Introduction
UV-curing resin TB3000 Series have the features of excellent workability in mass production line such as one-part, 100% reaction type, and a few seconds of fast curing and excellent physical properties of the cured object.

Because acrylic oligomers are used as main component in TB3000 series, they were requested to improve their water resistance and heat resistance.

Our researchers have conducted research based on the potential of UV-curing epoxy (hereinafter referred to as “UVE”) and succeeded in developing UVE series. Epoxy resins are widely used due to their excellent mechanical, electrical, and chemical properties.

UVE series have the cationic polymerization mechanism, which is different from conventional acrylic grades with the radical polymerization mechanism. As a result, the wider application has become available.

“SINX” is the development code name for “Weak-UV-curing Epoxy Resin,” developed as sister grades of this UVE series.
1. About Photopolymerization Reaction Mechanism

1-1. Comparison of Radical Polymerization and Cationic Polymerization

Reaction mechanism is classified roughly into the radical polymerization and the cationic polymerization type.

Table 1. Comparison of photopolymerization type

<table>
<thead>
<tr>
<th></th>
<th>Radical type</th>
<th>Cation type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resin</td>
<td>Various acrylates, Urethane, Polyester, etc.</td>
<td>Epoxy, Vinyl ether, etc.</td>
</tr>
<tr>
<td>Reaction mechanism</td>
<td>Free radical</td>
<td>Lewis acid, Bronsted acid</td>
</tr>
<tr>
<td>Curing speed</td>
<td>Fast</td>
<td>Medium</td>
</tr>
<tr>
<td>Oxygen blocking</td>
<td>Exist</td>
<td>Non</td>
</tr>
<tr>
<td>Curing shrinkage</td>
<td>Significant</td>
<td>Low</td>
</tr>
<tr>
<td>Adhesive property</td>
<td>Medium</td>
<td>Good</td>
</tr>
<tr>
<td>Heat resistance</td>
<td>Medium</td>
<td>Good</td>
</tr>
</tbody>
</table>

The radical type is composed of acrylate or unsaturated polyester/styrene. Therefore, as clearly shown in Table 1, although the curing speed is very fast, there are some problems regarding oxygen blocking, curing shrinkage, and adhesive property, etc., improvement of which are the objectives of our research.

1-2. Curing Process of Cationic UV Polymerization

UV light

UV (h ν)

Catalyst

Photodecomposition

Lewis acid/Bronsted acid

Start

Epoxy group

Propagation

Polymerization

1-3. Examples of Typical Cationic Polymerization (From catalyst type)

Table 2. Typical Cationic Polymerization Initiator

<table>
<thead>
<tr>
<th>No.</th>
<th>Type</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Diazonium salt</td>
<td>Coating</td>
</tr>
<tr>
<td>2</td>
<td>Iodonium salt</td>
<td>Coating, Encapsulant</td>
</tr>
<tr>
<td>3</td>
<td>Sulphonium salt</td>
<td>Coating, Encapsulant, Adhesive</td>
</tr>
<tr>
<td>4</td>
<td>Metallocene compound</td>
<td>Screen ink, Adhesive</td>
</tr>
</tbody>
</table>

The reaction mechanisms of the four types listed in Table 2 are shown below.

(1) Diazonium salt

\[
\text{R} - \underbrace{\text{N}^\ominus = \text{NBF}_3^+}_{\text{UV (h ν)}} \rightarrow \text{R} - \underbrace{\text{N}^\ominus + \text{N}_2 + \text{BF}_3^-}_{\text{(Lewis acid)}}
\]

\[
\text{BF}_3^- + \text{O}_\text{(Epoxy group)} \rightarrow \text{C} - \text{C}^\ominus + \text{C} + \text{C}^\ominus + \text{C} - \text{C}^\ominus + \text{C} - \text{C}^\ominus + \text{C} - \text{C}^\ominus
\]

(2) Iodonium salt

\[
\text{Ar}_2\text{I}^\ominus \overset{\text{UV (h ν)}}{\rightarrow} \text{Ar}_2\text{I}^\ominus + \text{Ar}^\ominus + \text{Solvent}^+ + \text{HX}^-(\text{Lewis acid})
\]

HX + M (Monomer) → Polymer

(3) Sulphonium salt

\[
\text{Ar}_2\text{S}^\ominus \overset{\text{UV (h ν)}}{\rightarrow} \text{Ar}_2\text{S}^\ominus + \text{Ar}^\ominus + \text{Solvent}^+ + \text{HX}^-(\text{Lewis acid})
\]

HX + M (Monomer) → Polymer
2. Product Form

Thanks to the excellent preserving property in epoxy resin, if filler or carrier fiber is selected properly, they can obtain the following various materials.

1) Compound products (including high-load products)
2) Pre-preg products
3) Composite products

1) The high-load compounds are liquid SINX resins, with which inorganic fillers such as silica powder, silica rock, talc, and glass chop are added. They are enclosed into the desired containers according to each characteristic and applications.

- Liquid, paste, putty, mortar, and bead
- Plastic bottle, syringe, aluminum tube, compaq aerosol can, cartridge, role of separate paper, aluminum pouch, and AE can

2) Pre-preg

Glass fibers impregnated with SINX resin for absorption.

- Glass cloth, mat, tape, roving, and code shape.
- Cover film is attached, roll magazine coiling

These pre-pregs are transformed to the requested shapes during curing. Then, FRP is obtained by UV irradiation. The molding methods include vacuum forming, posting molding, wrap around, filament winding molding, stitch method, and extrusion, etc.

3) Composite Materials

Composite materials are combination of the SINX resin and metal plates or glass or plastic moldings. They have been developed aiming at the simultaneous development of the features of the compositions.

- Metal sheet . . . . . Wire net, steel paper, aluminum foil, and copper foil, etc.
- Glass material . . . . . Glass bead and glass plate, etc.
- Polymeric materials . . PVC tube and hard polyurethane foam, etc.

The molding methods include compressive molding and tape lining, etc.

4) There are various technological ideas for special applications.

(Example) 3-D printed circuit board manufacturing process

- Static UV-curing powder coating
- Bolt/nut anti-loosing cap
- Assembly of filters

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(4) Metalloocene compound

$X = BF_3, PF_5, SbF_5, AsF_5$ etc.

$Ar = \text{CH}_3, \text{CH}_2$, etc.

$\text{CH}_3 \quad \text{O} \quad \text{et}$. etc.

\[ Fe \quad PF_5 \quad (\text{Lewis acid}) \quad \text{CH}_3 \]

\[ Fe \quad PF_5 \quad \text{O} \quad \text{C} \quad \text{R} \]

\[ Fe \quad PF_5 \quad \text{O} \quad \text{C} \quad \text{R} \]

1-4. What is SINX?

SINX is the abbreviation of Simultaneous Interpenetrating Polymer – Network of Experimental Grades

This is generated from a IPN (a polymer composed of intertwined circular polymers like the rings of the Olympic Games mark).
### 3. Product Lineup

#### Table 3. Product lineup

<table>
<thead>
<tr>
<th>Classification</th>
<th>Uncured object products</th>
<th>Cured object products</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Form</td>
<td>Package/Shape</td>
</tr>
<tr>
<td>Compound (liquid material)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Liquid</td>
<td>Bottle</td>
</tr>
<tr>
<td></td>
<td>Paste</td>
<td>Syringe</td>
</tr>
<tr>
<td></td>
<td>Cake</td>
<td>Aluminum tube</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Aluminum compound</td>
</tr>
<tr>
<td></td>
<td></td>
<td>333c.c. cartridge paste</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pre-preg</td>
<td>Glass fiber</td>
<td>Cloth mat</td>
</tr>
<tr>
<td></td>
<td>Tape</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Roving</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Composite Material</td>
<td>Metal sheet</td>
<td>Wire net</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Steel paper</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Aluminum foil</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Copper foil</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Bead</td>
</tr>
<tr>
<td></td>
<td>Glass</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Note: The photographs of the number (1), (2), (3),..., and (12) in the Table are shown in Photo 1, Photo 2, Photo 3,..., Photo 12, respectively.

« Part of application examples of the product lineup »

![Photo 1. SINX shell pack](image1.jpg)
Wire harness connection cured objects

![Photo 2. SINX solid resin](image2.jpg)

![Photo 3. Bolt/nut anti-loosening caps](image3.jpg)

![Photo 4. Polyvinyl chloride tube reinforcing cured objects using SINX pre-preg](image4.jpg)
Photo 5. SINX pre-preg cured objects

Photo 6. Providing rigidity to pre-preg (providing dent resistance to the doors of automobiles)

Photo 7. Vacuum forming of SINX pre-preg (oil pan)

Photo 8. Air filter adhesive materials of SINX pre-preg

Photo 9. Honeycomb moldings using SINX pre-preg

Photo 10. 3-D circuit boards using SINX pre-preg

Photo 11. Bonding SINX pre-preg and copper mesh

Photo 12. Bonding SINX pre-preg and stainless foil
4. Characteristics of UV-curing Type Cationic Polymerization Epoxy (SINX)

4-1. Characteristics

The characteristics of UV-curing type cationic polymerization epoxy resin are as follows:

The resins before curing have the characteristics listed below.

- One-component
- 100% reaction type
- Good preserving property
- Odor-free or light odor
- Lower toxicity

The cured objects are excellent in the characteristics listed below.

- Heat resistance
- Mechanical properties
- Electrical properties
- Chemical properties

Light-curing epoxy provided with these excellent workability and characteristics of cured objects shows the unique propagation curing property in addition. This is the property that once the (cationic) polymerization reaction starts, curing continues to be completed without external energy supply.

4-2. Curing by Sunlight (Weak UV)

After assembling the equipment below, put liquid SINX in it to the depth of 1mm. Take the equipment to the outside and check the curing time of SINX.

![Curing equipment by sunlight (weak UV)](image)

**Figure 1. Curing equipment by sunlight (weak UV)**

**Figure 2. Curing time by sunlight (weak UV)**
4-3. Depth Curing Property

After assembling the equipment below, fill the sleeve made from Teflon with liquid SINX.

And then, perform a given UV irradiation from above the Teflon sleeve and measure the thickness of the cured part of liquid SINX.

Internal diameter 10mm, length 40mm, and thickness 2mm
Sleeve made from opaque PTFE
Double-sided adhesive tape
UV irradiation conditions: 4kw High-pressure mercury lamp*1)
Irradiation distance 20cm
Irradiation time 14 seconds
Irradiation intensity 2000mJ/cm2

*1) Curedlight HMW-244-5CM made by ORC Mfg. Co. Ltd.
*2) UV actinometer UV-350 made by ORC Mfg. Co. Ltd.

Table 4. Exposure time and depth curing property after completing irradiation

<table>
<thead>
<tr>
<th>T: Time</th>
<th>H: Curing depth</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>4.8mm</td>
</tr>
<tr>
<td>1</td>
<td>5.2mm</td>
</tr>
<tr>
<td>4</td>
<td>5.4mm</td>
</tr>
<tr>
<td>8</td>
<td>6.5mm</td>
</tr>
<tr>
<td>24</td>
<td>8.7mm</td>
</tr>
</tbody>
</table>

Figure 3. Depth curing property measuring equipment

As shown in Table 4 and Figure 4, depth curing proceeds with elapsed time.
4-4. About Characteristics of SINX Compound (shell pack)

1) Properties and performance values

(1) Properties and performance

Table 5

<table>
<thead>
<tr>
<th>Appearance</th>
<th>Transparent</th>
<th>Non-fluid cake</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific gravity</td>
<td>1.14</td>
<td></td>
</tr>
<tr>
<td>Standard curing condition</td>
<td>10 seconds</td>
<td>Irradiator . . . . . . . . 4kw Focused cold mirror</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Illumination . . . . . . . . 142mw/cm^2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Irradiation distance . . . . . . . 15cm</td>
</tr>
<tr>
<td>Hardness (Shore D)</td>
<td>25°C . . . . . . 88</td>
<td></td>
</tr>
<tr>
<td></td>
<td>50°C . . . . . . 78</td>
<td></td>
</tr>
<tr>
<td></td>
<td>80°C . . . . . . 72</td>
<td></td>
</tr>
<tr>
<td></td>
<td>100°C . . . . . . 42</td>
<td></td>
</tr>
</tbody>
</table>

(2) Preserving property

Preserve at cool and dark place.
Avoid exposure to direct sunlight or weak UV (260nm), especially.

2) Curing property

(1) Objectives

Samples should be cured after they are UV-irradiated within 10 seconds or less.

(2) Irradiation method

After setting the shell pack together to put into an aluminum cup, deliver to the beltline, then irradiate from the above.

(3) Irradiator

Compare type 4000CM (ThreeBond Automation Equipment Co., Ltd.)
Output 4 kw
Lamp Focused cold mirror

(4) Irradiation conditions

Irradiation distance 15cm
Irradiation time 5 seconds, 10 seconds, and 15 seconds
Illumination 142mw/cm^2

(5) Decision

Measurement of curing
Measure the hardness of the cross sections by cutting the UV irradiated samples after each designated time.

3) Hardness

(1) Temperature - hardness

After exposing the samples, which were cured under the standard curing condition, for 24 hours, expose the cured objects at each temperature for 60 minutes for stabilization, then measure the hardness immediately.

Table 7

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Hardness (Shore D)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50°C</td>
<td>74 to 78</td>
</tr>
<tr>
<td>80°C</td>
<td>66 to 72</td>
</tr>
<tr>
<td>100°C</td>
<td>40 to 42</td>
</tr>
</tbody>
</table>

(6) Result

Table 6 (D Scale)

<table>
<thead>
<tr>
<th>Irradiation time</th>
<th>Elapsed time</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 seconds</td>
<td>10 seconds</td>
</tr>
<tr>
<td>After 12 hours</td>
<td>64 to 70</td>
</tr>
<tr>
<td>Low part is not cured</td>
<td>Completely cured</td>
</tr>
<tr>
<td>After 24 hours</td>
<td>68 to 74</td>
</tr>
<tr>
<td>Low part is not cured</td>
<td>Completely cured</td>
</tr>
</tbody>
</table>

(7) Conclusion

Since the measured hardness of the samples of 10 seconds and 15 seconds irradiation are ranged 82 to 86 after 3 days, the sample of irradiation curing of 10 seconds has passed with the above-mentioned conditions.
Table 8

<table>
<thead>
<tr>
<th>Sample</th>
<th>Thickness (mm)</th>
<th>Weight (g)</th>
<th>Bending rigidity (kg•mm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single steel sheet</td>
<td>0.3</td>
<td>19</td>
<td>4,000</td>
</tr>
<tr>
<td>+ Plain pre-preg</td>
<td>1.3</td>
<td>22</td>
<td>20,400</td>
</tr>
<tr>
<td>+ Single rib</td>
<td>1.3</td>
<td>23</td>
<td>75,900</td>
</tr>
<tr>
<td>+ Cross rib</td>
<td>1.3</td>
<td>24</td>
<td>93,000</td>
</tr>
<tr>
<td>Single steel sheet</td>
<td>0.38</td>
<td>24</td>
<td>8,100</td>
</tr>
</tbody>
</table>

- Chopped strand mat pre-preg 1.0mm
- 40mW/cm² × 30 seconds, from rib R3
- Cold-rolled steel sheet, JIS (Japanese Industrial Standard) G3141, 150 × 50 × 0.3mmt

Figure 5. The method to provide rigidity to thin steel sheet by SINX re-preg
1. Original sheet of the pre-preg
Dip the glass cloth into SINX undiluted solution to impregnate. And then, stick the separate paper on it and store it in dark place.

2. Cut to the standard size
Before using, take the original sheet of the pre-preg from the storage area and cut to the standard size.

3. Fix the rib
Place the pre-preg, which was cut to the standard size, on the master block, flow hot air by a dryer to adjust shape.

4. Cure the rib part (primary cured object)
Mask all the surface except the rib part. And then, irradiate UV to cure the rib part.

5. Stack storage
Store the pre-pregs made in the step (4).

6. Primer coating
Coat SINX primer on the thin steel sheet, and affix the pre-preg to the rib made in the step (4) together.

7. Curing (secondary cured object)
Irradiate UV to the whole to bond and cure the pre-preg.

As shown in the Table 8, SINX pre-preg values of bending rigidity are about 5 to 20 times higher, compared with thin steel sheet. Of course, the values may depend on the shape of the rib.

As these mentioned above, SINX pre-preg indicates a future direction in providing dent resistance (rigidity) while weight saving trend has progressed in various market.

5. Future Prospects and Objectives of UV-curing Type Cationic Polymerization Epoxy Resin

There are generally two-component type and one-component type epoxy resin adhesives. The two-component type is supplied with the epoxy resin and curing agent in liquid or paste. The two component are mixed to form adhesion layer and cured at room temperature or heat cured. The one-component type is supplied as the mixture with potential curing agent in paste, therefore users can use it immediately without mix work.

SINX belongs to the type containing potential curing agent in a broader sense. To achieve higher performance after the cationic catalyst curing system is measured in its own reactivity, it will be the key to research for new types of epoxy resin or system availability.

Conclusion

SINX is the newly developed product. Only part of the features has been introduced in this issue. We think that it has great future potential. We also wish to present the application part of SINX in the near future.

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