ThreeBond
TECHNICAL NEWS

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One-Part Epoxy Resin

Introduction

In addition to two-part epoxy resin, one-part epoxy resin has a wide range of applications. However, it seems that the product has not readily been and accurately understood by many people.

According to the survey conducted internally, one-part epoxy resin ranked high in both the "salable" and "difficult to sell" groups, giving a rather puzzling result. After all, though this is my own interpretation, sellers and buyers who have a certain degree of knowledge and understanding of one-part epoxy resins can select and use them, while those who consider it difficult to sell the resins may not understand the versatility and wide range of applications of epoxy resin.

This issue of the newsletter describes one-part epoxy resin, which has various properties and a wide range of uses, in order to increase understanding of the resin.

Contents

1. Summary

One-part epoxy resin has some commonalities with two-part epoxy resin. For example, they use the same epoxy resin, which is the fundamental ingredient thereof, and have employed very similar methods of improvement and development. In addition, the one-part technique is primarily dependent on the curing agents used. Therefore, the compounding techniques described in the present report should be understood as regarding general epoxy-resin compounds. Epoxy resin is characterized by the high degree of flexibility in its compounds due to its stability. Various compound techniques have been suggested and discussed for exploiting the flexibility and other good properties of the basic types of epoxy resin. This report describes the basic properties of the epoxy resin and the ingredients of the compounds and the roles thereof, and introduces the properties and uses of one-part epoxy resin.

2. Demand for epoxy resin in various fields

As shown in Table 1, there is demand for epoxy resin in a wide range of fields, including paints and electrical components. As a trend over the past decade, the focus of the demand has shifted from general paints to automobile paints, and then to electrical components. In particular over the past few years, there has been increasing demand for the resin as an encapsulating material of IC and LSI for electrical machinery such as FA and OA appliances.

3. What is epoxy resin?

The term "epoxy resin" is a generic name for compounds that have two or more oxirane rings (epoxy groups) in one molecule, and are cured three-dimensionally by a suitable curing agent. However, in most cases, the term refers to bisphenol-A diglycidyl ether (DGEBA), which is formed by the reaction between bisphenol A and epichlorohydrin, which currently commands a 75% share of the epoxy-resin market. Of the products of Three Bond, 50% to 60% of one-part epoxy resin and more than 90% of two-part epoxy resin are based on DGEBA or compounds containing DGEBA. Therefore, DGEBA is synonym for epoxy resin.

The following section describes the structure and performance of epoxy resin, using DGEBA as a representative example.

Table 1. Delivery quantity of epoxy resin organized by use (year on year (%)) 87-01-26

Uses \ Year		54		55		56		57		58		59	
Paints	Cans	5,643		4,973	88	6,378	128	5,836	92	7,234	124	8,258	114
	Automobiles			6,458	157	7,808	121	9,595	123	10,514	110	11,534	110
	Ships	3,739		4,929	132	7,533	153	7,496	100	6,888	92	7,572	110
	General purposes	11,191		10,578	95	10,153	96	9,713	96	10,974	113	13,412	122
	Total	24,676		26,938	109	31,872	118	32,640	102	35,610	109	40,776	115
Electrical components	Laminates	7,118		7,364	103	9,982	136	10,362	104	14,142	136	20,864	148
	Casting	5,282		5,367	102	4,574	85	3,658	80	4,079	112	5,266	129
	Others	2,231		2,260	101	3,413	151	3,652	107	5,483	150	11,122	203
	Total	14,631		14,991	102	17,969	120	17,672	98	23,704	134	37,252	157
Civil construction		6,901		6,558	95	7,411	113	8,002	108	9,446	118	9,469	100
Adhesives		3,582		3,659	102	3,832	105	3,609	94	3,731	103	3,882	104
Others		6,404		6,407	100	5,296	83	4,778	90	6,238	131	7,646	123
Domestic demand total		56,194		58,553	104	66,380	113	66,701	100	78,729	118	99,025	126
Export		915		902	99	568	63	866	152	1,330	154	1,729	130
Grand total		57,109		59,455	104	66,948	113	67,567	101	80,059	118	100,754	126

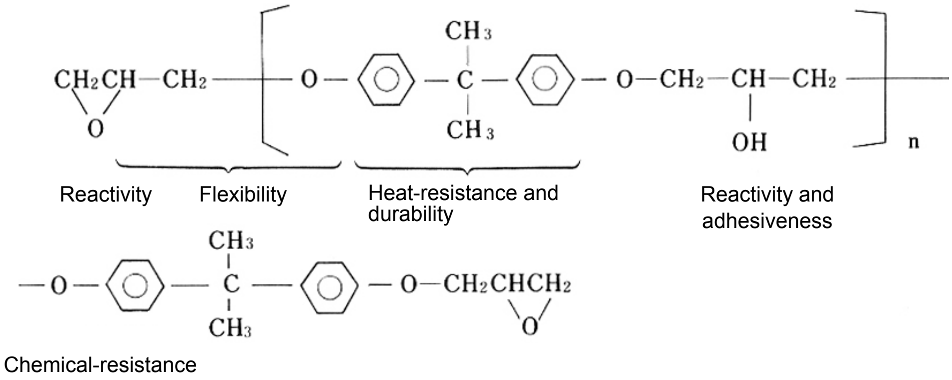


Fig. 1. Structure and properties of epoxy resin

The excellent properties of epoxy resin, such as durability and adhesiveness, depend largely on its structure. Fig. 1 shows the relationship schematically.

1) The epoxy groups at both terminals of the molecule and the hydroxyl groups at the midpoint of the molecule are highly reactive, allowing room-temperature and high-temperature curing using suitable curing agents, and a wide range of modifications. In addition, the resin is cured by ring-opening polymerization, and as a result has a smaller degree of cure shrinkage than other thermosetting resins.
2) The ether linkages included in the main chain improve the chemical-resistance and elasticity.
3) The benzene rings in bisphenol A provide chemical-resistance, adhesiveness, durability, heat-resistance and excellent electrical properties.
4) The coexistence of hydrophilic groups with hydrophobic groups in the molecule significantly increases the adhesion to various adherends.

60		61•Breakdown								61•Total	
		1～3		4～6		7～9		10～12			
8,327	101	2,051	93	2,697	116	2,397	127	2,279	119	9,424	113
12,473	108	2,988	101	3,095	91	3,013	100	3,103	100	12,199	98
7,437	98	1,411	73	1,584	78	1,515	85	1,514	88	6,024	81
13,122	98	3,294	104	4,100	121	3,561	113	3,497	103	14,452	110
41,359	101	9,744	95	11,476	103	10,486	107	10,393	103	42,099	102
18,652	89	4,436	100	5,973	133	5,453	110	5,791	121	21,653	116
5,565	106	1,663	121	1,873	136	1,898	139	2,142	148	7,576	136
10,849	98	3,215	102	4,044	144	4,130	193	3,689	135	15,078	139
35,066	94	9,314	104	11,890	137	11,481	136	11,622	130	44,307	126
9,349	99	2,210	92	2,017	96	2,347	96	2,273	95	8,847	95
4,059	105	1,019	105	1,358	138	1,316	133	1,478	133	5,171	127
7,768	102	2,007	95	1,751	97	1,867	101	1,925	97	7,550	97
97,601	99	24,294	98	28,492	115	27,497	117	27,691	113	107,974	111
1,423	82	583	139	521	180	420	111	437	130	1,961	138
99,024	98	24,877	99	29,013	116	27,917	117	28,128	113	109,935	111

As described above, many properties are ascribable to the structure, but such properties are largely dependent on the curing agents that cause the curing reaction, resulting in wide selectivity of the epoxy resin.

4. Compounding ingredients of epoxy-resin and roles thereof

As shown in Table 2, regardless of whether it is one-part or two-part, epoxy resin is rarely used alone as an epoxy-resin material, but rather is used in the form of compounds containing various modifiers and diluents in order to impart the resin's desirable properties, such as strength, flowability, and heat-resistance.

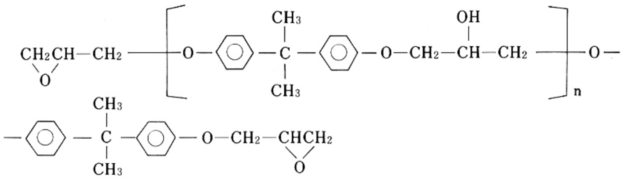
In addition to the agents described below, various agents can be mixed with epoxy resin. In such cases, epoxy resin causes remarkably less gelation and reaction inhibition than other reactive resins, which gives a significant advantage to the resin in the creation of compounds and allows anyone to make such compounds.

Table 2. Compounding ingredients of epoxy-resin and roles thereof

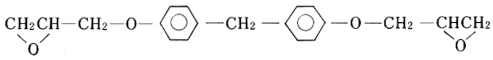
Constituents	Ingredients	Roles
Resin content	Epoxy resin	The bisphenol-A type is common. However, there are many other types of epoxy resin having different properties.
	Curing agents	Curing agents react with epoxy groups to form a three-dimensional network structure by crosslinking.
Modifying ingredients	Elasticity agents	Elasticity agents elasticate compounds to improve their peeling strength and extensibility, e.g., elasticizers and epoxy modifying resins.
	Shock-resistant agents	Shock-resistant agents eliminate brittleness from epoxy resin to prevent cracks and decrease distortion.
	Fillers	Fillers increase the weight in order to decrease costs and improving various types of mechanical strength, e.g., calcium carbonate and talc.
	Heat-resistant agents	Heat-resistant agents increase the heat-resistance and heat-deformation temperature through the use of multi-sensual types of epoxy resins such as novolac epoxy resin.
	Diluents	Diluents reduce viscosity and improve flowability and permeability. Reactive diluents having epoxy groups and nonreactive diluents having no epoxy group are available.
	Thixotropic agents	Thixotropic agents impart thixotropy to compounds in order to control flowability and increase viscosity.
	Other agents	Pigments, coupling agents, defoaming agents, leveling agents, etc.

4-1. Major types of epoxy resin

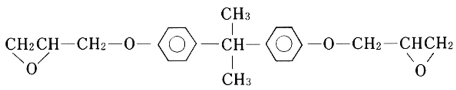
Bisphenol-A type (DGEBA); Commonly used



Bisphenol-F type; Characterized by having low viscosity



Bisphenol-A D type; Having intermediate characteristics between those of the DGEBA and bisphenol-F types



Most epoxy resins are composed on the basis of the above three types of resin. There are many other types of epoxy resins; however, most are not adaptable to a wide variety of applications, and rather are intended for special purposes such as modifications and improvements to heat-resistance and elasticity.

4-2. Various curing agents

Like epoxy resin, there are various types of curing agents for epoxy resin. In fact, there are so many types that they cannot be covered in this report; therefore, only the latent curing agent for one-part epoxy resin is described in this section.

The types of latent curing agents are classified as shown in Table 3. Including our products, those that are commercially available are primarily of the thermosetting type. Most thermosetting curing agents are of the dissolution-reactive type.

Table 3. Classification of latent curing agents

Activation means	Phenomena	Curing agents
Heat activation	Ionic reaction	Lewis-acid complexes (BF_3-ME-A, etc.)
	Dissolution	Dicyandiamide Modified imidazole, organic acids Hydrazides, DCMU
	Decomposition	Amine-imide compounds
	Elution	Molecular sieves
	Microcapsules	
Light (UV)	Decomposition	Aromatic diazonium salts, diallyl iodonium salts, triaryl sulfonium salts
Moisture	Decomposition	Ketoimine
	Elution	Molecular sieves
Pressure	Microcapsules	

Using dicyandiamide as a representative example, the following section describes the characteristics and properties of thermal-dissolution reactive curing agents.

<Dicyandiamide and derivatives thereof>

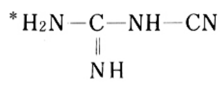
Dicyandiamides are crystals with a high melting point of 207°C to 210°C. When dispersed in epoxy resin in the form of fine powder, they will have a pot life of 6 to 12 months, and will remain stable for a greater length of time than imidazole. Four to ten parts of them are added to DGEBA.

Dicyandiamides require heating at 160°C to 180°C for one hour to several hours for curing, and generate a large quantity of heat upon curing. They tend to sediment due to their high specific gravity, and thus are not suitable for casting. They are used for coating, adhesion, and lamination.

In many cases, to decrease the curing temperature, which is a weakness of dicyandiamides, an accelerating agent is added, as shown in the following example of compound, in order to accelerate curing at a lower temperature. New accelerating agents have actively been developed.

<Example of compound>

DGEBA 100
DICY (dicyandiamide*) 8
Dimethyl urea 3



<Properties of the compound>

Curing conditions 120 °C × 30 minutes
Shearing strength 150 kgf/cm^2
Glass transition point 125 °C

The compound has found a wide range of applications: as an adhesive in electric and electronic applications, as an encapsulating material for terminals due to the fact that it does not cause metal corrosion, as a structural adhesive due to its strong adhesiveness, and for pre-preg and powder coating due to its low cost.

4-3. Elasticity and shock-resistant agents

Despite its high strength, (cured) epoxy resin has the problem of brittleness due to its poor elasticity. One-part epoxy resin, when it has not been particularly elasticated, has shearing adhesive strength of 150 to 200 kg f/cm^2, which is relatively high for an adhesive; however, it has peeling adhesive strength of 0.5 to 1 kgf/25 mm width in a T-peel test, which is equivalent to that of instant adhesives. This is due to the fact that the cured resin is relatively low in extensibility. If this insufficiency is redressed by a elasticity agent, the resin may have shearing adhesive strength of 250 kgf/cm^2 or higher, and peeling adhesive force of 20 kgf/25 mm width in a T-peel test.

The elasticated agents are described below.

The purposes of adding elasticated agents include the following: 1) improvements in mechanical strength, 2) prevention of cracks due to thermal distortion, and reduction of distortion, and 3) improvements in adhesiveness, particularly improvements in peel strength by imparting elasticity to disperse stresses.

The method of compounding elasticated agent is as follows: an elastic structure is introduced to the main chain polymer, side chain or terminal of a bisphenol type resin (see Fig. 2). However, the introduction of polymers having a rubber structure or a straight chain inevitably causes a significant increase in the viscosity of the material and deterioration of the properties of the material, such as heat-resistance, due to the decrease in the crosslinking density.

To avoid such deteriorations in properties, a special elasticated agent, carboxyl-terminal butadiene-acrylonitrile copolymer liquid rubber (CTBN), may be added. CTBN has mutual solubility with epoxy resin, but does not have it with cured epoxy resin and therein forms a dispersed rubber particle phase, and serves as a cushioning material to prevent cracks (see Fig. 3). This elasticated agent is said to provide elasticity without deteriorations in properties, due to the fact that it does not remain in the epoxy-resin layer.

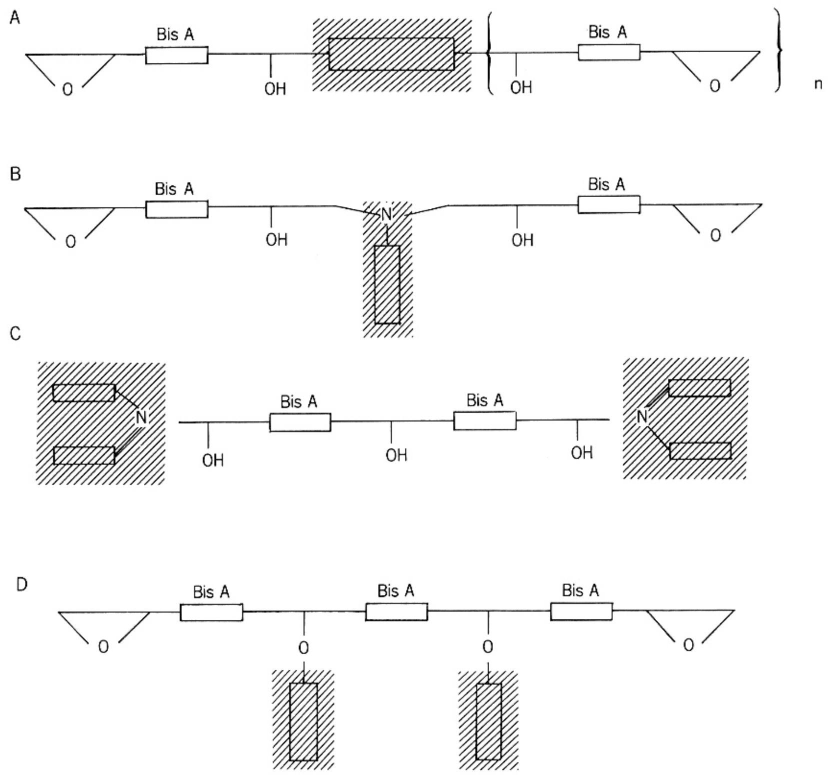


Fig. 2. Schematic structure of modified resins

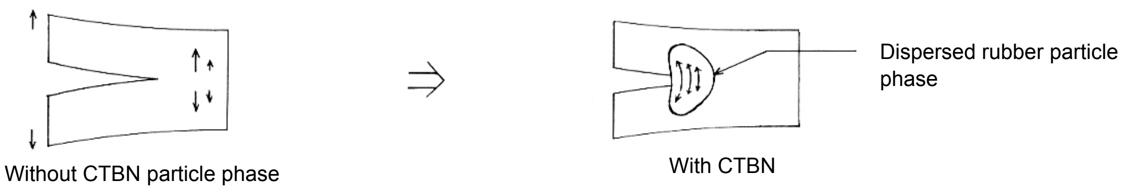


Fig. 3. Effect of CTBN

4-4. Heat-resistance improvers

The heat-resistance of compounds depends primarily on the epoxy resin contained therein. In one-part epoxy resin, the usable curing agents are limited, and thus the heat-resistance depends primarily on the type of selected epoxy resin .

It can be generally concluded that improvements in crosslinking density contribute to improvements in heat-resistance, and thus resins with a short distance between epoxy groups, or multifunctional types of epoxy resin are commonly used.

Representative examples are given below.

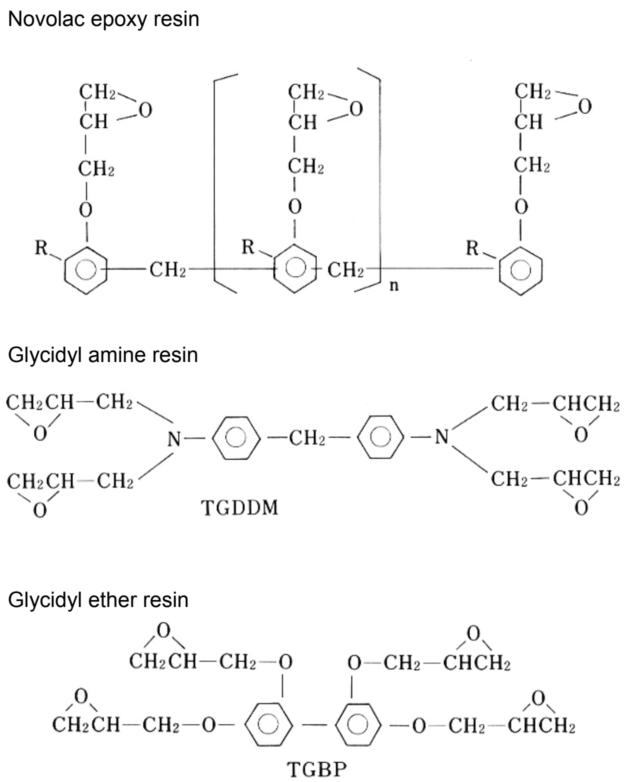


Fig. 4. Representative heat-resistance agents

4-5. Fillers

Fillers tend to be regarded merely as bulking agents, but their roles cannot be neglected due to the fact that increasingly rigorous properties are required of epoxy resin. It is therefore necessary to select and add appropriate fillers.

The effects of fillers include the following:

1) Improvements in mechanical strength
2) Reduction in thermal distortion and dimensional change
3) Improvements in electrical properties, particularly insulating and dielectric properties
4) Cost reduction due to the increase in weight
5) Improvements in fire retardancy

6) Improvements in heat conductivity

4-6. Diluents

As previously mentioned, when various materials are added to epoxy resin in order to improve its properties, the viscosity of the composition correspondingly increases. Bisphenol-A-type epoxy resin itself does not have low viscosity, and thus it inevitably requires adjustment (reduction) of its viscosity. For this purpose, diluents are used.

The influence of diluents on performance must be minimized, and thus the preferably used fillers are those that can have a significant effect with as small amounts as possible. One-part epoxy resin requires diluents having a low vapor pressure, as it undergoes a heating process.

Diluents fall into two types: reactive ones having epoxy groups and unreactive ones having no epoxy group. Most one-part epoxy resins are used reactive diluents, as unreactive diluents serve as a elasticizer in the cured resin. Fig. 5 shows the major diluents. Their handling requires caution, as they have a low molecular weight and readily permeate through the skin to cause irritation.

4-7. Thixotropic agents

Thixotropy is a property of liquids containing flocculating components. Flocculating components are destroyed by repeated stirring and the liquids show flowability; however, once stirring is stopped, the components reflocculate and the liquids return to the nonflowable state.

This property is required in applications in which sagging causes a problem, such as the thick coating of paints and the adhesive sealing of gaps. Commonly used effective thixotropic agents include silica fine powder (Aerosil), and colloidal hydrated aluminum silicate/organic complex (Orben).

However, the effect varies among thixotropic agents. Some exert their effect in heating, and others disappear in heating, become ineffective when cured, or deteriorate over time. Their selection is difficult even for experts.

5. Major functions and uses of one-part epoxy resins

Table 4 lists the major properties and uses of one-part epoxy resin, and Photograph 1 shows examples of the usage of one-part epoxy resin.

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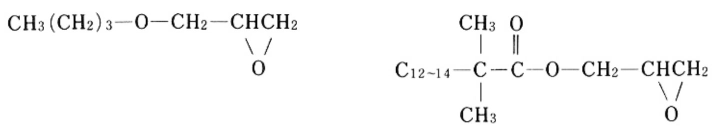

Fig. 5 Representative reactive diluents

Table 4. Major properties and uses of one-part epoxy resin

Properties	Uses	Characteristics	Product name ("TB" is an abbreviation for Three Bond.)
Heat-resistance	(1) Impregnating fixation of armature coils	Moderate impregnation properties and strength with heating at 160 °C or higher Resistance to continuous heating at 220 °C	TB2068K, TB2068H TB2064C
	(2) Heat-resistant adhesion	Glass transition temperature of 170 °C, strength with heating 200 °C, 50 kgf/cm^2, peeling strength of 14 kgf/25 mm width	TB2064C
	(3) Adhesion of motor magnets	Moderate flowability, strength with heating at 150°C or higher	TB2068M
Dimensional stability	(1) Encapsulation of heads and electrical components	Low coefficient of thermal expansion, high moisture-resistance, high purity, resistance to P.C.T. (pressure cooker test)	TB2071B
Thixotropy	(1) Antisagging, temporal adhesion of chips, fixation of coil terminals	High thixotropy, screen printability Fast curing at 150 °C, curing in one to two minutes	TB2065, TB2065M
	(2) Terminal seal for prevention of penetration	Moderate flowability, curing at a low temperature of 80 °C to 100 °C	TB2062B, TB2062D
	(3) Joint sealants	High thixotropy, high viscosity	TB2065, TB2062K
Fast curing	(1) Adhesion of syringe needles	Moderate permeability, white cured substance, curing at 150 °C in one to three minutes	TB2062D, TB2065L
	(2) Coating of stepping motors	Curing at 150 °C in one to three minutes, machinability	TB2065, TB2065C
Machinability	(1) Joint sealants for bus bodies	High shock adhesive force, slump property, and machinability	TB2063C
Impregnation	(1) Low-viscosity impregnating adhesion, impregnation of cut cores	Low viscosity, long shelf life	TB2076, TB2076C
	(2) Potting agent for small coils	Low viscosity, low shrinkage ratio	TB2071C
Elasticity	(1) Thermal shock, adhesion of motor magnets	Absorption of the thermal distortion of magnets/yokes, prevention of cracks in vibration-absorbing magnets	TB2064, TB2064B
	(2) Terminal seal for halogen-lamp	Thermal shock, conformity to terminal bending, adhesion to engineering plastics	TB2064
	(3) Adhesion of headlights (iron/glass)	Rubber elasticity	TB2067E, TB2067F TB2067D
Structural adhesion	(1) Adhesion of automobile hemming	High adhesive strength, peeling adhesive force	TB2068G
	(2) Adhesion of joints in chainsaw fuel tanks	High adhesive strength, peeling adhesive force	TB2063, TB2063D
Filling adhesion	(1) Potting of inhibitor switches	Moderate flowability, heat-resistance, weather-resistance	TB2068M, TB2068P TB2068I, TB2063J
	(2) Adhesion sealing of plastic cases	Moderate permeability, soldering heat-resistance	TB2062C, TB2062J
	(3) Encapsulation of printer heads	Moisture-resistance, flowability, low-temperature fast-curing property	TB2065E, TB2065F

Photograph 1 Examples of the usage of one-part epoxy resin

Conclusion

Three Bond has been selling one-part epoxy resin for more than ten years. In that time, we have developed various grades of products, such as a simple compounds composed of a bisphenol-A-type epoxy resin, dicyandiamide, and a filler, and those containing a low-temperature active curing agent for curing at 80 °C, as well as those comprising a heat-resistant resin to achieve high heat-resistance and those allowing a peeling adhesive force of 10 kg/25 mm width or more through rubber modification. The performance of these products has been proven.

Thanks to an increase in the demand for one-part epoxy resin and the development of various functional materials as a result of the efforts of material manufacturers, we have successfully developed proven products. We will continue to work to expand the possibilities of one-part epoxy resins.

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ThreeBond TECHNICAL NEWS

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