ThreeBond
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# Development Trend of Epoxy Resins 2006

## Introduction

We have developed and sold a wide variety of adhesives and sealants using epoxy resins as materials so far. Their supply is increasing year by year, and their deployment to new fields is expected by providing new characteristics.

However, development to comply with the regulations of substances of environmental concern is required so that it is clear that raw materials used for manufacturing are restricted and the option of resin design is narrower than before.

Under these circumstances, we have marketed products provided with various characteristics with curing properties, which characterize epoxy resins, and physical properties of cured objects are retained the balance.

There are examples of the value-added products that are added to light-curing property, anaerobic curing property, or high purity. Many of these products have been used for specific fields and places, making their application deployment difficult. As the result, small-lot production causes high cost, which is a factor to narrow further deployment.

To break through the current status, we have developed products from the view of general-purpose deployment. We will introduce development concept, characteristics, and future direction of our development products in this issue.

## Contents

## 1. About Low-temperature Fast-curing One-part Epoxy Resins

On one hand, thermal curing one-part epoxy resins (hereinafter referred to one-part epoxy resins) are relatively low cost and provided with good workability. On the other hand, there are some cases where they cannot be used for adherends with low heat resistance because heating up to as high as 100 to 150 °C or so is required during curing. In addition to our release of low-temperature-curing type one-part epoxy resins: ThreeBond 2200 Series and 2210 Series, we have developed ThreeBond 2277 that faster curing is enabled by using newly developed fast-curing epoxy resin and fast-curing agent this time.

### 1-1. About ThreeBond 2277

ThreeBond 2277 (hereinafter ThreeBond is abbreviated as TB) has the following characteristics:

1) Low-temperature fast curing (80°C×10min. or 60°C×15min.)
2) High adhesive strength (tensile shearing adhesive strength: 15MPa)
3) Phenomenon of uncuring due to separation of curing agent during curing of interstice does not occur

### 1-2. Comparison of Physical Properties

A comparison of physical properties of our current low-temperature-curing grade (TB2202) and the competitor's low-temperature fast-curing product is shown in Table-1 and a comparison of curing behavior, which indicates fast-curing property, is shown in Figure-1.

Table-1. Physical property table

| Characteristics/ physical properties | Unit | Competitor's low-temperature fast-curing product | TB2277 | TB2202 | Test method |
|---|---|---|---|---|---|
| Color and appearance | – | Creamy-white | Black | Black | 3TS-201-02 |
| Viscosity | Pa•s | 23 | 30 | 13 | 3TS-208-03 |
| Specific gravity | – | – | 1.14 | 1.14 | 3TS-213-02 |
| Hardness | – | 88 | 85 | 88 | 3TS-215-01 |
| Tensile shearing adhesive strength | MPa | 18 | 21 | 10 | 3TS-301-11 |
| Peeling adhesive strength | N/m | 1,000 | 1,200 | 160 | 3TS-304-21 |
| Glass transition point | °C | 42 | 80 | 105 | 3TS-501-05 |
| Linear expansion coefficient $\alpha_1$ | /°C | $40\times10^{-6}$ | $50\times10^{-6}$ | $74\times10^{-6}$ | 3TS-501-05 |
| Linear expansion coefficient $\alpha_2$ | /°C | $125\times10^{-6}$ | $138\times10^{-6}$ | Not measured | 3TS-501-05 |
| Uncured part due to separation | – | Existed | Not Existed | Existed | – |
| Storage condition | – | Freezer storage | Freezer storage | Cold storage | – |
| Curing condition of test piece | – | 80°C×30min. | ← | ← | – |

TB2277 has the great characteristics of high tensile shearing adhesive strength and no development of uncured part due to separation compared with TB2202 and the competitors' products.

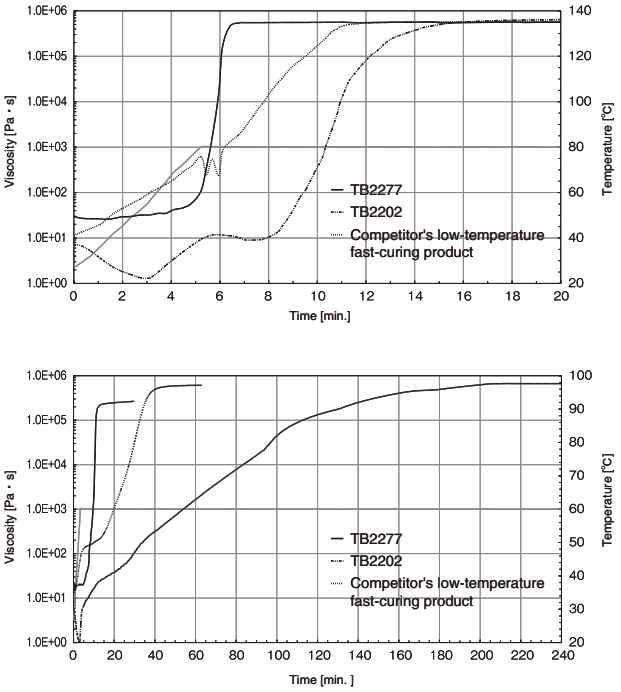


Figure-1. Comparison of curing behavior (Upper: curing at 80°C; Lower: curing at 60°C)

As shown in Figure-1, the curing reaction of TB2277 is so fast that it reaches the almost ultimate viscosity in 8 min. at 80°C and in 15 min. at 60°C. In addition, since no viscosity reduction occurs during heating with TB2277, the phenomenon of uncuring due to separation does not occur.

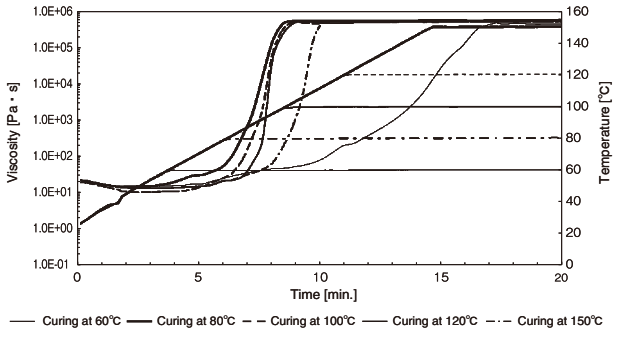


Figure-2. Comparison of curing behavior (TB2277)

Figure-2 shows the curing behavior of TB2277 for each curing temperature. It is confirmed that it has been cured within 10 minutes at temperature of above 80°C. Especially at temperature of above 100°C, it is confirmed that it has been cured before reaching the processing temperature.

This is a great feature of this newly developed fast-curing epoxy resin.

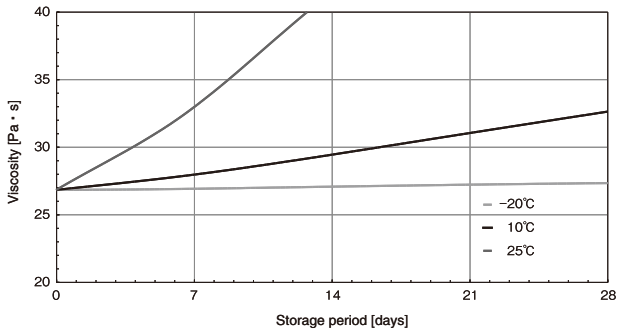


Figure-3. Storage data (TB2277)

Figure-3 shows data of storage stability (viscosity change) at each temperature. At room temperature (25°C), the viscosity almost doubled in 10 elapsed days.

### 1-3. Development Trend in Future

Although TB2277 is the product designed to place the highest priority on the fast-curing property using unprecedented fast-curing epoxy resin and fast-curing agent, it has the following disadvantages:

1) Freezer storage
2) High cost

We are planning to improve TB2277 for more general use in the future. Table-2 shows the target specifications.

Table-2. Target specifications

| | Unit | TB2277 improved product | TB2277 | TB2202 | Test method |
|---|---|---|---|---|---|
| Curing condition (60°C) | – | Good (Within 60 min.) | Excellent (15min.) | Fair (180min.) | – |
| Viscosity | Pa•s | 10 ～ 100 | 30 | 13 | 3TS-208-03 |
| Storage stability | – | 10°C | –20°C | 10°C | – |
| | | 4 months or more | 3 months or more | 7 months | |
| Glass transition point | °C | Excellent (120 or more) | Fair (80) | Good (105) | 3TS-501-05 |
| Tensile shearing adhesive strength | MPa | Excellent (20 or more) | Excellent (21) | Fair (10) | 3TS-301-11 |
| Uncuring due to separation | – | Not Existed | Not Existed | Existed | – |
| Price (/kg) | – | Good | Fair | Excellent | – |

We will improve the followings.

1) Cost reduction
2) Storage condition (cold storage)
3) Tensile shearing adhesive strength (20MPa or more)
4) Tg (120°C or more)
5) Curing condition (within 60 min. at 60°C)

Figure-4 shows the position of the improved product.

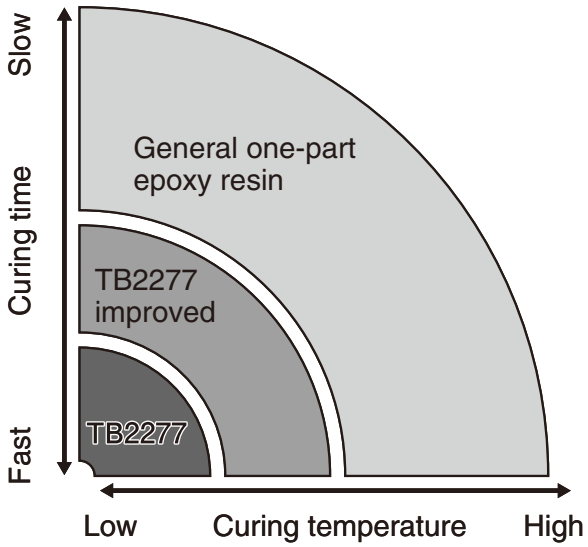


Figure-4. Positioning map of current product group (low-temperature-curing one-part epoxy)

Although it is inferior to TB2277 in fast-curing property at low temperature, we believe that there are enough advantages of workability and the like by developing products with cold storage capability. We are planning further cost reduction and improvement in specifications.

Besides them, we are examining UV-curing property added types and repairability added types as well.

## 2. About Structural Adhesives

It is generally known that epoxy resins have excellent shearing adhesive strength to adherends such as metal, glass, concrete, and wood, and they are used in various fields. In recent years, as the demand for additional applications increases, high performance in peeling adhesive strength, heat resistance, creeping property, and durability against time degradation is required as well as shearing adhesive strength.

The application of structural adhesives, which bond conventionally physically fastened parts by welding, bolt screwing, and the like is especially requested. For structural adhesives, improvement in not only shearing adhesive strength but also peeling adhesive strength is required.

However, in general, as the cured objects harden, although the shearing adhesive strength of the adhesives increases, the peeling adhesive strength tends to decrease inversely proportional to it. It is not easy to improve both adhesive strengths at the same time. Therefore although general epoxy resin based adhesives have high shearing adhesive strength, they do not satisfy the high peeling adhesive strength and flexibility of absorbing vibration and shock required for structural adhesives and the like. To satisfy these requirements, the methods to bind with chemical reaction, blend, or alloy [1] thermoplastic resins to epoxy resins are employed.

However, although it was possible to improve both shearing adhesive strength and peeling adhesive strength with these methods in a balanced manner, the obtained strength was still insufficient and it was in lack of reliability for use as structural adhesives. The development of resins excellent in both shearing adhesive strength and peeling adhesive strength is required.

### 2-1. About ThreeBond 2249G

So we have developed one-part heat-curing epoxy resin provided with both shearing adhesive strength and peeling adhesive strength.

Table-3 shows data of TB2249G, extra-strength one-part heat-curing epoxy resin.

Table-3. Characteristics and properties of TB2249G

| Test items | Unit | Characteristics | Test method |
|---|---|---|---|
| Color and appearance | – | Gray | 3TS-201-02 |
| Specific gravity | – | 1.59 | 3TS-213-02 |
| Viscosity | Pa•s | 75 | 3TS-210-02 |
| Hardness | – | D90 | 3TS-215-01 |
| Tensile shearing adhesive strength | MPa | 39 | 3TS-301-11 |
| T-type peeling adhesive strength | kN/m | 8 | 3TS-304-21 |
| Glass transition temperature | °C | 104 | 3TS-501-05 |
| Linear expansion coefficient | /°C | $42\times10^{-6}$ | 3TS-501-05 |

*Curing condition: 160°C×30min.

It has been confirmed that TB2249G is an epoxy resin provided with excellent adhesive strength that tensile shearing adhesive strength (SPCC-SD steel plate: 1.6×25×100mm) is 39.0MPa and T-type peeling adhesive strength (SPCC-SD: 0.5×25×150mm) is 8.0kN/m.

Figure-5 shows S-S chart [2] of tensile shearing adhesive strength of TB2249G and S-S chart of general epoxy resin (TB2252) as reference.

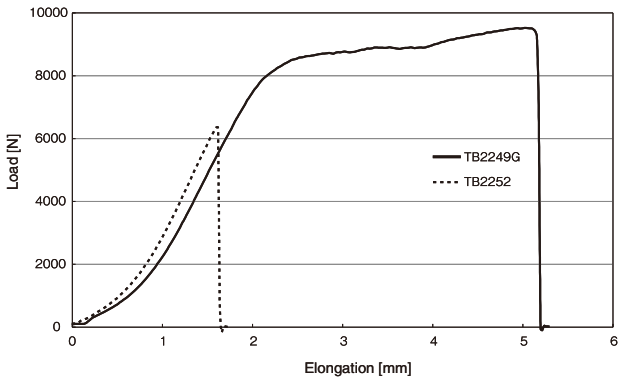


Figure-5. Shear S-S chart of TB2249G and TB2252

From the S-S chart above, it is recognized that TB2249G is provided with excellent toughness. During measurement of tensile shearing adhesive strength, resins with insufficient toughness will fracture before reaching the equilibrium state on the S-S chart due to elongation of the test piece. However, thanks to excellent toughness, TB2249G tolerates elongation of the test piece and has excellent tensile shearing adhesive strength. For this reason, after the tensile shearing adhesive strength test, elongation of the test piece was observed as shown in Photo-1.

In proportion to this toughness, it is provided with excellent adhesive strength at T-type peeling adhesive strength test as well. Photo-2 shows the appearance of the measurement of T-type peeling adhesive strength test. As shown in the photograph, it is recognized that cohesive failure has occurred, which indicates it is provided with high adhesion and bonding strength.

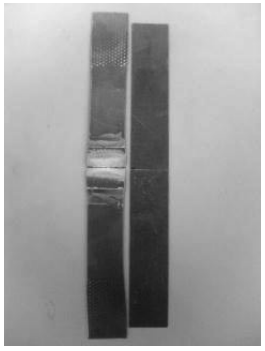

Photo-1. Test piece for tensile shear test
Left: After the test, Right: Before the test

Photo-2. Appearance of T-type peeling test

Since it was proved that it is provided with excellent adhesive strength to the SPCC-SD steel plate, adhesive properties to various adherends (metal) have been examined. The results of tensile shearing adhesive strength are shown in Table-4 and the results of T-type peeling adhesive strength are shown in Table-5. The data of TB2252 is listed as reference.

Table-4. Tensile shearing adhesive strength of various adherends

| TP type | Tensile shearing adhesive strength (MPa) | | Length of test piece (mm) |
|---|---|---|---|
| | TB2249G | TB2252 | |
| SPCC-SD | 39 | 26 | 1.6×25×100 |
| SUS430 | 36 | 19 | 1.5×25×100 |
| A1050P | 22 | 19 | 2.0×25×100 |
| SPCC-SB (Ni plating) | 35 | 23 | 2.0×25×100 |
| SPCC-SB (hexavalent chromium plating) | 38 | 24 | 1.6×25×100 |
| SPCC-SB (trivalent chromium plating) | 31 | 20 | 1.6×25×100 |

* Test method: 3TS-301-11

Table-5. T-type peeling adhesive strength of various adherends

| TP type | T-type peeling adhesive strength (kN/m) | |
|---|---|---|
| | TB2249G | TB2252 |
| SPCC-SD | 8.0 | 4.5 |
| SUS430 | 3.6 | 0.6 |
| A1050P | 4.5 | 3.0 |
| SPCC-SB (Ni plating) | 4.0 | 2.0 |
| SPCC-SB (hexavalent chromium plating) | 5.0 | 2.0 |
| SPCC-SB (trivalent chromium plating) | 2.7 | 1.0 |

* Test method: 3TS-301-11

Although inferior to the SPCC-SD steel plate, it has been confirmed that it is provided with excellent bonding strength to various adherends.

TB2249G has the following features:

- Includes modified epoxy resin to improve toughness and adhesion.
- Selects fillers to eliminate brittleness of the resin.
- Selects curing agent to provide toughness to the resin and eliminate brittleness.

## 2-2. Development Trend in Future

At present, we are examining various grades of TB2249G.

- Low-temperature-curing type (curing time: 100°C×60min. or so)
- High Tg type (glass transition temperature: about 150°C)

By developing these grades, one-part heat-curing epoxy resins with very high reliability for various fields and applications can be provided.

1) Alloy type
2) Elongation – load chart

## 3. About Frozen Epoxy Resin

Frozen epoxy resin are new type adhesives, which are provided to users in the retained temperature of −20°C after mixing and stirring of main agent and curing agent, which are sold as two-part epoxy resin conventionally.

They have the following advantages compared with conventional one-part epoxy resins.

(1) Uncuring due to separation does not occur.

Since the curing agent is liquid component, there is no uncuring due to separation. With conventional one-part epoxy resins, the issue of uncuring due to separation has not been completely solved, but there is no problem with the frozen epoxy resins.

(2) Low viscosity (5Pa•s or less) can be achieved.

Since many of the curing agents of conventional one-part epoxy resins have been solid, there was a limit to the effort to make the resin with low viscosity; however, since the curing agents of frozen epoxy resin are liquid, it is possible to make it with low viscosity.

(3) Curing temperature can be controlled.

Since curing agent for two-part epoxy resin is used, curing temperature can be set widely to range from 25 to 150°C. Furthermore, since the curing agents, which could not be used conventionally for one-part type, can be used, unprecedented chemical resistance and heat resistance can be achieved.

Moreover, compared with conventional two-part epoxy resins, since the operation of mixing and stirring is not required, they can be used easily without worrying of uncuring caused by measuring mistakes and insufficient stirring.

On the other hand, disadvantages are that they must be frozen (−40 to −20°C) when storing and transporting and they cannot be restored once they have been used at room temperature. Therefore the quantity is required to use up at one time.

### 3-1. About Status of Development

Prototype 20X-343 is the first frozen epoxy resin manufactured in our company. The characteristics are shown in Table-6.

Table-6. Characteristics and physical properties of prototype 20X-343

| | Unit | Measured value | Test method |
|---|---|---|---|
| Color and appearance | – | Transparent light brown | 3TS-201-02 |
| Viscosity | Pa•s | 2 | 3TS-210-05 |
| Specific gravity | – | 1.14 | 3TS-213-02 |
| Pot life | min. | 60 | *1 |
| Tensile shearing adhesive strength | MPa | 20 | 3TS-301-11 |
| Volume shrinkage ratio | % | 2.54 | 3TS-228-01 |
| Glass transition point | °C | 111 | 3TS-501-05 |
| Storage modulus | Pa | $2.5\times10^{9}$ | 3TS-501-04 |
| Linear expansion coefficient | /°C | $63\times10^{-6}$ | 3TS-501-05 |

*1. Until the viscosity increase of up to 40% (25°C)
* Curing condition: 150°C×5min.

Figure-6 shows the viscosity change by freezer storage. Although small amount of viscosity increase was observed during freezer storage, it has a slight effect on the pot life.

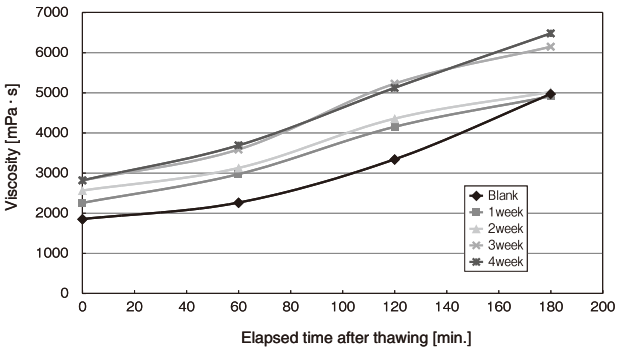


Figure-6. Viscosity change of prototype 20X-343 by freezer storage

As mentioned above, to use its own low viscosity and high reliability, which one-part epoxy resins cannot perform, we have considered it for use to adhere small areas, where heat resistance and chemical resistance are required.

### 3-2. Development Trend in Future

At present, we are developing some types with extended pot life with the same curing conditions. They enable us to make available operating time elongated and increase in the quantity used at once is possible.

In addition, we are examining reduction in curing time, low-temperature curing, improvement in various characteristics, and the like as well. As a development example, the characteristics of prototype 20X-382B are listed below.

Table-7. Properties of prototype 20X-382B

| | Unit | Measured value | Test method |
|---|---|---|---|
| Color and appearance | – | Light yellow | 3TS-201-02 |
| Viscosity | Pa•s | 8.0 | 3TS-210-05 |
| Specific gravity | – | 1.15 | 3TS-213-02 |
| Pot life | h | 10 or more | *1 |
| Tensile shearing adhesive strength | MPa | 25 | 3TS-301-11 |
| Volume shrinkage ratio | % | 3.15 | 3TS-228-01 |
| Glass transition point | °C | 113 | 3TS-501-05 |
| Storage modulus | Pa | $2.9\times10^{9}$ | 3TS-501-04 |
| Linear expansion coefficient | /°C | $74\times10^{-6}$ | 3TS-501-05 |

*1. Until the viscosity increase of up to 40% (25°C)
* Curing condition: 100°C×1h

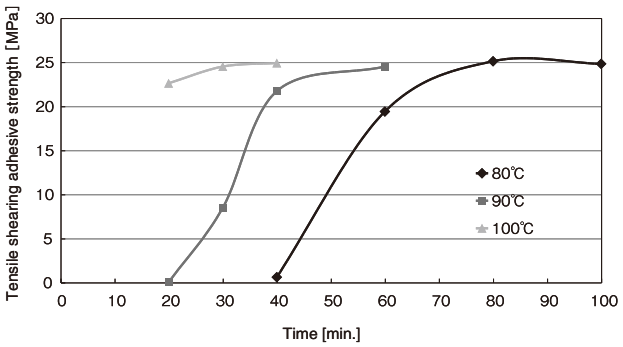


Table-7. Low-temperature-curing property of prototype 20X-382B

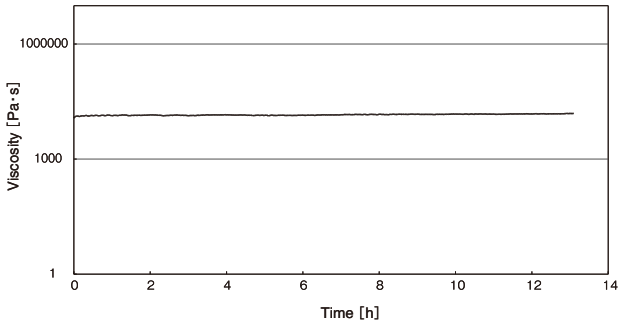


Figure-8. Viscosity change at room temperature

As listed above, low-temperature curing, pot life of 10 hours or more, high adhesive strength, and the like have been achieved.

Table-8. Comparison with prototype 20X-382B and general products

| | Separation | Pot life | Low-temperature curing | Storage |
|---|---|---|---|---|
| 20X-382B | Good | Good | Good | Poor |
| General-purpose one-part epoxy resin | Fair | Good | Fair | Fair |
| General-purpose two-part epoxy resin | Good | Poor | Good | Good |

Here, we introduce a special prototype for low viscosity. Prototype 20X-343-20 has been developed as an underfill agent. Basic characteristics and physical properties are as follows:

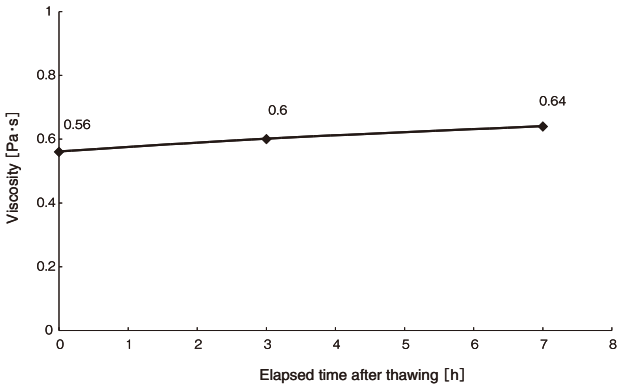


Figure-9. Viscosity change at 25°C of prototype 20X-343-20 after thawing

Prototype 20X-343-20 has achieved low viscosity of 1 Pa•s or less, and it has also high permeability even at room temperature.

Table-9. Physical property of prototype 20X-343-20

| | Unit | Measured value | Test method |
|---|---|---|---|
| Tensile shearing adhesive strength | MPa | 14 | 3TS-301-11 SPCC SD |
| Glass transition point (TMA method) | °C | 104 | 3TS-501-05 |
| Storage modulus (DMA method: E") | °C | 102 | 3TS-501-04 |
| Loss modulus (DMA method: tanδ) | °C | 122 | |
| Storage modulus | Pa | $1.5\times10^{9}$ | |
| Linear expansion coefficient | /°C | $83\times10^{-6}$ | 3TS-501-05 25°C ～ 80°C |

* Curing condition: 150°C×10min.

Furthermore, prototype 20X-343-20 is so excellent adhesive strength and heat resistance that it can be cured in a short time curing.

Utilizing these features, frozen epoxy resins are expected for applications in a variety of fields including small relays, and adhesion of various parts of HDD as well as underfill agents.

## Conclusion

The history of epoxy resins goes back a long way and our products have been used for various fields.

We are considering what kinds of features should be provided to epoxy resins, which have high performance as raw materials.

In this issue, we have introduced some characteristics of epoxy resins: low-temperature curing, extra strength, and frozen technology.

Regarding above mentioned development products, we are now taking the long view of product lineups not only for specific fields but also for general use.

We will comply the regulations of substances of environmental concern and continue to develop products, which can be widely used for you by advancing further reform and improvement in the future as well.

In addition, we are planning to market products, which match your needs, timely.

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