Epoxy Resin Adhesives

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Epoxy resin adhesives excel in adhesive properties, chemical resistance, heat resistance, mechanical properties, and electrical properties, and they are widely used even in joints that are subject to large loads over a long period in fields such as automotive, civil engineering, electronics, and space industries thanks to their high reliability. This article introduces the epoxy resin systems of our company, which meet the recent demands in adhesive applications, including environmental measures and durability improvement.

Epoxy resin

An epoxy resin is a compound which contains two or more epoxy groups in a molecule. It is usually used in combination with an epoxy resin curing agent (hereinafter referred to as the curing agent) to obtain the cured product of an epoxy resin (hereinafter referred to as the cured product) with various properties depending on the reaction.

Typical epoxy resins include bisphenol A-based epoxy resin with excellent electrical insulation and chemical resistance; novolak-based resin with multiple functions and high thermal resistance; and alicyclic epoxy resins with low viscosity and good color stability, and they are all used appropriately according to the characteristics of each to suit the purpose.

Our company markets "GLYCIALE PP-300P," which is made by glycidyl etherification of polyether. It can deliver a cured product that excels in flexibility when cured by combining it with bisphenol A-based epoxy resin, etc. **Table 1** shows examples of its properties.

Epoxy resin curing agent

There are various types of epoxy resin curing agents, and the curing conditions and working life are determined depending on the type and amount used. They also add various properties to the cured product **(Table 2)**.

● Polyamide polyamine-based curing agent

Polyamine-based agents are the most common type among the curing agents, and they deliver cured products with excellent adhesive properties. Of these, polyamide polyamine is synthesized by dehydration condensation reaction between carboxylic acid and polyamine, and it can be used to deliver many products with different levels of viscosity, amine values, and levels of reactivity depending on the types of raw material and their composition ratio. It has a relatively wide allowable range of the composition ratio to epoxy resin and a long pot life. Those with large molecular weights in particular show less skin irritation and can deliver cured products with high plasticity and flexibility, thereby improving the toughness and adhesiveness of cured products. They are used in highly versatile applications such as adhesives and paints to utilize these excellent features. Our company markets polyamide polyamine-based curing agents as the "POLYMIDE L" Series. **Table 3** shows a summary of the series.

● Acid anhydrate-based curing agent

Another characteristic curing agent is the acid anhydride curing

Table 1 Examples of the properties of "GLYCIALE PP-300P"

Name of product	Appearance	Viscosity (mPa·s)	Epoxy equivalent (g/eq)	Hydrolyzable chlorine mass (%)	Total chlorine mass (%)
GLYCIALE PP-300P	Light yellow liquid	Approx. 43 (25°C)	Approx. 296	Approx. 0.07	Approx. 0.18

Table 2 Types and characteristics of epoxy resin curing agents

Type	Main characteristics	Primary applications
Aliphatic polyamine	Excellent cold curing property and adhesive property	Casts, adhesives
Polyamide polyamine	High adhesive property	Civil engineering/ construction
Aromatic polyamine	High heat resistance, chemical resistance	Composite materials, laminated plates
Acid anhydride	Low viscosity, excellent electrical properties	Electric and electronics, powder paints
Mercaptans	Low-temperature curing	Adhesive
Phenol novolak resin	Excellent chemical resistance, electrical properties	Semiconductor sealing materials
Dicyandiamide	Latent curing agent	Composite materials, laminated plates, paints

agent. The acid anhydride curing agent has low viscosity, good workability, a long pot life of the mixture, and smaller shrinkage and heat generation from curing than other curing agents. However, it has disadvantages such as the need for heating to high temperatures for curing and susceptibility to the effects of humidity. The cured products also excel in electrical insulation, mechanical properties, and heat resistance, and cause less skin irritation than amine-based agents. It is thus also used for large molded products, electrical and electronic applications, etc. Our company markets alkenyl succinic anhydrides "DSA" and "PDSA-DA." Of the acid anhydrate-based agents, these are especially easy to handle thanks to their long pot life as well as low shrinkage and heat generation from curing, and they can deliver cured products with excellent physical and electrical properties. **Table 4** shows the properties of "DSA" and "PDSA-DA."

Epoxy Resin Adhesives

Since the cured products obtained by the reaction between epoxy resin and curing agents have good electrical properties, mechanical properties, adhesion with the base material, chemical resistance, water resistance, heat resistance, and dimensional stability, they are widely used as adhesives, paints, sealing materials, and casting resins in fields including electricity/electronics, civil engineering and construction, transportation machines, and ships. In particular, adhesives have become a major application because of their excellent adhesive property.

Epoxy resin adhesives come as liquid type in general, and are classified into; two-liquid types or one-liquid types.

Of these, two-liquid types which react at room temperature have good curing and workability and are widely used, as the cured products also have additional advantages such as adhesive strength, durability, and water resistance.

Utilizing our proprietary denaturation and compounding technologies, our company develops and distributes two-liquid type adhesives mainly for the civil engineering and construction fields. The adhesives for civil engineering and construction are described below.

Adhesives for civil engineering and construction

Adhesives for civil engineering and construction are used for building reinforcement and repair, lining on walls and floor materials, bonding and filling of anchors and screws, waterproofing of concrete, etc. Environmental consideration, improvement in production efficiency with reduction in man-hours, etc. are desired in adhesives. Higher durability is also desired depending on the intended use, and our company has developed products that meet these needs.

Application type permeable waterproof material "DOUBLE COAT S"

An epoxy resin system (which combines the resin, curing agent, additives, etc.), which is applied to the construction surface to form a waterproof layer, is used in many types of waterproofing works such as

Table 3 Overview of "POLYMIDE L" Series

Name of product	Appearance	Color number (Gardner)	Viscosity (mPa·s)	Total amine value	Adhesion performance test		
					Compounding ratio for adhesive (mass ratio)		Adhesive strength*2 (Mpa)
					Epoxy resin*1	POLYMIDE L	
L-45-3	Yellowish brown liquid	7	4,800 (40°C)	320	100	43	10
L-55-3	Yellowish brown liquid	4	1,700 (20°C)	380	100	43	10
L-504	Brown liquid	5	2,000 (25°C)	300	100	100	9
L-2513	Brown liquid	5	2,250 (30°C)	290	100	67	12
L-4051	Yellowish brown liquid	4	300 (20°C)	345	100	43	12

*1 Mitsubishi Chemical Corporation, jER828 (epoxy equivalent of 184 to 194 g/eq) *2 JIS K 6850

Table 4 Examples of properties of "DSA" and "PDSA-DA"

Name of product	Main ingredients	Appearance	Kinematic viscosity [mm^2/s]	Acid value	Specific gravity	Thermal reduction*3 (decomposition start temperature)
DSA	Dodecenyl succinic anhydride	Yellow liquid	Approx. 400 (25°C)	Approx. 412	1.00	186°C
PDSA-DA	Pentadecenyl succinic anhydride	Yellowish brown liquid	Approx. 850 (30°C)	Approx. 345	1.00	197°C

*3 Thermogravimetric analysis (under N_2 atmosphere, heating at 10°C/min)

water purification plants, sewage treatment plants, subways, pools, building foundations, pump rooms, elevator rooms, and water tanks.
As described above, there are also needs for environmental consideration and productivity improvement in these applications.
Our company's "DOUBLE COAT S" is an environment-friendly aqueous adhesive, as it is a system consisting of a solvent-free aqueous epoxy resin, aqueous polyamide polyamine and aggregate.
These are then combined at the construction site and applied to substrates such as concrete and vinyl chloride plate to form a waterproof layer with excellent alkali and acid resistance that is cured. Application to the substrate is relatively easy by means of trowels, rollers, sprays, etc., and it is also possible to apply it on wet surfaces.
Additionally, it delivers excellent adhesive strength between the "DOUBLE COAT S" layers applied on top of one another, and high adhesive strength to polyurethane and epoxy paints.
Taking advantage of these features, the "DOUBLE COAT S" System is used for many waterproof construction works.

Tables 5 and **6** show an outline and performance examples of the "DOUBLE COAT S" System.

Solventless epoxy resin Adhesive "EPOTIGHT"

In addition to reduction in the global environmental burden, adhesives for civil engineering, and construction have seen a shift toward solvent-free adhesives, water-based adhesives, and formaldehyde-free adhesives in consideration of the effects on the health of the workers.
"EPOTIGHT," our company's two-liquid type epoxy resin adhesive, has been designed to cure at the ordinary temperature and not to be designated as a deleterious substance by containing no solvents or formaldehyde. Inorganic filler is dispersed in both the main agent (epoxy resin) and the curing agent (polyamine), so that it cures at the room temperature.
"EPOTIGHT" has the following features:
[1] Workability and mechanical properties
To suit the environment of use at construction sites and other places, it is necessary that the product has an appropriate viscosity that can be applied to the adherend, sufficient pot life that can ensure the time to do the work, and drip resistance even when it is applied on vertical surfaces such as walls.
While thixotropy-imparting agents such as silica are often used in adhesives containing dispersed inorganic fillers for prevention of dripping and precipitation of the filler, this method has a disadvantage in the limited amount of inorganic fillers that can be used as the viscosity of the adhesive increases.
By combining with a high molecular weight polyether, our company has achieved excellent workability with the inorganic filler even while using a thixotropy-imparting agent, through high-concentration filling.
Due to the high content of the inorganic filler, it has high compression strength, and can also be used as an adhesive (structural adhesive) in joints that are subjected to large loads over long periods.
[2] Water resistance
Since "EPOTIGHT" is designed with hydrophobic raw materials and water has little effect on it even when the adhesive has not cured, it delivers sufficient strength even if there is a sudden rainfall after application at an outdoor construction site. Moreover, the cured products have excellent water resistance.
[3] Labor saving
"EPOTITE" is a two-liquid cartridge type product in which the epoxy resin component and the polyamine component are each filled in a cartridge container. To use, a static mixer is set to the two-liquid cartridge and the two liquids are mixed in a special extrusion device.
Since the two-liquid cartridge type does not require compounding processes such as weighing and mixing at the construction site, it results in labor saving for the workers and improvement in production efficiency. There is also no concern about using the wrong compounding ratio for the

Table 5 Outline of "DOUBLE COAT S" System

Name of product	DOUBLE COAT S-1	DOUBLE COAT S-2	DOUBLE COAT S-3
Outline	Main agent	Curing agent	Aggregate
Main ingredients	Epoxy resin	Polyamide polyamine	Water-cured inorganic material
Appearance	White liquid	Light yellow liquid	Grayish white powder
Formulation	5 kg	5 kg	25 kg

Table 6 Example of performance of "DOUBLE COAT S" System

Test item	Substrate	Test result	Test method
Adhesive strength	Pressed concrete plate	2.5 (MPa)	Test using a Building Research Institute type adhesion tester
	Vinyl chloride plate	1.5 (MPa)	
Pressurized water permeability	Concrete	0.14	In compliance with JIS A 1404 (tested under water pressure of 0.3 MPa) (Measurement values are expressed as water permeability ratios)

adhesive or insufficient mixing. Additionally, it is economical as only the necessary amount is used.

Non-shrinkage epoxy resin adhesive

While "EPOTITE" delivers such excellent characteristics, internal stresses are generated during the solidification process just like in other two-liquid type adhesives. The internal stress is known to be caused by the curing shrinkage stress that occurs during curing and the thermal shrinkage stress that occurs when it is cooled from the curing temperature to room temperature. When the internal stress increases, the stress on the interface between the adherend and the adhesive part causes problems such as decrease in adhesive strength and breakdown of the joint **(Fig. 1)**.
In order to reduce the internal stress and improve the durability, our company developed a solvent-free two-liquid curing epoxy resin adhesive that reduces the volume shrinkage from adhesive curing to almost zero.
The "developed product EP" is a two-liquid epoxy resin adhesive based on the previously described "EPOTITE," in which the reactive inorganic expansion agent is dispersed, and we were able to successfully reduce the volume shrinkage of the cured product to nearly zero by making adjustments so that the expansion agent expands in accordance with the curing rate of the epoxy resin. Additionally, since the inorganic expansion agent does not reduce the strength of the cured product, high adhesive strength is ensured. Application as a structural adhesive in the automotive field is also expected in addition to civil engineering and construction applications.
Tables 7 and **8** show the outlines of the "EPOTITE" and "developed product EP" Systems.
The demands for the products in the civil engineering and construction fields are expected to grow further in the future due to the increase in the number of public projects and housing operations, earthquake disaster recovery projects, and infrastructure establishment for the Olympics. The needs for epoxy resin adhesives have diversified in concurrence with this; including high adhesive strength, durability, and environmental measures. In order to respond to such diversifying needs, we will continue to improve our products and expand their applications.

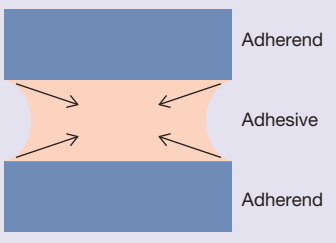

Fig. 1 Adhesive stress effect on the adhesive surface

References (Directly translated of Japanese title)

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[Contact (about the product)]
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Table 7 Characteristics of "EPOTITE" and "developed product EP" Systems

Item		Unit	EPOTITE	Developed product EP
Characteristics of mixture solution*4	Viscosity	mPa·s	55,000	52,000
	Thixotropic index	–	6.1	6.8
	Pot life	min.	55	35
Mechanical properties	Compression yield strength*5	N/mm^2	100	105
	Compressive elasticity modulus*5	N/mm^2	4,300	4,500
	Tensile strength*6	N/mm^2	33	35

*4 In compliance with JIS K 7117-1, test solution temperature: 25°C
*5 In compliance with JIS K 7181, test speed: 2 mm/min
*6 In compliance with JIS K 7161, test speed: 1 mm/min

Table 8 Adhesive strength to adherend

Item	Unit	EPOTITE	Developed product EP
Rate of volume change	%	▲3	0
Tensile shear strength [steel plate/steel plate]*7	N/mm^2	13.2	17.1

*7 In compliance with JIS K 6850, test speed: 10 mm/min