2-cyanoacrylic acid ester. The molecule contains strong electrophilic groups such as cyano and carbonyl groups that result in nonuniform molecular electron density distributions, with sites of higher and lower electron density. Basic compounds such as water or amine readily attack sites of low electron density as nucleophiles, with anion polymerization progressing as shown in Figure 1. The instant bonding of instant adhesives results from this extremely sensitive anion polymerization.

The sensitive anion polymerization dominates the curing mechanism of instant adhesives, therefore, radical polymerization with heat or light is small and almost negligible. Thus, trace amounts of acidic substances are added to these adhesives to improve preservation stability. This means that when bonding mutual adherends, water adsorbed to the surfaces of the adherends neutralizes the acidic material. Curing begins when the entire adhesive comes to alkaline region. Radical polymerization inhibitors are generally added as well to prevent gradual radical polymerization in preservation, although such reactions tend to be slow.

1-2. Advantages and disadvantages of instant adhesives

Table 1 summarizes the characteristics of instant adhesives.

The quick curing property of instant adhesives alone tends to attract attention. However, instant adhesives also happen to create powerful bonds on virtually any material. This versatility is a powerful advantage, and therefore, instant adhesives are used broadly in homes and industries and for medical services.

On the other hand, it is a fact that instant adhesives have disadvantages, as listed in Table 1. Thus, bleaching effect discourages applications for which appearance is important. Since cured instant adhesive tends to be hard and brittle, bonded areas have low impact, peeling, and thermal shock resistance.

The selection of monomer types and new additives is gradually removing such disadvantages. For example, adding rubber to instant adhesives improves impact resistance and peeling resistance.[1)]

For the bonding of optical materials and ornaments, bleaching effect is probably one of most significant disadvantages of instant adhesive, due to degradation of the appearance and contamination of bonded object materials by the adhesive. The following subsection briefly discusses the principles of bleaching.

Table 1: Advantages and disadvantages of instant adhesives

Advantages	Disadvantages
1. Quick curing at room temperature 2. One-part nonsolvent 3. High bonding strength (Shearing and tension strength) 4. Capable of bonding a wide range of materials 5. Capable of bonding different materials 6. Highly transparent cured objects 7. Small consumption	1. Possible bleaching 2. Inflexible cured objects 3. Low shock resistance 4. Low heat resistance (80°C) 5. Unsuitable for large gaps or filling adhesion 6. Low water resistance 7. Highly adhesive to skin

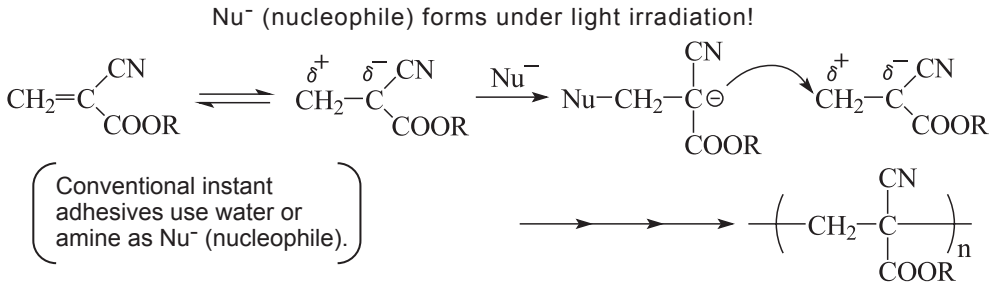
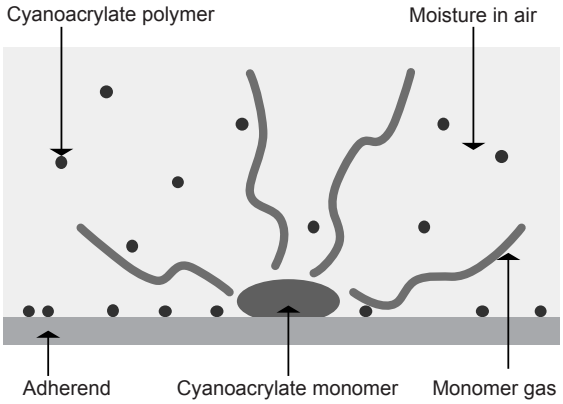
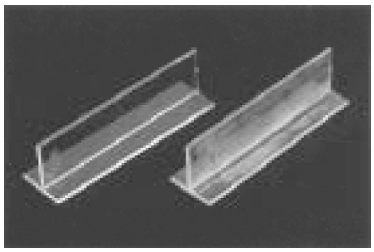


Figure 1: Overview of photo anion polymerization reaction mechanism

1-3. Bleaching effect

Bleaching effect is a phenomenon in which the gas evaporated from the instant adhesive monomer reacts with airborne moisture to form a white powder that adsorbs to adherends, lending a cloudy appearance, as shown in Figure 2. Bleaching effect is particularly disadvantageous for optical materials and ornaments.





Left: Bonding without bleaching
Right: Bonding with bleaching

Figure 2: Principles of bleaching and bonding examples

Given below are several approaches to avoiding bleaching effect.

(1) Method that forces curing with curing accelerator

This method cures the adhesive before the monomer gas evaporates, thereby preventing bleaching effect. However, this method still results in an unattractive adhesive finish. Rapid curing of the adhesive also creates large internal stresses, which tends to reduce bonding strength. Lastly, the accelerator is an organic solvent that poses problems for the working environment. Nevertheless, this method offers remarkably rapid curing. (ThreeBond 1796 series)

(2) Using odor free, low bleaching adhesives

The monomer vapor pressure varies with the type of ester in the 2-cyanoacrylic acid ester. Longer ester structures result in lower vapor pressure, impeding evaporation. Keeping the gas from evaporating generally prevents bleaching effect. However, large ester structures also tend to slow setting times and reduce bonding strength. (ThreeBond 1721C)

(3) Precise coating using a coater

Since bleaching effect is caused mainly by gas vaporizing from excess monomer, using a coater to control the amount of coating would resolve the problem. This method would also increase coating precision, reliability, and speed. However, it fails to address the root cause of bleaching effect. (Coater S-II, SMF-02B)

(4) Using a light-curing instant adhesive

Adding a photo polymerization initiator to an adhesive to generate anion species enables curing of instant adhesives by exposure to light. Since excess adhesive is cured by light, this technique avoids bleaching effect without impairing appearance and decreasing bonding strength. However, light-curing requires an initial investment for various equipment, including the light source irradiator. (ThreeBond 1770 series)

Table 2 summarizes the preceding discussion. In general, light-curing instant adhesives represent the best choice for preventing bleaching effect.

The next and subsequent subsections describe various details of light-curing instant adhesives.

Table 2: Characteristics of methods for preventing bleaching effect

	With accelerator	Low-bleaching type TB1721C	With coater	Light-curing instant adhesives
Anti-bleaching capability	◎	△	△～○	◎
Ease of use	△	◎	◎	○
Curing speed	◎	△～○	○	◎
Bonding strength	△～○	△	◎	◎
Cosmetic aspects	△～○	○	○	◎
Cost effectiveness	○	○	△	△
Environmental safety	△	◎	◎	○

2. Characteristics of light-curing instant adhesives

2-1. Curing mechanism

As shown in Figure 1, a light-curing instant adhesive cures on irradiation by ultraviolet or visible light, thanks to a photo polymerization initiator contained in the adhesive that decomposes and generates anion species (Nu^- (nucleophile)), which then advances anion polymerization.

Conventional light-curing resins include radical polymerization and cation polymerization type resins. Much technological expertise has accumulated for radical polymerization type resins in particular, resulting in a wide range of adhesives based on various resin combinations.

Among these, anion types (including instant adhesives) that use anion species as polymerization initiators remain at the stage of basic research due to their instability and handling difficulty. Only several studies have been reported to date. Kutal and Yamaguchi et al. (University of Georgia, 2)) reported that 2-cyanoacrylic acid esters undergo photo-induced polymerization with the addition of metallocene derivatives such as benzoylferrocene. However, the report addresses only aspects such as: "increased viscosity" and "gelation," with no discussion of preservation stability. In short, the report is not useful in advancing practical adhesive applications.

Our research has shown that radical generators significantly activate the reactivity of the above ferrocene derivative. We have succeeded in developing light-curing instant adhesives with excellent light-curing properties and good preservation stability through concurrent use of adhesives and radical generators.

As shown in Figure 3, light-curing instant adhesives are activated by light irradiation, which cures excess adhesive that laps from the adherends of bonded materials. Based on instant adhesives, the portion between the adherends cures instantly by moisture curing, as do conventional instant adhesives.

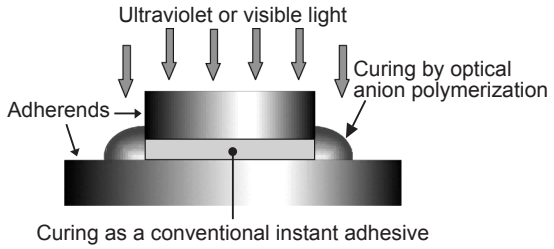


Figure 3: Curing mechanism

2-2. Characteristics of light-curing instant adhesives

Light-curing instant adhesives combine both light curing and moisture curing. This combination reduces bleaching effect and improves surface curing and filling bonding properties, and vastly expands applications.

Table 3 compares the characteristics of light-curing instant adhesives, conventional instant adhesives, and typical light-curing resin.

Table 3: Characteristics of light-curing instant adhesives

	Instant adhesives	Light-curing instant adhesives	Light-curing resins
Bonding of light-blocking materials	○	○	×
Curing of excess portions	×	○	○
Surface curing property	×	○	△
Bleaching	×	○	○
Temporary retaining jigs	Not required	Not required	Required

(1) Good bonding properties for light-blocking materials

Although transparent materials pose no problems, ordinary light-curing resins fail to cure when used to bond light-blocking materials, as shown in Figure 3, since the materials block light. In contrast, light-curing instant adhesives cure instantly via moisture curing in the gaps between adherends. Light-curing instant adhesives are thus associated with lower incidence of curing failures than light-curing resins due to insufficient light irradiation, even for transparent adherends.

(2) Good surface curing of excess adhesives prevents bleaching effect

While conventional instant adhesives cure instantly in the gaps between adherends, excess adhesive remaining as a liquid cures slowly, reacting with airborne moisture. This behavior is due to an imbalance between the acid stabilizer and the alkaline initiator, with too much stabilizer for the amount of moisture. Under these conditions, the monomer gas evaporates readily and promotes bleaching effect. In contrast, light-curing instant adhesives and light-curing resins require only light to cure.

It should be noted that oxygen inhibits the curing of light-curing resins that cure by radical polymerization, resulting in poor surface curing characteristics.

(3) No fixing jig required at bonding

While light-curing resins require fixing jigs until exposed to light, most light-curing instant adhesives have the advantage of adhering when applied to the adherends, eliminating the need for fixing jigs. This extremely useful characteristic reduces labor costs and increases speed of production lines.

2-3. Properties of light-curing instant adhesives

Table 4 shows the properties for ThreeBond 1771E, 1773E, and 1776E.

Table 4: Properties of light-curing instant adhesives

	Items		Unit	TB1771E	TB1773E	TB1776E
Monomer	Color and appearance		-	Transparent yellow liquid		
	Main component		-	2-cyanoacrylic acid ester		
	Viscosity		mPa·s	2	150	1000
Polymer	Linear expansion coefficient (0℃-100℃)		$\times 10^{-6}$/℃	81-103	75-99	70-99
	Glass transition temperature Tg		℃	124	123	117
	Standard curing conditions	Ultraviolet curing	kJ/m^2	10	10	10
		Visible light curing	kJ/m^2	0.4	0.2	0.2
	Dielectric breakdown voltage		kV/mm	27.0	26.0	25.8
	Volume resistivity		Ω·m	5.4×10^{13}	5.9×10^{13}	5.4×10^{13}
	Surface resistivity		Ω	1.2×10^{13}	5.9×10^{12}	1.2×10^{13}
	Dielectric constant	1MHz	-	3.27	2.69	2.90
		1MHz	-	4.05	3.34	3.61
	Dielectric tangent	1MHz	-	0.0511	0.0529	0.0555
		1MHz	-	0.0522	0.0534	0.0548

2-4. Setting time and bonding strength of light-curing instant adhesives

Light-curing instant adhesives offer good bonding properties for various substrates, similar to conventional instant adhesives. Table 5 shows an example of the setting time and bonding strength of light-curing instant adhesives. The tension shearing adhesive strength in the table is assessed in a tension shear test after applying adhesives under conditions of 25°C and 50% humidity, followed by 24 hours of curing. Except for materials (such as metals) that are stronger than the adhesives themselves, most adherends exhibit material break (i.e., the material breaks before the adherends due to the strength of the bond).

Not shown in Table 5 is another advantage of light-curing instant adhesives, this being that nonpolar or highly crystalline resins, generally regarded as difficult to bond, can bond strongly. For example, in combination with a primer (ThreeBond 1797), light-curing instant adhesives create strong bonds when used with polyethylene, polypropylene, polyacetal, soft polyvynyl-chlorides including large amounts of plasticizer, silicone rubber, and EPDM rubber.

Figure 4 shows the curing speed for moisture curing and light curing. As previously discussed, conventional instant adhesives are moisture-curing type. However, moisture-curing adhesives do not cure fully when initially applied to adherends. Although bonding strength increases rapidly at first, to complete curing generally it requires 12 to 24 hours at room temperature.

Light irradiation allows a bond to attain final strength in approximately 10 seconds. Thus, the optimal curing method is to temporarily fix the

adherends by moisture curing, then to cure completely by light irradiation.

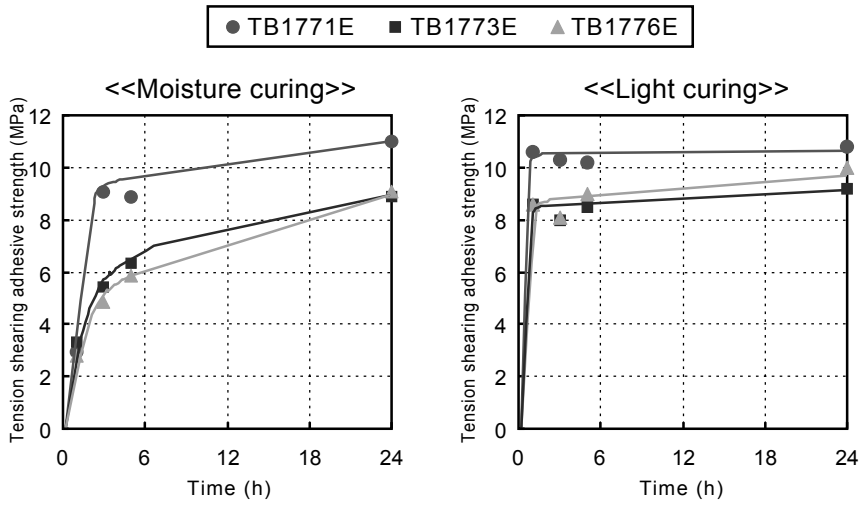
Instant adhesives generally function also as reactive "solvents" capable of dissolving the surfaces of certain plastic materials, including acrylic, polycarbonate, and ABS. Table 5 shows that the setting times for acrylic and polycarbonate are relatively slow. This is due the mutual solution of instant adhesive and the plastic in the bonding area.

Since they cure instantly, light-curing instant adhesives can prevent the dissolution of plastic surfaces in such cases.

Table 5: Setting time and bonding strength of light-curing instant adhesives

Adherends	Setting time (seconds)			Tension shearing adhesive strength (MPa)		
	TB1771E	TB1773E	TB1776E	TB1771E	TB1773E	TB1776E
Polycarbonate	12	15	20	11.0 (*)	8.9 (*)	9.1 (*)
ABS	2	3	7	7.4 (*)	6.7 (*)	7.0 (*)
6-nylon	5	7	15	7.1 (*)	7.1 (*)	7.2 (*)
PET	2	7	10	12.2 (*)	12.9 (*)	12.8 (*)
Acrylic	15	25	45	5.8 (*)	8.4 (*)	8.5 (*)
NBR	2	2	2	0.5 (*)	0.5 (*)	0.5 (*)
Paper (woody paper)	5	15	30	- (*)	- (*)	- (*)
Iron	3	5	10	15.1	15.9	16.8
Stainless steel	3	7	15	11.9	11.3	12.4
Aluminum	3	10	20	10.6	11.2	11.4
Copper	3	7	20	11.5	13.5	11.5
Brass	3	5	15	9.2	10.3	10.9

Test method: 3TS-220-04 (Setting time) (*) indicates material breaking.
3TS-301-11 (Tension shearing adhesive strength) [Tension speed 10 mm/min]



(Note) The light irradiation condition is 3.5 kJ/m^2 with a 4-kW high-pressure mercury-vapor lamp.
Moisture curing is performed in shade at 25°C and 50% humidity.

Figure 4: Comparison of curing speed for moisture curing and light curing (Adherends: polycarbonate)

2-5. Applications of light-curing instant adhesives

Light-curing instant adhesives offer a vast range of applications, including electric and electronic components, fields in which conventional instant adhesives are not used, and precision components. They are used not just to create surface bonding with various adherends, but for applications involving sealing, potting, and fixing. Additionally, since light-curing instant adhesives have the advantage of curing at lower illumination than typical light-curing resins, that is, since they cure faster, they should improve productivity in fast production lines. Major applications are listed below.

(1) Electric, electronic, optical, and general components requiring non-bleaching properties
(2) Fixing and bonding of supports around optical lenses
(3) Fixing and bonding of various light-blocking adherends
(4) Reinforcement of IC attachment
(5) Bonding of fitting sections such as printer heads and bearings
(6) Bonding of the fitting section of a drum motor and main shaft
(7) Fixing and bonding of ornamental materials
(8) Assembly of hypodermic needles and syringes
(9) Creation of Braille characters and graphics

Advancing miniaturization and driving to reduce weight has resulted in single components having extremely fine structures. Even the portions that could conventionally be irradiated with sufficient light, now the irradiation often causes problems. In such cases, light-curing instant adhesives that use both light and moisture curing are effective in providing reliable curing and bonding.

With increasing miniaturization, printed circuit boards use less solder. But since bonding strength must be maintained, light-curing instant adhesives are used to reinforce solder.

For metal plated plastic components, conventional light-curing or anaerobic resins sometimes fail to bond the adherends. In some cases, light-curing instant adhesives are used, due to their even broader bonding capabilities for a wide range of materials.

Components such as hypodermic needles and syringes have direct effects upon the human body. Reliable complete bonding and curing is critical in their assembly. Light-curing instant adhesives are also used for Braille characters and graphics, since the surface curing of light-curing resins is relatively poor due to oxygen-induced curing inhibition, as already discussed, and touching incompletely cured portions with hand may result in skin irritations. Light-curing instant adhesives are not affected by curing inhibition with oxygen. It can be said a better adhesive.

3. Summary

In view of recent trends toward international green technologies, the effectiveness and benefits of light-curing technology (including reduced use of organic solvents) in the areas of environment and energy are being recognized once again. Adding light curing properties overcomes the disadvantages of instant adhesives. The range of potential applications for light-curing adhesives continues to expand rapidly.

We plan to pursue the commercialization of shock-resistant and highly peel-resistant products, with the goal of overcoming the remaining disadvantages of the materials discussed, thereby exploiting new applications and new markets.

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