ThreeBond
TECHNICAL NEWS

ThreeBond Technical News
Issued July 1, 2018

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New Instant Adhesive Products

Introduction

As the name implies, instant adhesives enable bonding to adherents in a matter of seconds. These solvent-free adhesives demonstrate their bonding instantaneously at room temperature without releasing any environmentally hazardous substances, making them an excellent choice in point of protecting our planet. Even so, they are not without their weak points. We have tried a myriad of ways to overcome these, such as improving cyanoacrylate monomer synthesis and additive compounds.

At ThreeBond, we have developed and launched ThreeBond 7721 and ThreeBond 7761, instant adhesives that can handle a variety of usage environments and conditions, and also boast improved reduction of the blooming that is one of the weak points of instant adhesives.

Furthermore, to support the diversification of instant adhesive use seen in recent years, these also support medical applications. We also offer products compliant with ISO 10993: Biological Evaluation of Medical Devices, the most widely used international standard for assessing the biocompatibility of medical devices. Most of these products have been given light curing properties, which improves surface and thick film curing performance, both weak points of conventional instant adhesives.

In this article, we are pleased to present our low odor and non-blooming instant adhesive, as well as our light-curing instant adhesive for medical equipment use.

Hereafter, ThreeBond is abbreviated as TB.

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1. The Reaction Mechanism of Instant Adhesives

The main component of instant adhesives is α-cyanoacrylate monomer, which contains within its molecules strong electron-withdrawing groups, such as the cyano and carboxyl groups. These molecules contain large deviations in charge as well as polarity. As a result, basic components within moisture in the air, etc., act as a nucleophilic agent, driving anionic polymerization (Fig. 1).

The instantaneous bonding of instant adhesives comes from the fact that this anionic polymerization is extremely sensitive, so the reaction advances within moments.

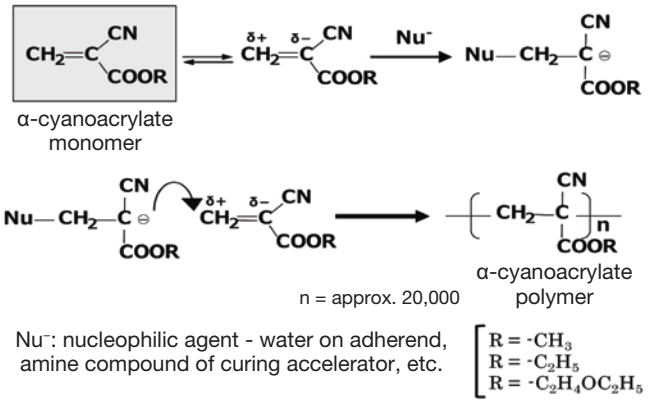


Fig. 1 The Reaction Mechanism of Instant Adhesives

The majority of the instant adhesive reaction mechanism is dominated by this sensitive anionic polymerization. The amount of radical polymerization caused by sources such as heat and light is low enough to be negligible, so small amount of various acidic substances are added to improve maintainability. This is because when adherends are bond to each other, the acidic substances are neutralized with a minimum amount of water (alkaline component), etc., and curing begins once entirely shifted to the alkaline range. Though the speed is gradual in storage, the radical polymerization reaction gradually progresses, so radical polymerization inhibitors are usually added to prevent this.

2. Advantages and Disadvantages of Instant Adhesives

Main Advantages

(1) Fast room-temperature curing

(2) Single-component solvent-free for excellent workability

(3) High sheer bond strength

(4) Adheres to a wide range of materials

(5) Colorless and transparent cured adhesive layer

Main Disadvantages

(1) Generates blooming

(2) Low heat resistance (up to 80°C)

(3) Hard and low-flexibility cured product is inferior in terms of impact resistance

(4) Inferior moisture and water resistance

(5) Inferior thick film curing performance

In additions to curing quickly, instant adhesives strongly bond to almost any adherend, and not needing to worry about materials used is a distinct advantage. This has led to their adoption in a wide variety of fields, such as general housing, industry and medical uses.

However, some weak points remain, even though various additives supplement the α-cyanoacrylate monomer. Through research from a variety of viewpoints, we have succeeded in improving these weak points.

Among these achievements, looking at the issue with the goal of refining the α-cyanoacrylate, the main component of instant adhesives, improved weak points while adding new function through the addition of the ethoxyethyl group. The ester moiety of commercially available instant adhesives is either the methyl ($-CH_3$) or ethyl ($-C_2H_5$) group. Introducing the ethoxyethyl group ($-C_2H_4OC_2H_5$) into this

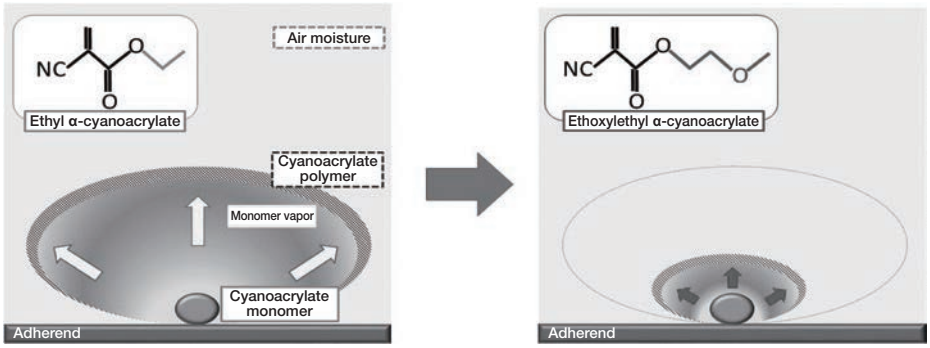


Fig. 2 Comparison of Blooming

ester moiety lowers the vapor pressure of the monomer to inhibit vaporization. Increasing the molecular weight in this way enables the suppression of blooming. Furthermore, the lengthening of this ester moiety makes it more flexible than the methyl group, and enables delayable curing speed and adjustable curing strength (Fig. 2).

3. Low-Odor Non-Blooming Instant Adhesive, ThreeBond 7721 and 7761

As mentioned above, introducing the ethoxyethyl group to α-cyanoacrylate led to the development of TB7721, with suppressed irritating odors and blooming as well as TB7761, with delayable curing speed and adjustable curing strength.

3-1. Non-Blooming Instant Adhesive, ThreeBond 7721

TB7721 is a rapid-curing instant adhesive which uses ethoxyethyl α-cyanoacrylate as its main component. Introducing the ethoxyethyl group into this ester moiety lowers the vapor pressure of the monomer to inhibit vaporization, leading to a product where blooming is suppressed. This eliminates irritating odors almost entirely, and makes it excellent for bonding to porous materials such as wood, paper, cloth or leather due to incredibly fast curing.

1) Bonds instantly (within 2 seconds to 3 minutes).
2) Very little characteristic irritating odor and suppressed blooming.
3) Incredibly fast curing for quick bonding to a variety of materials (porous materials, acidic substances, etc.).

3-2. Instant Adhesive for Impregnation, ThreeBond 7761

TB7761 is an instant adhesive for impregnation coating which uses ethoxyethyl α-cyanoacrylate as its main component. Conventionally, porous materials are utilized in a variety of industrial applications. Among these, gypsum is used in a variety of fields, such as industrial product and dental model applications. In recent years, it has been used for laminated 3D printer materials, and modeling use requires high dimensional accuracy. Basically, the thinner the coating agent, the higher the model accuracy, but both sufficient hardness and strength are required.

Required Performance

1) Permeation throughout the finest details of the molding
2) Control of permeation (curing) rate

1) Permeation throughout the finest details of the molding

Viscosity and surface tension are high in conventional instant adhesives, so it was difficult to permeate to the deepest parts of the molding. So, we added a solvent with moderate compatibility with the cyanoacrylate main component which has the functionality of low surface tension and viscosity. As a result, we succeeded in improving permeation performance without lowering curability or maintainability.

2) Control of permeation (curing) rate

Adjustment of curing rate is vital to the control of permeation rate. Mainly by slowing down curing, we made it possible to minimize uncured parts so as to develop sufficient reinforcement strength in laminated materials. In order to control the permeation rate, we utilized formulation technology to adjust the polymerization rate, which led to maintained practical strength without impairing permeability.

TB7761 has excellent permeability for gypsum molding shaped by 3D printers, and demonstrates reinforcement and color pigmenting via impregnation. Furthermore, the cyanoacrylate main component has almost no irritating odor.

3-3 Properties and Characteristics

The properties and basic performance of TB7721 and TB7761 are shown in Table 1.

Table 1 TB7721 and TB7761 Basic Properties

Features		Unit	TB7721	TB7761	Testing method
Appearance		—	Light yellow, transparent	Light yellow, transparent	3TS-2100-020
Viscosity		mPa·s	4.8	5.0	3TS-2F00-001
Specific gravity		—	1.07	1.08	3TS-2500-002
Setting time	Fe	sec	15	180	3TS-3140-004
	NBR		2	120	3TS-3140-001

Adhesive strength for various adherends is shown in Table 2.

Table 2 Adhesive Strength for Various Adherends

Adherend material	Tensile Shear Bond Strength (MPa)	
	TB7721	TB7761
Fe	18.4	16.0
Al	12.9	13.9
SUS	7.7	12.7
Brass	10.8	12.9
Cu	12.4	13.6
Nickel	7.5	13.8
Galvanized chromate	7.1	10.5
PC	7.6 (*)	6.5 (*)
6-nylon	2.9	3.3 (*)
6,6-nylon	8.1	5.3
Noryl	5.5	1.9
ABS	4.1 (*)	6.0 (*)
Glass epoxy	11.1	9.1
PBT	1.8	0.2
PET	7.3	6.1
PPO	5.1	3.1
PPS	1.9	0.6
HIPS	3.9 (*)	3.5
Acrylic	6.4 (*)	7.4 (*)
POM	0.8	0.7
NR	0.4 (*)	0.3 (*)
CR	0.6 (*)	0.4
NBR	0.8 (*)	0.3
SBR	1.6 (*)	0.4
EPDM	0.8 (*)	0.7 (*)

*Material failure

4. Light-Curing Instant Adhesives

4-1. Light-Curing Instant Adhesives for Medical Devices

Here, we introduce products with improved α-cyanoacrylate to suppress the blooming which has been a weak point for instant adhesives until now. We also enabled suppression of blooming through the use of light-curing instant adhesive which combines light and moisture curability. We added a photoinitiator that generates anions in the instant adhesive and utilized technology that also cures in photoirradiation for our light-curing instant adhesive. This improved surface hardening and thick film curing performance for expansion into a wide range of applications.

Table 3 shows a comparison of the features of our light-curing instant adhesive with those of conventional instant adhesives and general light-curing resins.

Table 3 Light-Curing Instant Adhesive Features

	Instant Adhesives	Light-Curing Instant Adhesives	UV-Curing Resin
Adhesion to light-shielded (shaded) material	○	○	×
Curing of protruding parts	×	○	○
Blooming	×	○	○
Surface curing	×	○	△
Temporary fixing jig	Not required	Not required	Required

Table 4 shows our lineup of light-curing instant adhesives designed for medical devices. These light-curing instant adhesives are also utilized in the medical device field for parts that contact the human body, such as injection needles and syringe assemblies (Fig. 4). Parts like these require considerably reliable and safe bonding and curing in addition to durability.

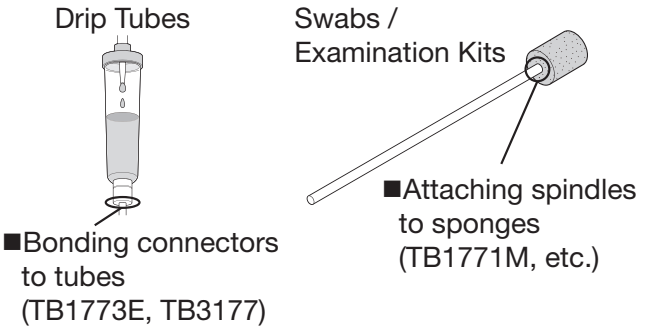


Fig. 4 Medical Device Applications

We are engaged in risk management as a part of comprehensive medical device evaluation designed to protect the human body from potential biological risks related to the use of these medical devices. At ThreeBond, we provide ISO 10993: Biological Evaluation of Medical Device-compliant products which are often required for the commercial release of medical equipment. This evaluation utilizes the standards that are the most widely used for the biological evaluation of medical devices and materials,

Table 4 Lineup of Light-Curing Instant Adhesives for Medical Devices

Features		Adherend	Unit	TB1771E	TB1771M	TB1773E
Appearance		—	—	Light yellow to light green, transparent	Light yellow to light green, transparent	Light yellow to light green, transparent
Viscosity		—	mPa·s	2	2	150
Setting time (25°C, 50% RH) (when moisture curing)		NBR	sec	2	2	2
		Fe		3	10	5
Tensile shear bond strength		PC	MPa	11.0 (*)	10.8 (*)	8.9 (*)
		Fe		15.1	17.5	15.9
Coefficient of linear expansion (0°C to 100°C)		—	$\times 10^{-6}$/℃	81 to 103	90	75 to 99
Glass transition temperature Tg		—	℃	124	125	123
Standard curing (UV curing)		—	kJ/m^2	10.0	10.0	10.0
Dielectric breakdown voltage		—	kV/mm	27.0	29.0	26.0
Volume resistivity		—	Ω·m	5.4×10^{13}	2.9×10^{13}	5.9×10^{13}
Surface resistivity		—	Ω	1.2×10^{13}	6.4×10^{15}	5.9×10^{13}
Permittivity	1MHz	—	—	3.27	3.30	2.69
	1kHz	—	—	4.05	3.90	3.34
Dielectric loss tangent	1MHz	—	—	0.0511	0.033	0.0529
	1kHz	—	—	0.0522	0.036	0.0534

and act as a framework for determining the appropriate biocompatibility evaluation grade when planning biological evaluation. Table 5 shows the items assessed for this.

Table 5 ISO 10993 Assessment Items

ISO 10993 (biological safety evaluation) assessment items				
Cyto-toxicity	Skin sensitivity	Dermal irritation reaction	Acute systemic toxicity	Subacute systemic toxicity
○	○	○	○	○

* For use in medical devices requiring heat generation, implantation and blood compatibility. Do not employ for uses other than those intended.

* When using this product for their products, customers are responsible for checking and determining compatibility with their intended application and purpose before use.
Furthermore, customers bear the full burden of responsibility stipulated in the Pharmaceuticals and Medical Devices Act.

4-2. ThreeBond 3177

Here, we introduce TB3177 which is ISO 10993: Biological Evaluation of Medical Device-compliant and features heat and moisture resistance better than that of conventional light-curing instant adhesives. TB3177 is a single-component, solvent-free light-curing instant adhesive which is a hybrid of acrylic-based light-curing adhesive and instant curing adhesive. Adding a crosslinking component to the instant adhesive's base monomer increases areas that crosslink between resins during curing. In this way, the crosslinking component builds a wall to greatly slow moisture entry, supplementing the heat and moisture resistances which are weak points of instant adhesives. This combination of the durability and reliability of acrylic-based light-curing adhesive with the fast drying and versatility of instant adhesive enables use with an array of materials in a wide range of environments. Cures quickly via UV rays in the 200 to 450 nm wavelength as well as visible light what reduces blooming.

Table 6 TB3177 Properties and Characteristics

Features	Adherend	Unit	Measured value	Testing method
Appearance	—	—	Light yellow to light green, transparent	3TS-2100-020
Viscosity	—	mPa·s	1200	3TS-2F00-001
Specific gravity	—	—	1.06	3TS-2500-002
Setting time (25°C, 50% RH) (when moisture curing)	NBR	sec	20	3TS-3140-001
	PC		60	3TS-3140-004
			90	
Tensile shear bond strength (25°C, 50% RH) x 24h	NBR	MPa	0.8 (*)	3TS-4100-011
	PC		5.8 (*)	
	Fe		19.5	
Tensile shear bond strength ($10kJ/m^2$)	PC	MPa	7.3 (*)	
Standard curing conditions (when UV curing)	—	kJ/m^2	10	UV-LED
	—	kJ/m^2	10	4 kW high-pressure mercury vapor lamp

4-3. Features of ThreeBond 3177

The properties of TB3177 are shown in Table 6.

● Humidity resistance

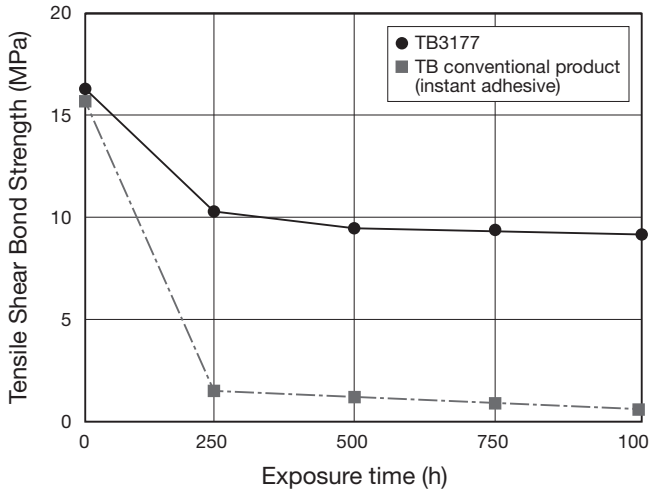
Figures 5 and 6 show TB3177 moisture resistance during moisture curing (adherend: Al) and light curing (adherend: PC), respectively.

Figure 5 shows that moisture resistance is remarkably improved compared to our conventional instant adhesives. TB3177 also demonstrates better moisture resistance than our conventional UV-curing adhesives (type with moisture curing).

● Heat cycle resistance

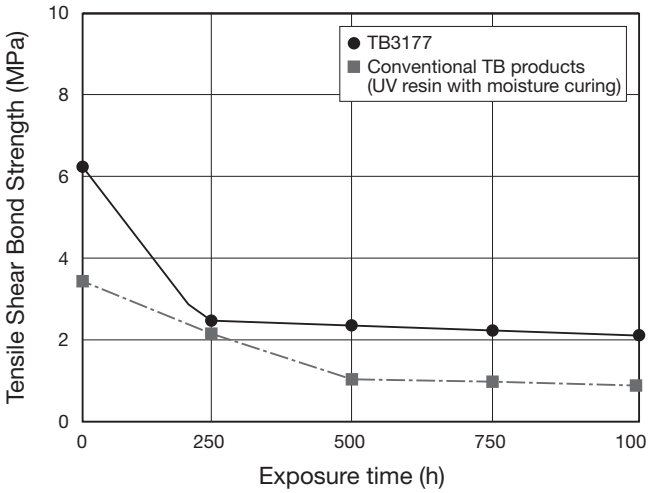
Figures 7 and 8 show heat cycle resistance during moisture curing (adherend: Al) and light curing (adherend: PC), respectively. The test pieces, created in the same way as for moisture resistance, were exposed to specific heat cycles for 30 min. each from −40°C to 120°C, then returned to 25°C and measured.

Figures 7 and 8 show a remarkably high heat cycle resistance superior to our conventional instant adhesives and UV-curing adhesive with moisture curing.



Exposed for a given time in a 85°C 85% RH temperature and humidity testing chamber after 24 hours of exposure in 25°C 50% RH, then returned to room temperature and measured (10mm/min).

Fig. 5 Moisture Resistance (for Al)



Light-cured with an 10 (kJ/m^2) light integral 4kW high-pressure mercury vapor lamp, exposed to a 25°C 50% RH environment for 20 hours, then exposed to 85°C 85% RH and measured.

Fig. 6 Moisture Resistance (for PC)

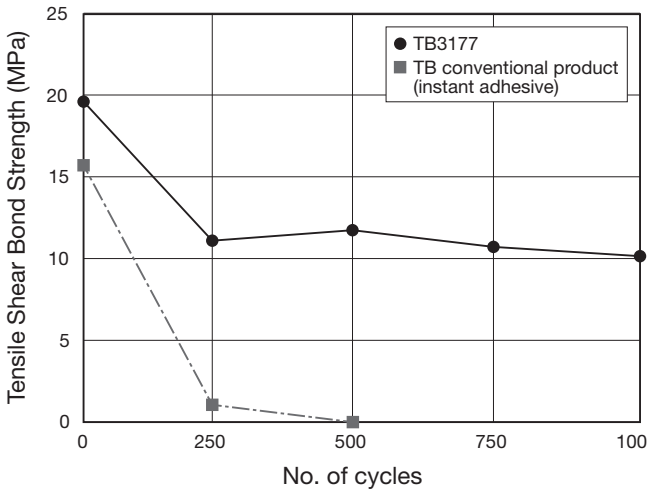


Fig. 7 Heat Cycle Resistance (for Al)

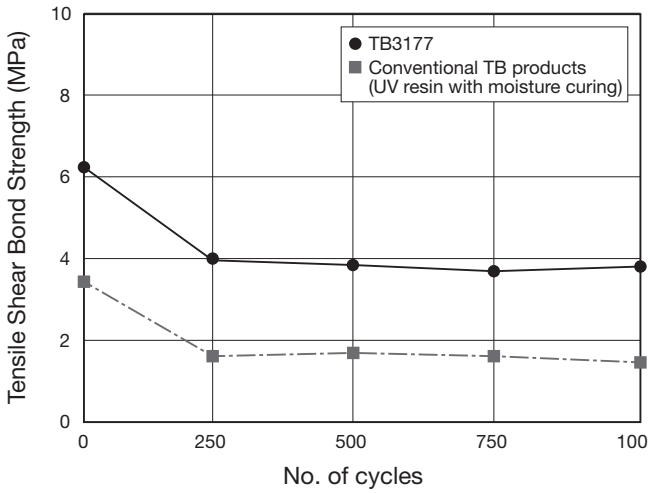


Fig. 8 Heat Cycle Resistance (for PC)

4-4. Bonding to Various Adherends

Table 7 shows TB3177 bonding to various adhesives, such as metal and plastic.

Because TB3177 is an acrylic-based instant adhesive hybrid, it demonstrates particularly strong bonding with aluminum (Al), zinc die cast (ZnDC) and other metals compared to our conventional UV-curing adhesives. Furthermore, it contains instant adhesive, so it can be used with our TB7797 instant adhesive primer for difficult bonding. As a result, it can bond to polyethylene (PE), polypropylene (PP), polyacetal (POM), and other materials said to be difficult to bond to. This is a noteworthy feature not commonly found in UV-curing adhesives.

Table 7 TB3177 Bonding to Various Adherends

Curing type	Moisture curing		Conventional product (UV resin with moisture curing)
Adhesive	TB3177	TB3177	
Primer	—	TB7797	
PC/Al	7.7 (*)	—	2.4
PC/SUS	10.5 (*)	—	3.1
PC/ZnDC	7.3 (*)	—	2.8
PC/PBT	1.5	5.8	4.1
PC/PPS	2.9	4.8	1.4
PC/POM	2.4	5.9 (*)	1.1
PC/PE	0.4	5.0 (*)	0.4
PC/PP	1.0	6.3 (*)	0.8

Closing

Cyanoacrylate-based adhesives demonstrate many excellent features that differ from conventional adhesives, and it has been more than half a century since they were adopted into practical use. Today, a variety of products are offered by many different companies, and these adhesives continue to be demanded in a wider array of fields. Instant adhesive functionality depends largely on the cyanoacrylate that is its base monomer, but these adhesives are considered to have great potential. Moving forward, it is important to make improvements that further enable utilization of advantages while covering weak points.

The products introduced here utilize the features of ethoxyethyl α-cyanoacrylate to suppress the blooming that is a weak point of instant adhesives. As a result, we believe they can be used for optical and decorative materials for which the dirt of blooming would have made application to these adherends difficult.

This enables use of UV-curing instant adhesives in a wide range of fields, from electronic and electrical to medical devices. In this way, weak points exhibited by single component, solvent-free instant adhesives with both light and moisture curing are covered, and we are certain this will lead to future research and application of cyanoacrylate-based adhesives.

At ThreeBond, we will continue to respond to every customer demand as we pioneer new applications and commercial development.

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