Measurement method for curing shrinkage rate and shrinkage stress of epoxy resin

AcroEdge Co., Ltd.
Kenichi Nakaushu

Diverse the applications of functional resins

Functional resins are used in a wide range of applications

Electric, Electronic devices

Chemical products

Automobile equipment

Precision devices








These products are highly affect to the device/machine performance

Functional resins require high specifications

Application of adhesive technology

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Electronics and display

Semiconductor resist
- Liquid resist
- Dry film resist
- Colored resist
- Dicing tape
- PDP electrode material
- Prism sheet
- Nanoimprint

Plastic coating

PVC flooring
- Bicycle lenses and reflectors
- Interior
- Hard coat
- Functional film

Wood products

Clear coating
- Colored coating
- Floor coating
- Filler
- Sealer

Printing plates and inks

Overprint coating
- Clear coating
- Offset
- Screen
- Letterpress
- Ink jet

Can coatings
- Overprinting

Metal coating

Tube pipe
- Name plate
- Wire

Adhesive bonding

Pressure-sensitive adhesive
- Optical lens
- Laminate

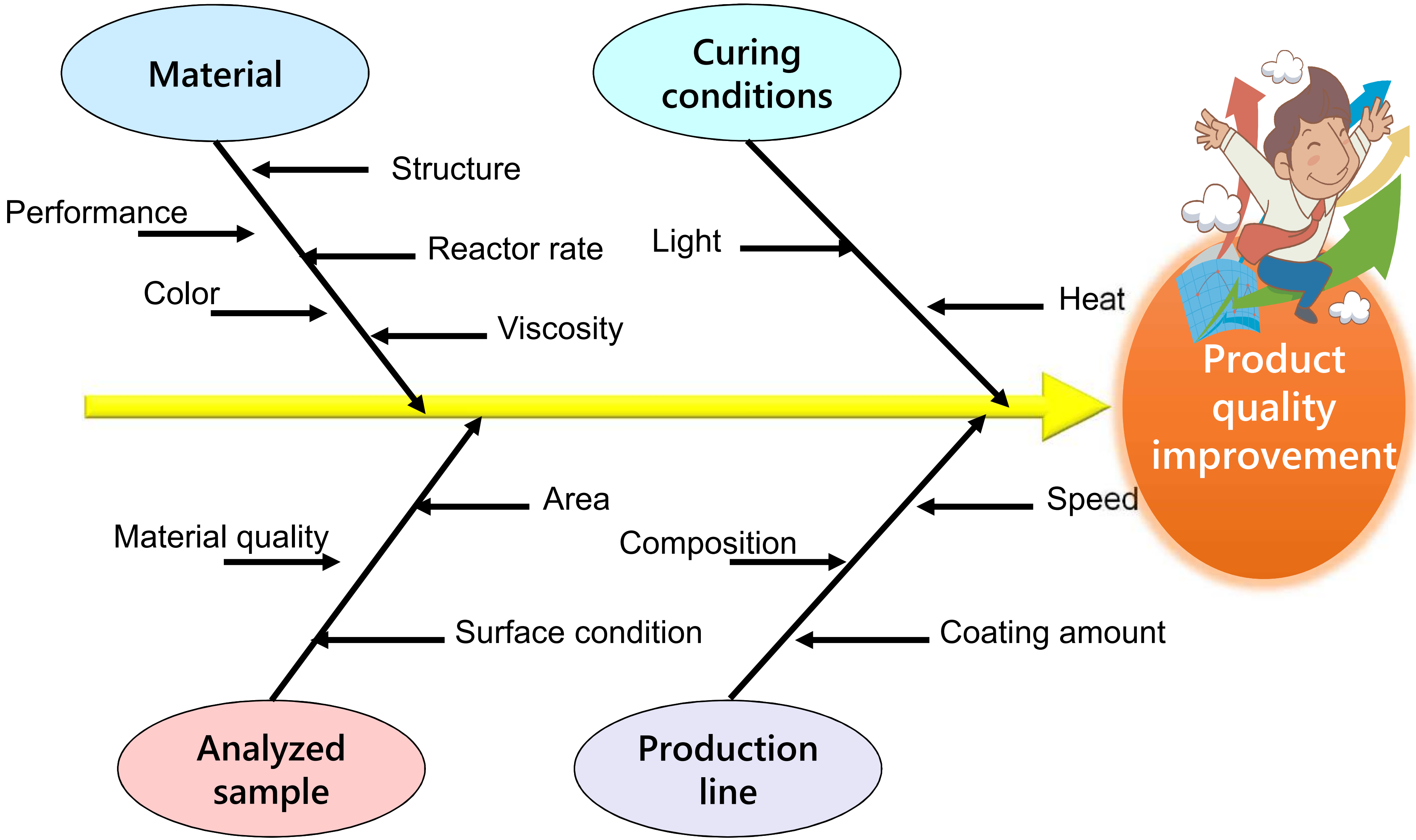
Fiber coating
- Optical fiber

Dental material

3D optical modeling

Silicon release paper

Factors that affect each other



Requirements for resin performance

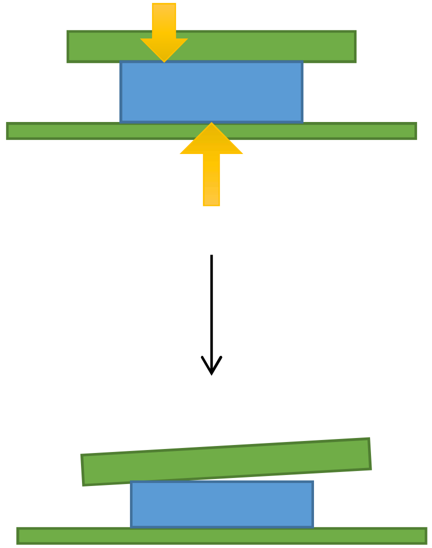
What are the necessaries for resin performance?

- **Performance of the resin itself**
- **Performance due to interaction with the object**

It is necessary to understand the history of resin behavior

Adhesion and curing shrinkage stress

Stress expression



Adhesive bonding

1. Diffusion theory
2. Chemical absorption theory
3. Anchor theory

Balance with resin stress

Current state of the curing shrinkage rate measurement

- Densitometry (JIS K-56002 4)

Measure the density before and after curing and calculate the cure shrinkage from the density change.
Volume shrinkage rate:

$$r = \frac{ds - dl}{dl} \times 100$$

where:

dl: specific density of liquid before curing
measured by specific gravity bin method
ds: specific gravity of solid after curing
individual specific gravity measurement method (tactics in liquid)

- General test methods for thermosetting plastics (JIS K6911)

Cure the 20 x 1.0 x 1.0 cm rod-shaped mold and measure the shrinkage rate in longitudinal direction

5.2.1 Specific gravity cup method

5.2.1.1 Apparatus

Analysis device, as following:

a) Gravity cup

5.2.1　比重カップ法

5.2.1.1　装置

装置は，次による。

a) **比重カップ**　比重カップは，図 **1** に示す形状・寸法であって，内容積が 100 ml のもの。材質は，黄銅製クロムめっき仕上げをしたもの又はステンレス製のもので，カップの質量は 200 g 以下とする。吹き出し穴は，試料の流動性などによって，適切な大きさのものを選ぶ。

b) **温度計**　温度計は，**JIS B 7410** に規定するタグ密閉式低引火点用温度計（TAG-50），又はこれと同等の精度のもの。

c) **恒温槽**　恒温槽は，かき混ぜ装置のあるもので，23 ℃±2 ℃の一定温度に保つことのできるもの。

d) **はかり**　はかりは，ひょう量 100 g 以上，かつ，感量 100 mg 以下のもの。

単位　mm

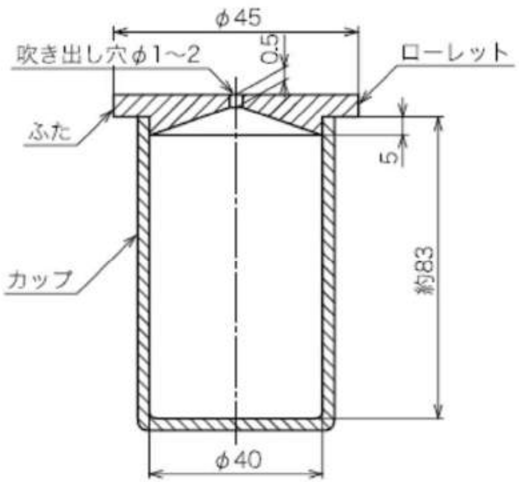


図 1－比重カップの形状・寸法

JIS K 6833

5.2.1.2　手順

b) 室温まで放冷した後，ふたとともに，その質量 (W_1) をはかる。

c) 測定温度付近に調節した水を，泡が入らないように，ふたの吹き出し穴からあふれ出す量を比重カップに入れ，ふたをする。測定温度に保った恒温槽中に 1 時間保持する。

d) 比重カップを恒温槽から取り出し，あふれた水をぬぐいとり，外面に付着した水滴などを清浄な布でよくふき取る。この比重カップの質量 (W_2) をはかる。水及び比重カップは，あらかじめ温度 23 ℃ ±2 ℃に保っておく。

e) 比重カップを乾燥した後，水の代わりに試料を用い，c) ～d) と同様の操作で，試料を満たした比重カップの質量 (W_3) をはかる。

f) 同一試料で 3 回測定を行う。また，測定温度を記録する。

5.2.1.3 試験結果の表し方

計算は，次によって行う。

a) 比重 (S_G) は，式 (1) によって算出する。

$$S_G = \frac{W_3 - W_1}{W_2 - W_1} \quad \cdots\cdots (1)$$

ここに，
S_G： 比重
W_1： 比重カップの質量 (g)
W_2： 水を入れた比重カップの質量 (g)
W_3： 試料を入れた比重カップの質量 (g)

b) 密度 (D) は，式 (2) によって求める。

$$D = d \times S_G \quad \cdots\cdots (2)$$

ここに，
D： 密度 (g/cm^3)
d： 測定温度における水の密度 (g/cm^3)（23 ℃では，0.997 54）
S_G： 比重

c) 3 回の測定の平均値を求め，小数点以下 2 けたに丸める。

5.2.2 比重瓶法

5.2.2.1 装置

装置は，次のものを用いる。

a) **比重瓶** 比重瓶は，図 2 に示す形状のガラス製のもので，容量 25 ml のもの。

エポキシ樹脂 及び 硬化剤の比重試験方法　K 7232-1986

（1992 確認）

Testing Methods for Specific Gravity of Epoxide Resins and Hardeners

3.Test method, as following:

3.1. Test method of liquid epoxy resin as well as hardener

1) Pycnometer method (specific gravity bottle method)
2) Specific gravity cup method
3) Floating method

3.2. Test method for hardened epoxy and hardener

1) Water displacement method
2) Pycnometer method (specific gravity bottle method)

Typical thermal analysis techniques

Table 1: Typical thermal analysis techniques

Name		**Measurement target**	**Measurement unit**
示差熱分析	Differential Thermal Analysis: DTA	Temperature difference	^{O}C, μV*
示差走査熱量測定	Differential Scanning Calorimetry: DSC	Heat flow	W (=J/sec)
熱重量分析	Thermal Gravimetric Analysis: TGA	Mass	g
熱機械分析	Thermalmechanical Analysis: TMA	Length	m
動的熱機械測定	Dynamic Mechanical Analysis: DMA	Young’s modulus	Pa (N/m^2)

Differential Scanning Calorimetry (DSC) principle

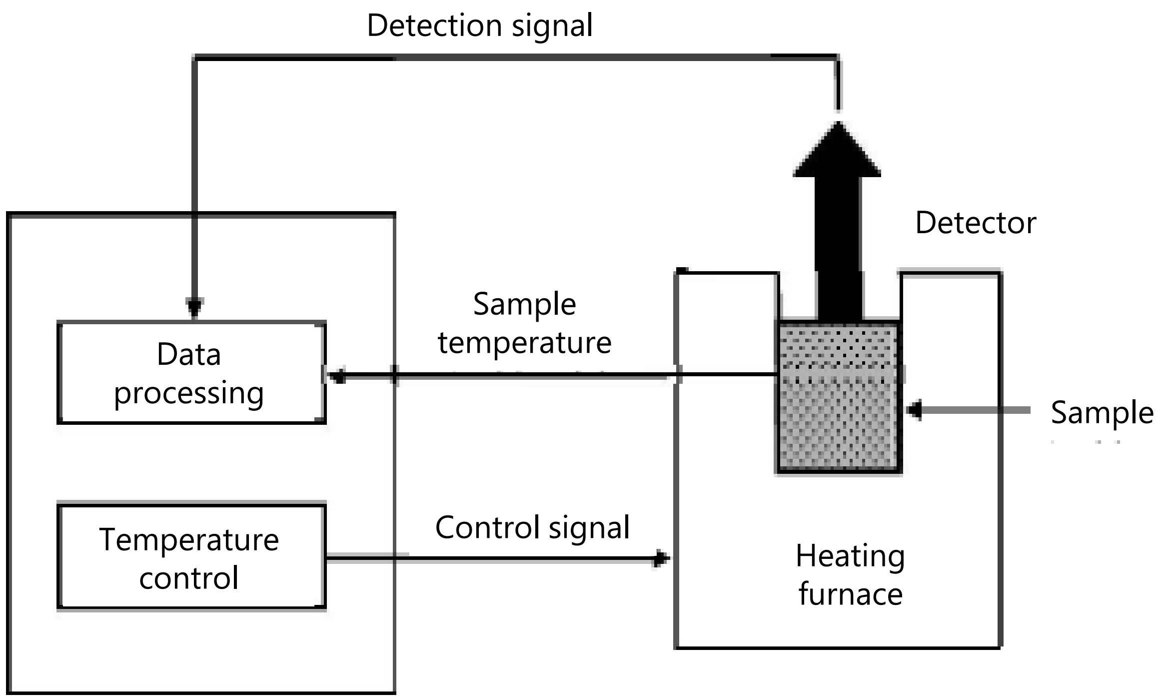


Figure 1: Schematic diagram of thermal analysis device

Differential Scanning Calorimetry (DSC) techniques

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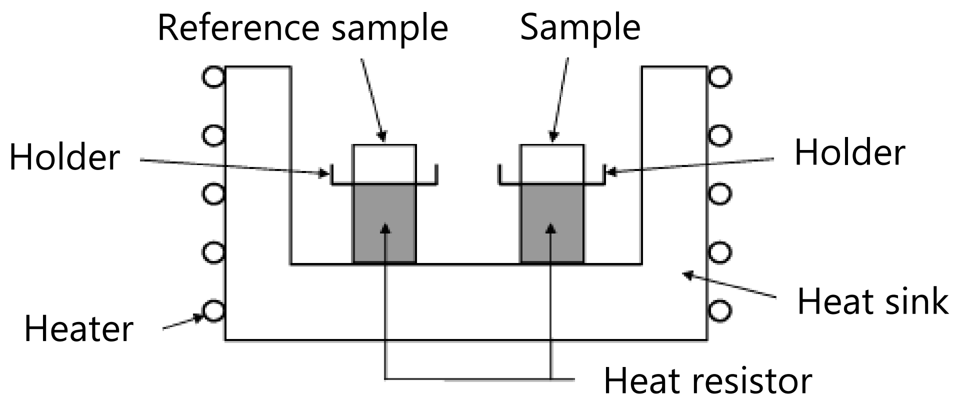

Figure 8: Schematic diagram of DSC device

Phenomenon		Obtained information
Phase transition, etc.	Melting	Temperature. Heat capacity
	Crystallization	Temperature. Heat capacity
	Glass transition	Glass transition temperature Specific heat capacity difference
	Crystal transition	Temperature. Heat transfer
	Evaporation. Volatilization. Sublimation	Temperature. Heat capacity
	Magnetic phase transition	Transition temperature
Chemical reaction	Curing reaction	Temperature. Heat capacity
	Oxidation reaction	Temperature. Heat capacity
	Self-reaction	Temperature. Heat capacity
	Chemisorption. Desorption	Temperature. Heat capacity
Others	Precipitation	Temperature. Heat capacity
	Micelle formation	Craft point. Heat capacity
	Heat denaturation	Temperature. Heat capacity
	Gelation. Gelatinization	Specific heat capacity

Thermalmechanical Analysis (TMA) equipment

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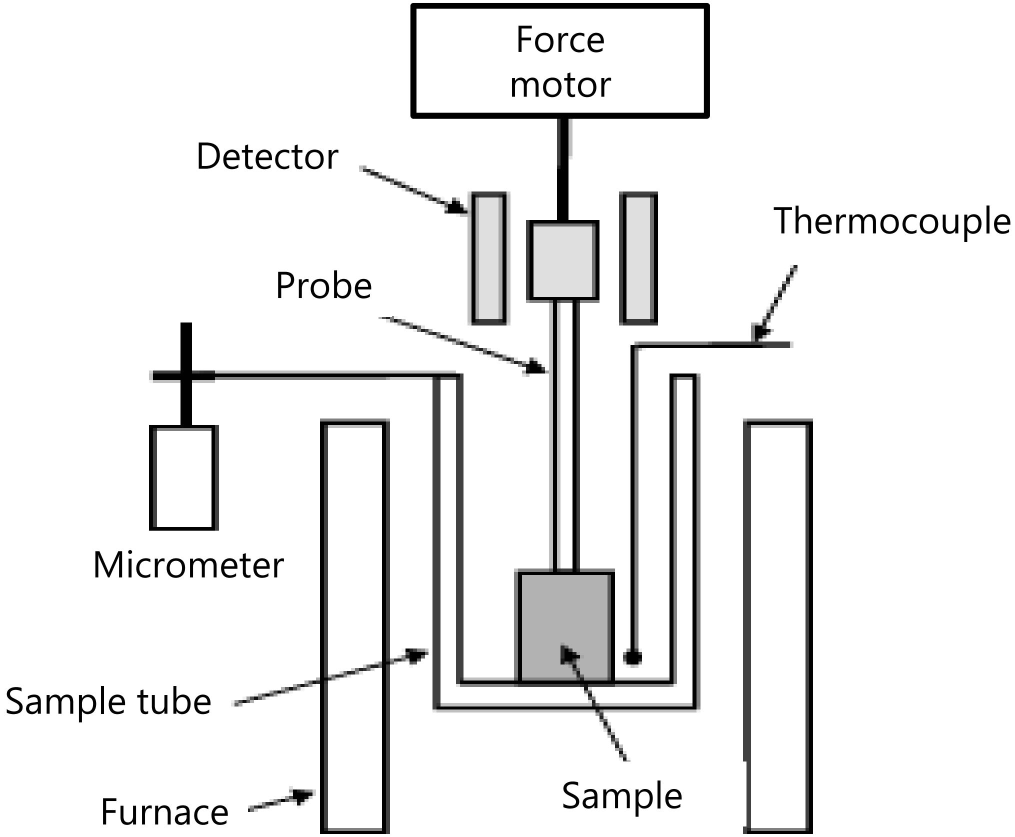


Figure 8: Schematic diagram of TMA device

Current state of curing shrinkage measurement

Strain method

A method for calculating the magnitude of the curing shrinkage stress by applying resin to a thin plate then cure it, depending on the amount of warp, the curing shrinkage is calculated.

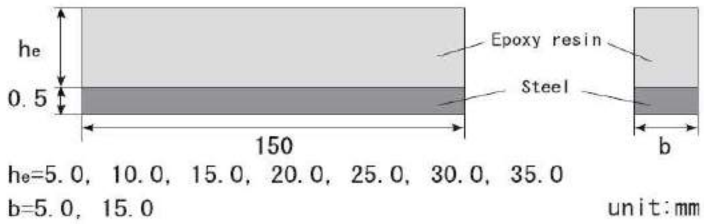
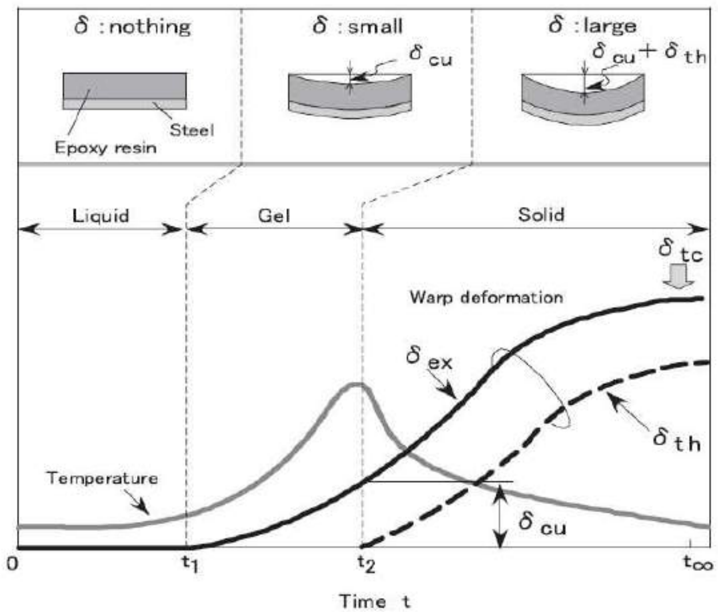


Fig.1 Laminated body



Source 広島工業大学紀要研究編 第44巻（2010）pp.17-24

論 文

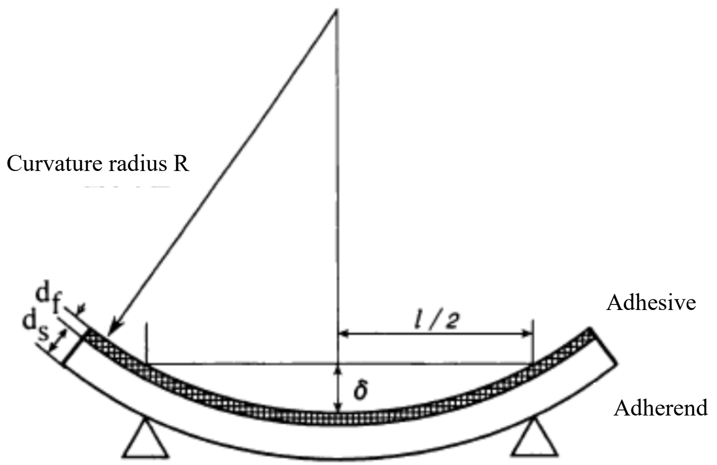


Fig.1: Warped rectangle by residual stress of adhesive - adherend

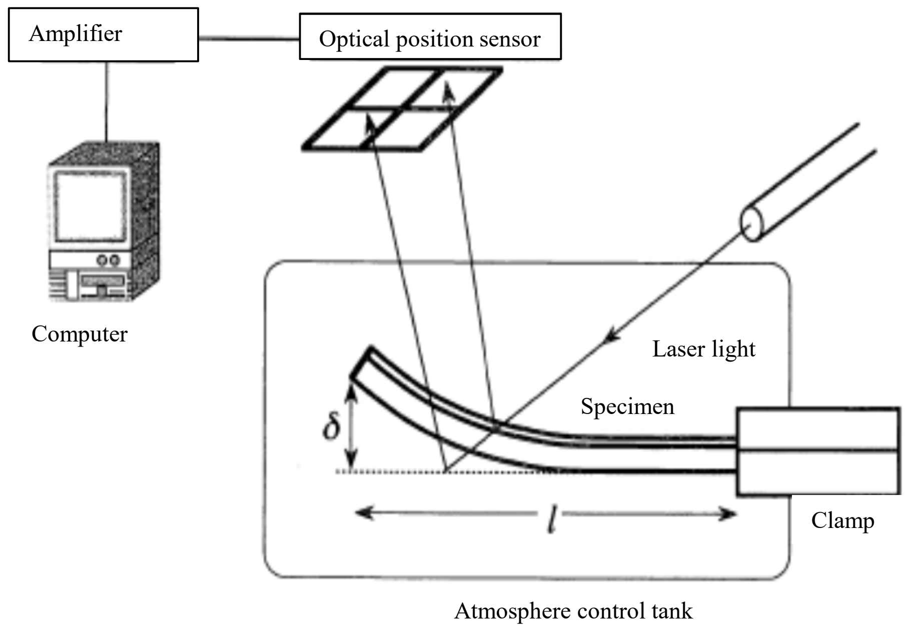


Fig.2: Measurement method of residual stress using laser displacement meter

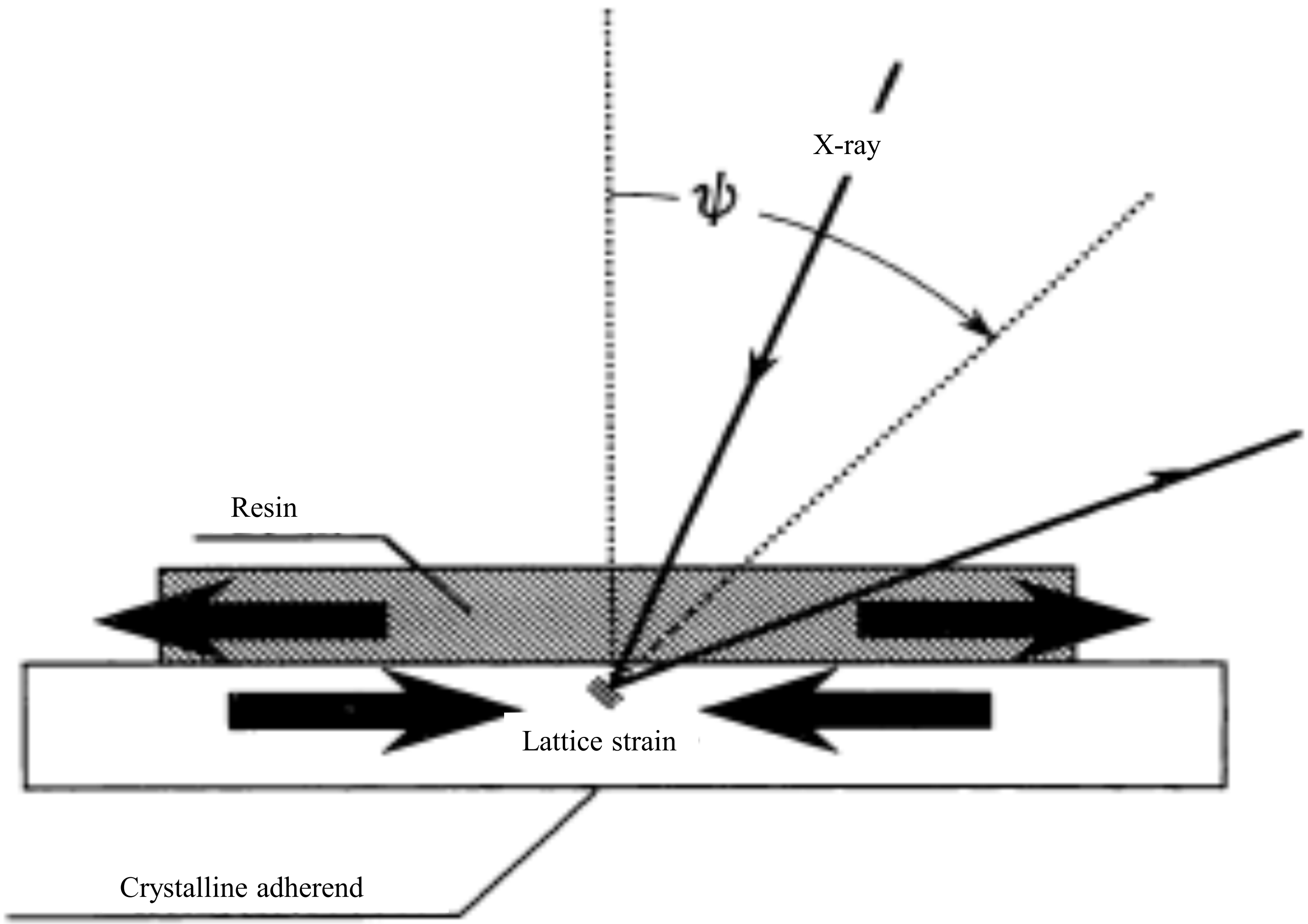


Fig.4: Principle of residual stress measurement by X-ray diffraction method

Current state of the curing shrinkage rate measurement

◆Cure shrinkage stress measurement method

There are some indirect measurement techniques such as applying adhesive to a thin plate a and converting the warp of the plate by curing shrinkage and measuring it, however, there is no direct measurement method has not been established yet.

◆Issues

- A complicated calculation for conversion the measurement results is required .
- In indirect measurement techniques, errors due to external factors occur.

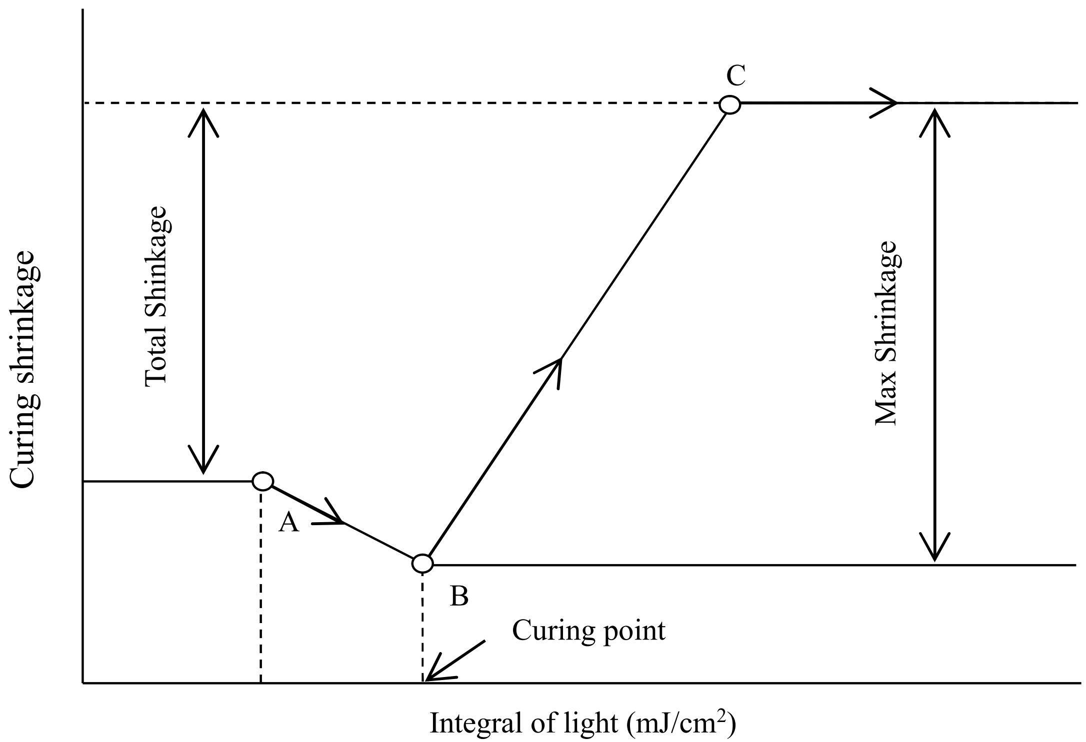
Compliance and compare of required performance, etc. and Required Performance, etc. of Similar Models

		Selection Model		Rating machine model			
Product name, model, etc.		A. Resin cure shrinkage stress measuring equipment – 1 set Acroedge Co., Ltd. **EU201C-Pro** (Composition) - EU 201 C-Pro Main unit - Including installation adjustment cost		B. Thermomechanical analyzer – 1 set Hitachi High-Tech Science Co., Ltd **TMA7100** (Composition) - TMA7100 Main unit		C. Viscosity and viscoelasticity measuring equipment – 1 set Thermo Fisher Scientific Co., Ltd. **HAAKE MARS** (Composition) - HAAKE MARS Main unit	
Quotation							
Required ability, etc.		Performance, standards, etc.	Evaluation	Performance, standards, etc.	Evaluation	Performance, standards, etc.	Evaluation
Item	Performance, standards, etc.						
Cure shrinkage	Continuous measurement of curing shrinkage rate is possible.	Continuous measurement of curing shrinkage rate can be made from pre-curing to post-curing and time elapsed.	○	Measurement is not possible	×	Measurement is not possible	×
Hardened shrinkage stress	The continuous measurement of the hardened shrink stress is possible.	Continuous measurement of curing shrink stress from pre-curing to post-curing and relaxation of internal stress is possible.	○	Measurement is not possible	×	Measurement is not possible	×
Continuous shrinkage rate and stress information observation by setting the time of acquired information from pre-reaction to post-reaction	Information (data) can be acquired continuously from 0.1 second intervals.	The curing shrinkage rate, curing shrinkage stress, and the temperature of the resin surface can be measured.	○	It is possible to predict the reaction rate by analogy of the reaction heat.	△	Reaction rate can be measured by continuously measuring the increase or decrease of functional groups.	◎
Resin internal stress relaxation measurement	Relaxation of internal stress can be measured from after curing process to room temperature or being left at room temperature.	The internal stress relaxation (shrinkage rate, shrinkage stress) can be measured from after curing to room temperature or being left at room temperature.	○	Allow detailed measurement of phase transition	△	Measurement is not possible	×
Temperature programming during the curing process	The temperature programe of the heating/cooling curve during the curing process can be set optionally.	Optional temperature programme can be set by the heating unit and circulating cooling unit.	○	Original function and measurable.	◎	Measurement is not possible	×

Details of Required Performance, etc.

Requirements	Required Performance, Standards, etc.	Reason for the necessary
Curing shrinkage	Continuous measurement of curing shrinkage rate shall be possible.	By continuously measuring the curing shrinkage rate, it is necessary to understand the behavior (change) of the curing process and evaluate the performance to the product rather than the adhesive only.
Curing shrink stress	The continuous measurement of curing shrinkage stress is possible.	By continuously measuring the curing shrinkage stress, it is necessary to understand the behavior (change) of the curing process and evaluate the performance to the product rather than the adhesive only.
Continuous shrinkage rate and stress information observation by setting the time of acquired information from pre-reaction to post-reaction	Information (data) can be acquired continuously from 0.1 second intervals.	In the curing reaction, detailed observation of resin behavior is necessary by obtaining data at micro-intervals. In addition, it is necessary to observe the resin behavior over a long period of time by lengthening the acquisition time.
Resin internal stress relaxation measurement	Relaxation of internal stress can be measured from after curing to room temperature or being left at room temperature.	In thermosetting resin, stress accumulates inside the resin due to the curing conditions and gradually relaxing due to the standing conditions. For this reason, stress relaxation of the resin under annealing or under natural storage should be observed.
Temperature programme setting during the curing process	The temperature programme of the heating/cooling curve during the curing process can be set optionally.	The curing performance of the thermosetting resin changes due to changes in the heating rate as well as the curing temperature. Therefore, it is necessary to change the heating and cooling speeds and observe the difference in curing resin performance.

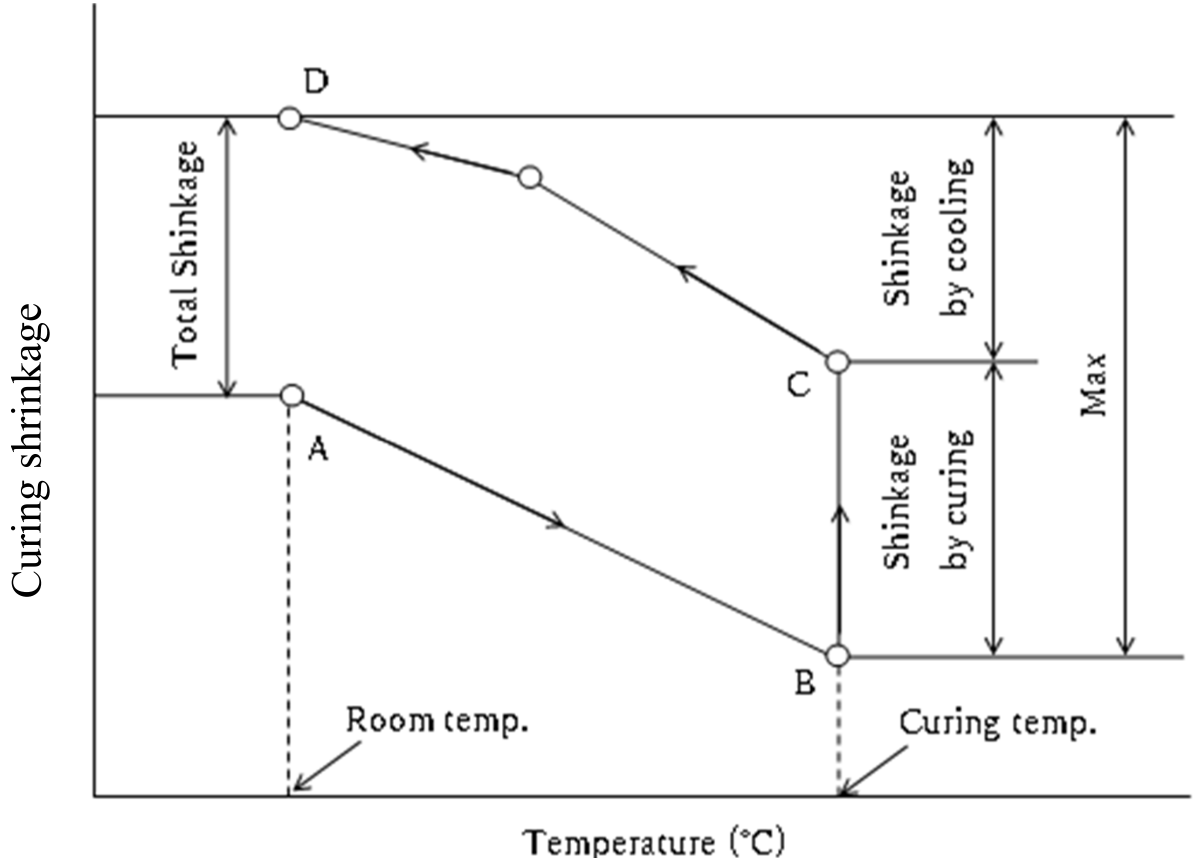
Curing shrinkage of UV curable resin



A: Irradiation start point
B: Shrinkage start point
C: Shrinkage end point

Fig.4: Behavior of ultraviolet curable resin after UV irradiation

Curing shrinkage of thermosetting resin



A: Heating start point
B: Curing reaction starting point
C: Curing reaction end point
D: Shrinkage terminal point

Room temperature: T_A ,T_D , Room temperature: T_B ,T_C :

Fig.2: Behavior of thermosetting resin during heating and cooling process

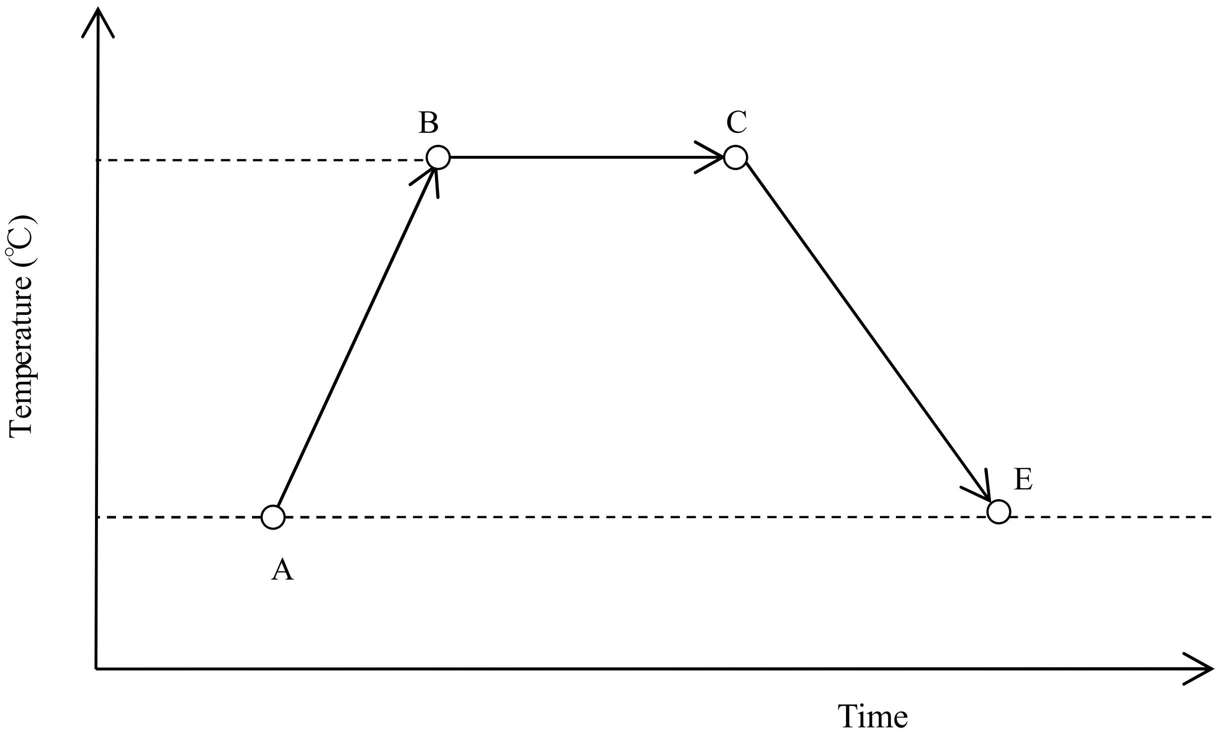


Fig.3: Temperature condition of thermosetting resin

Internal stress reduction method

1. Decrease in glass transition temperature Tg
2. Decrease in linear coefficient of expansion in the vitreous area
3. Decrease in elasticity of the vitreous area

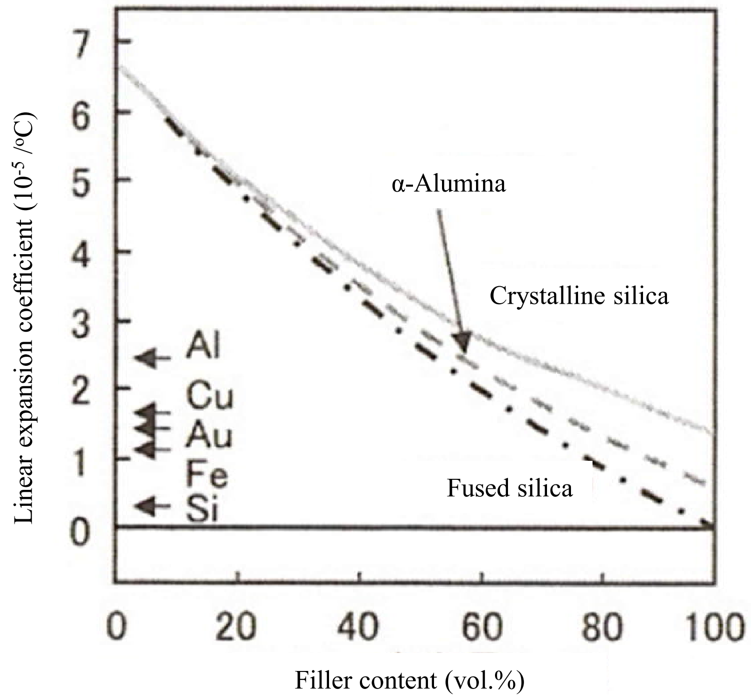


Fig.7: Relation between filler content and linear expansion coefficient

Device characteristics

- Directly measure and quantify the cured shrink stress of the resin.
- Possible to continuously measure all processes: before, during, and after reaction.
- Cure shrinkage in accordance with cure shrinkage stress
- Expansion, thermal reaction, and stress changes along with temperature change

  } Measurable over time

- The program allows the user to freely combine the UV irradiation terms and temperature conditions (heating, cooling, setting range ambient temperature to 200°C).

Device characteristics

- Temperature change on the resin surface can be measured
- Measurement during UV irradiation is possible.
- Applicable for various types of resin, such as UV curing resin, thermosetting resin, and 2-component liquid adhesive
- It can be measured in small amount (0.1 cc).
- Easy measurement by anyone without having skilled measurement technique.

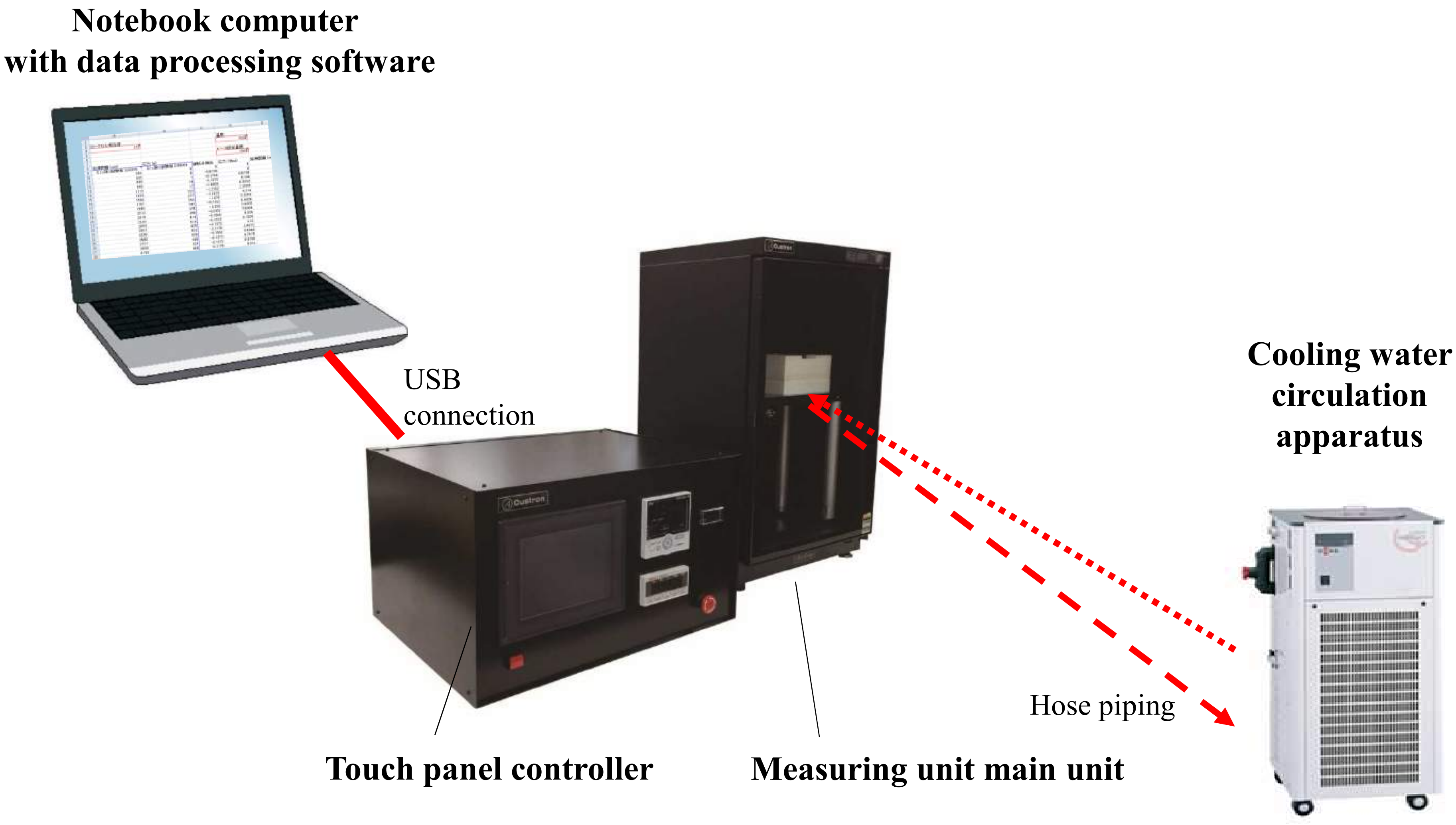
Principle

By continuously measuring the film thickness curing of the resin before and after curing using a small amount of sample, the film thickness change rate is obtained to obtain the change shrinkage rate.

Note 1: For fluid sample, since the cross-section area in the container does not change, the film thickness is proportional to the volume.

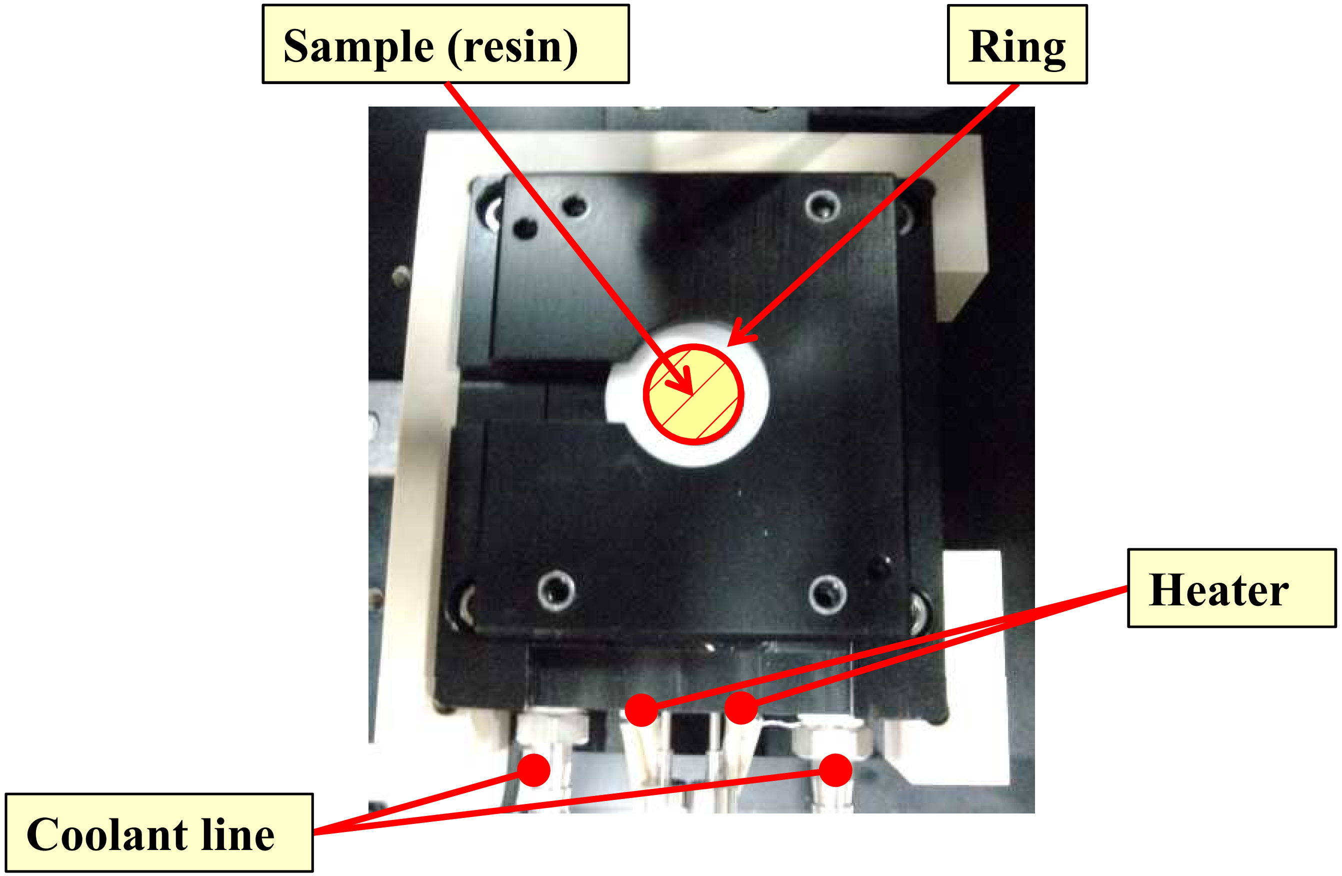
Note 2: When a general UV curing resin undergoes UV irradiation, it expands immediately after irradiation then hardening progresses (see Fig.1). Reaction, shrinkage may start immediately as soon as it cures quickly. In addition, when heated, thermosetting resin expands while increasing temperature, when it reaches the curing temperature and begins to cure, the thermosetting resin begins to shrink and the shrinkage continues until returning to room temperature (see Fig.2).

Equipment configuration



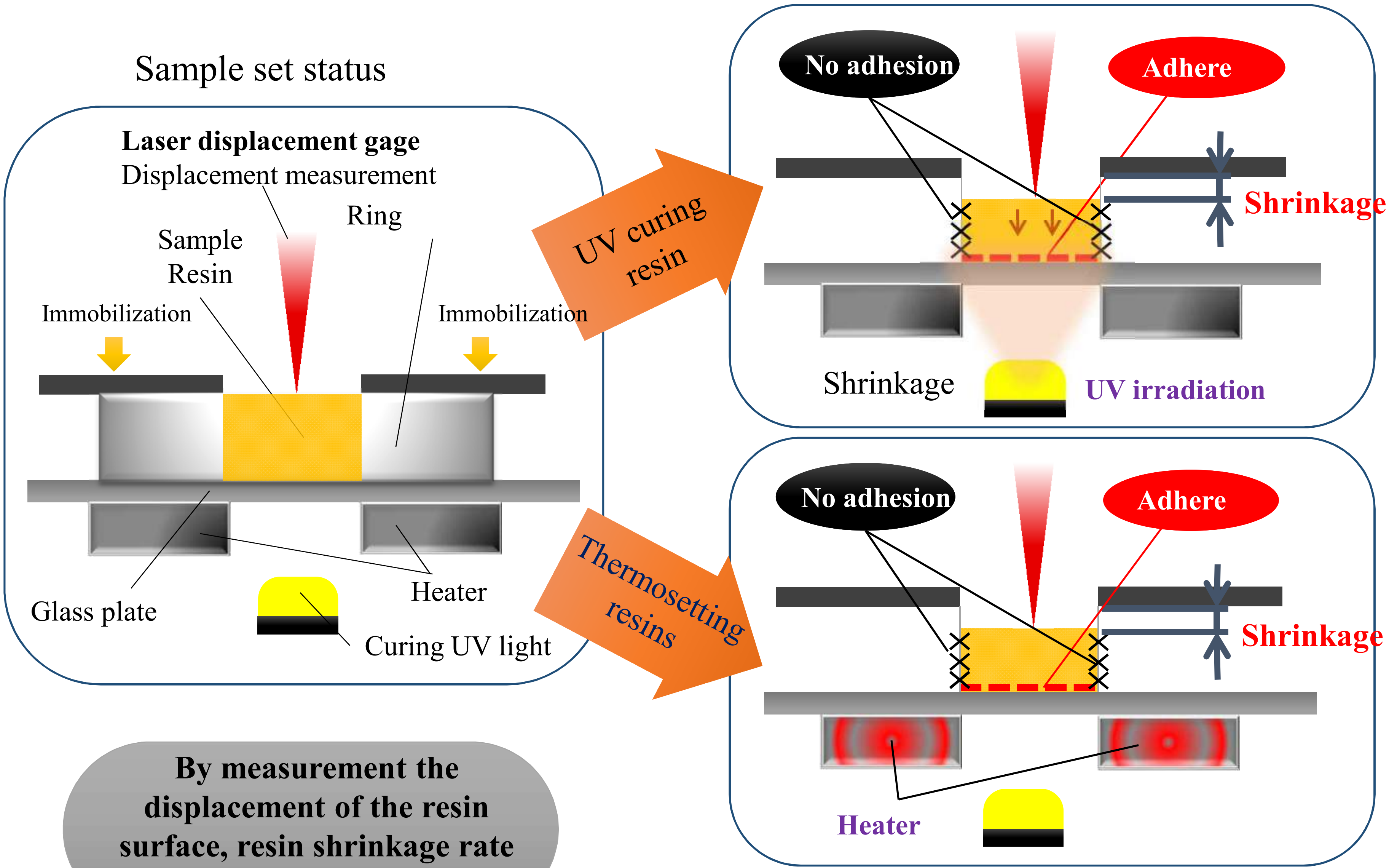
Configuration of measuring unit

[Sample set part in the main unit of the measuring unit]



- The product can be programmed to increase temperature or cooling from room temperature to 180^{o} C

Curing shrinkage measurement principle

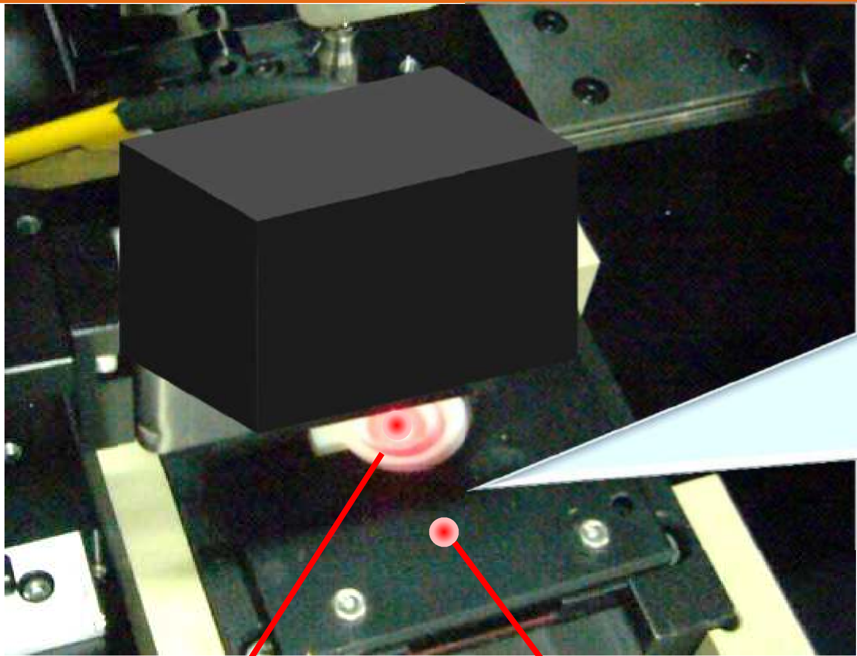


By measurement the displacement of the resin surface, resin shrinkage rate can be known

UV irradiation and heater heating can be performed at the same time.

Measurement

Cure shrinkage measurement



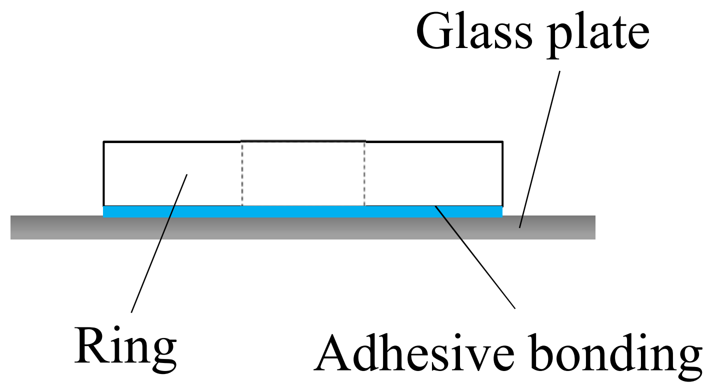
Since expansion and shrink at baseline are measured simultaneously and the expansion and contraction rates are measured based on the difference, accurate measurements can be made regardless of the material's expansion coefficient.

Laser beam for shrinkage measurement

Laser beam for baseline correction

Measurement procedure

①Place an 1 mm thickness Ring on glass instead of dam with glass plate as an adhesive.



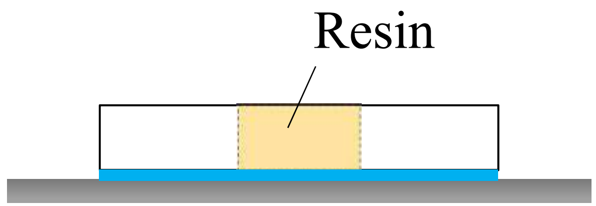
◆Adhesion of the Ring into the slide glass allows the measurement to be made for a low viscosity, a stainless steel ring can be used instead of the glass plate for measuring even lower viscosity (measurable range: 1cps～tens of thousands cps).

Since the Rings have a small affinity for the polymer, it is possible to minimize lateral adhesive stress, allowing only vertical shrinkage from the glass surface to be measured.

Measurement procedure

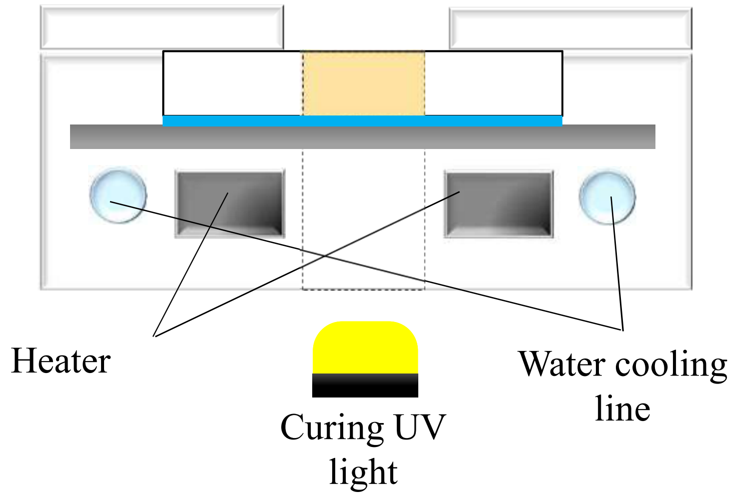
2. Inject resin therein

Injection volume: inside diameter Ø=10mm,
When dropping in a thickness of 1mm → 0.08cc
(Ring thickness: 0.5 ~ 2 mm)



3. Place on top of measurement table

→Complete of setting



Measurement procedure

4. On the touch panel, set the resin curing condition (see the example of the touch panel operation screen)

5. Start measurement (continue to be automatically measured until the end)

6. Measured capture data can be min 0.1 sec ~ 1 msec (option)

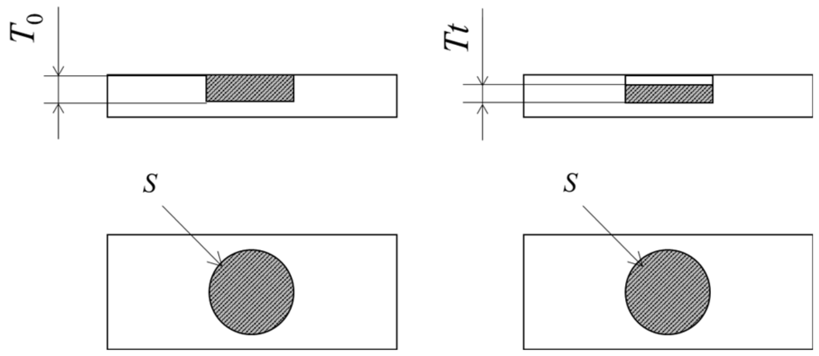
7. Display data and graphs in Excel after completion of measurement (see example PC data loading software screen)

Formula for cure shrinkage rate

$$A(t) = \frac{V_0 - V_t}{V_0} \times 100\% = \frac{T_0 - T_t}{T_0} \times 100\%$$

where:

A(t): depending on arbitrary curing condition, the curing shrinkage rate at the time t (%)
t: elapsed time after starting curing
V_0 : initial volume at time t=0
$V_0 = T_0$ x S
V(t): volume at the time t
S: cross section of sample
T_0 : initial sample thickness at t = 0
T_t : depending on arbitrary curing conditions, sample thickness at time t

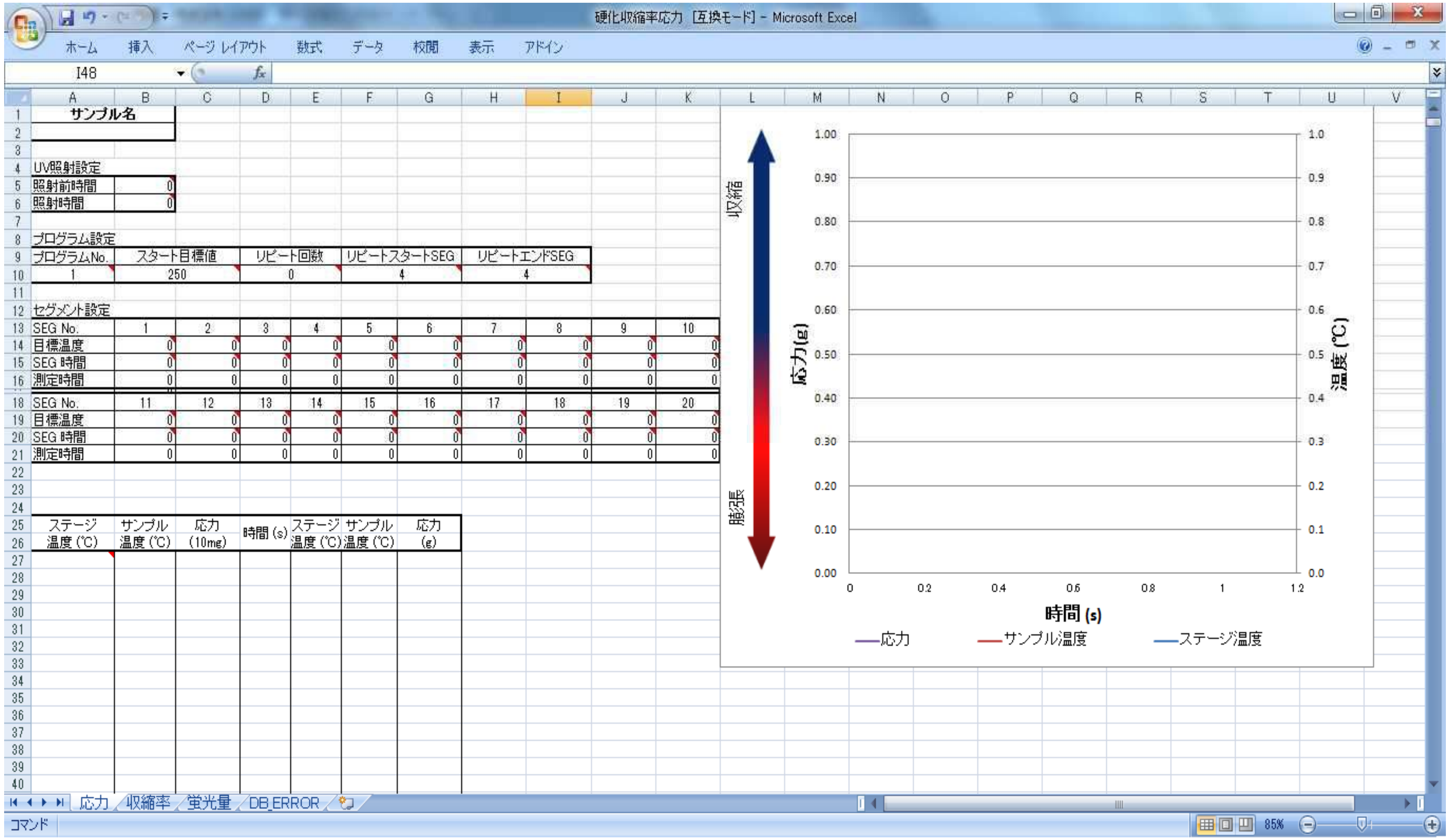


Touch panel operation scree (example)

Simple operation with touch panel allows setting of various curing conditions.

※The display and layout of the touch panel may be changed without notice in advance

PC data loading software screen (example)



※The display and layout of the loading software may be changed without notice in advance

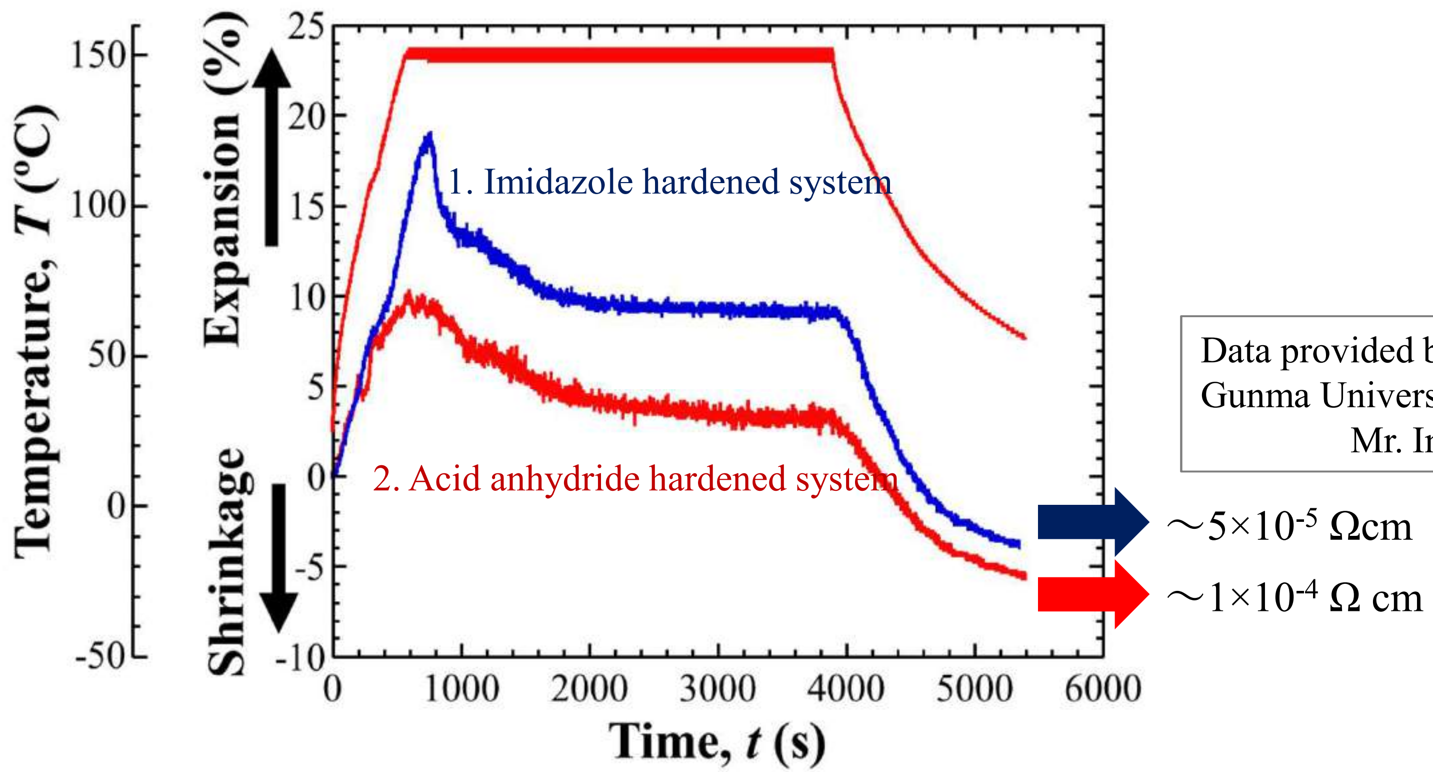
Power supply	100V±10%	
Detector	Load cell for measurement shrinkage stress	1) Standard rating 5 N (other options 500mN, 1N, 2N, 10N, 20N) 2) Non-linearity ±0.5% RO or less 3) Repeatability accuracy ±0.5% RO or less
	Laser displacement gage for shrinkage measurement	1) Repeatability accuracy 2μm 2) Red-semiconductor laser 655 nm (visible light) 3) Laser class 1(FDA CDRH Part1040.10) 4) Output 220μW
	Radiation thermometer for measurement resin temperature	1) Detection temperature 0-500℃ 2) Detection element thermopile 3) Detection wavelength 8-14 μm 4) Repeatability ±0.5℃
Setting temperature range	5～200℃ (* Temperature range when Coolant is used)	
Device dimension	Measuring unit W450 x D400 x H900 mm	Weight 40 kg
	Control unit W500 x D420 x H310 mm	Weight 15 kg
Maximum number of measurements	30000 points	

Measured data conductive adhesive

Shrinkage ratio

<Relationship between the shrinkage rate after hardened and coolant and the electrical resistivity>

※Electrical resistivity is not simply proportional to shrinkage rate



Data provided by
Gunma University
Mr. Inoue

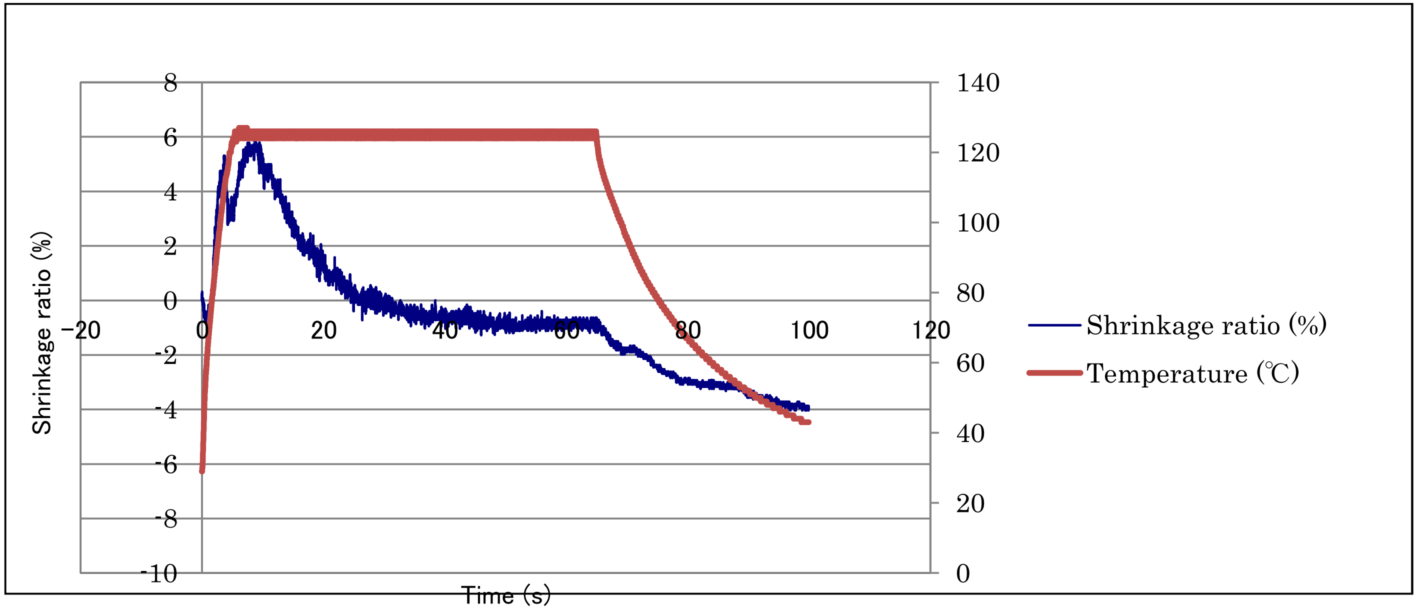
○ Electrical resistivity of the acid anhydride-based conductive adhesive is ～1x 10^{-4} Ωcm.

○ Electric resistivity of the imidazole-based conductive adhesive is ～5 x 10^{-5} Ωcm.

Thus, the higher shrinkage acid anhydride system has a lower electrical resistivity.

Measured data conductive adhesive

<Typical thermosetting epoxy resin measurement> Epicoat 828 + hardener + binder

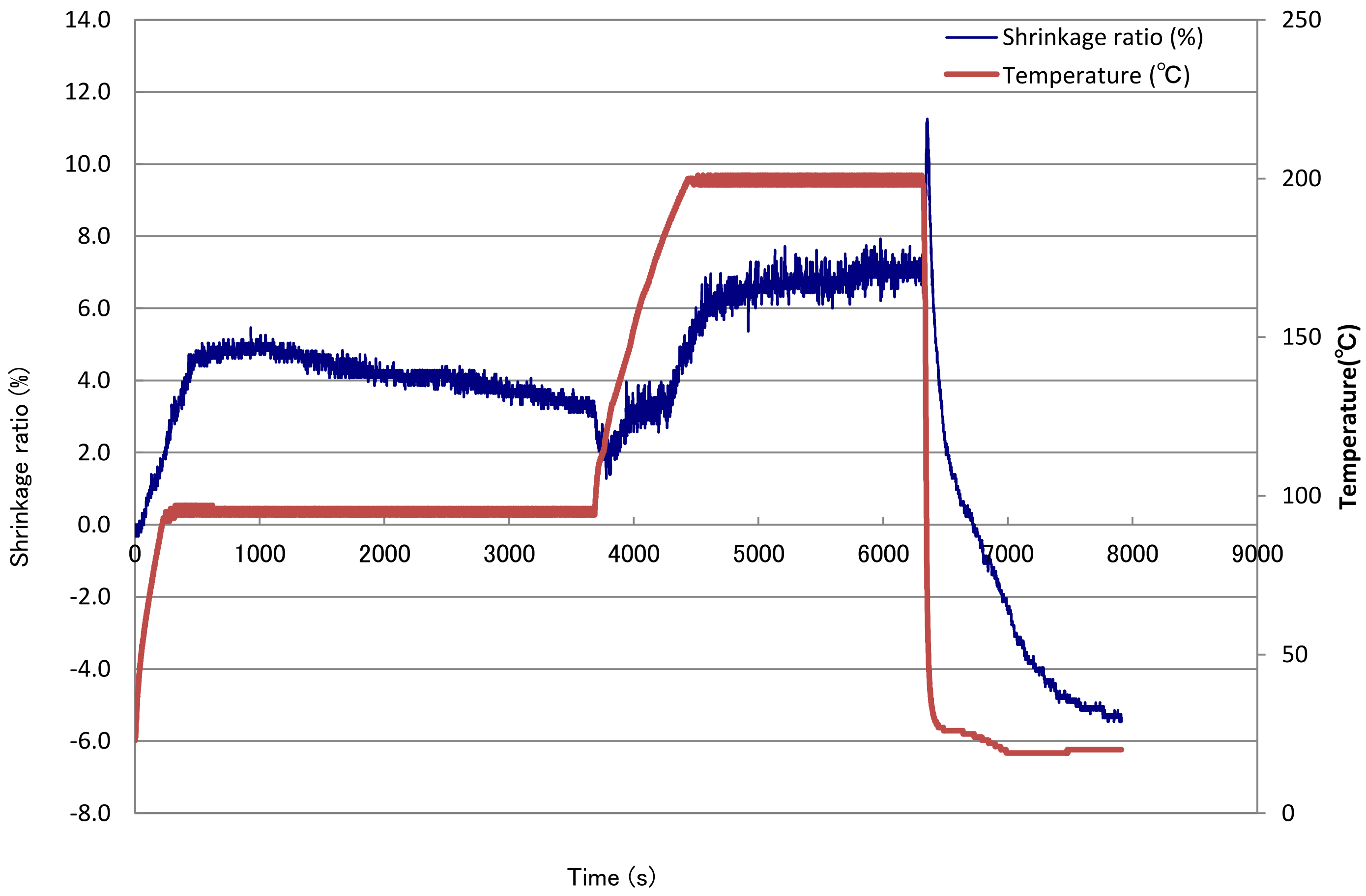


Heat the temperature to 130°C, keep it for 60 minutes, and cool naturally

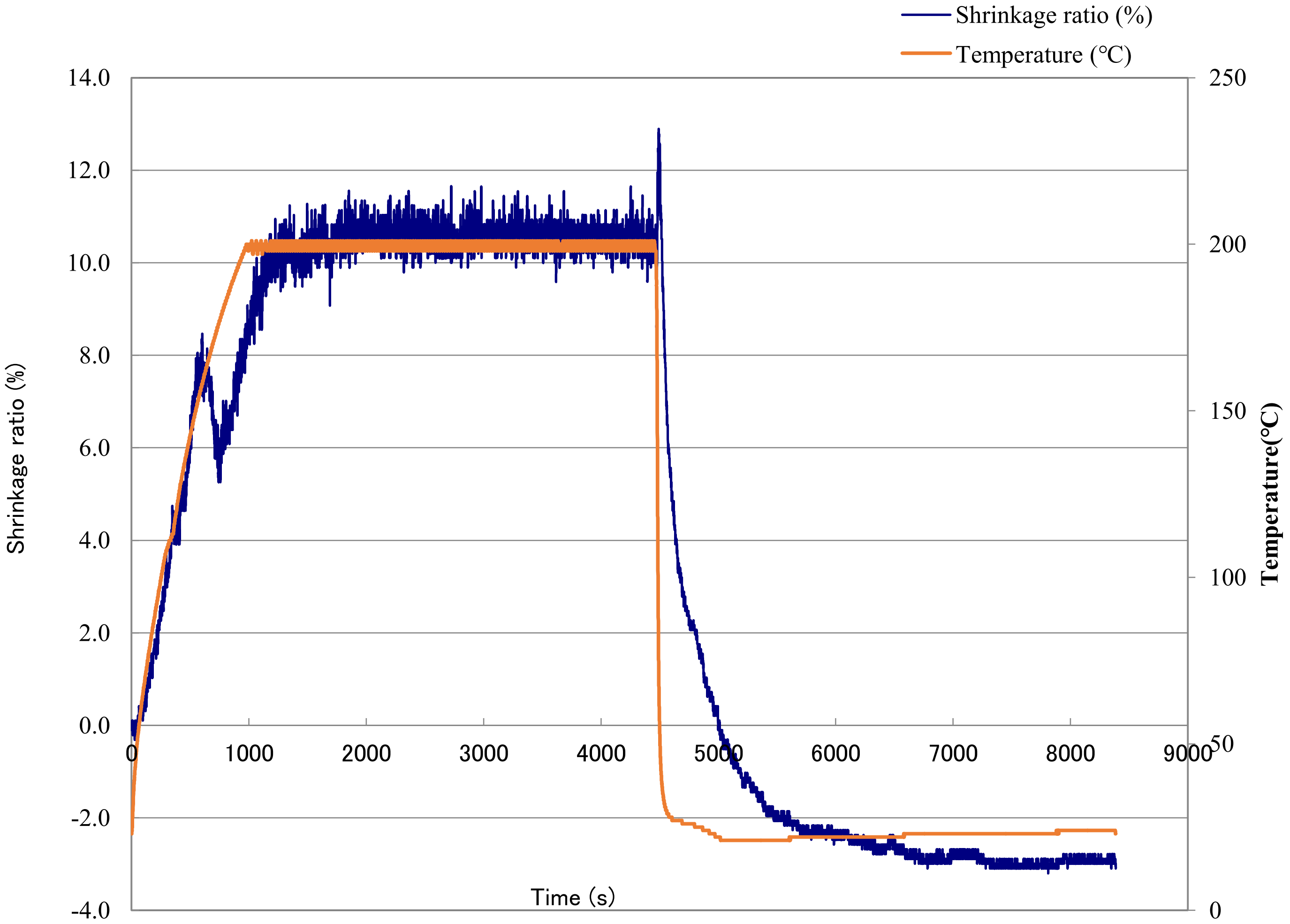
- It can be seen from the graph it expands approximate 5% at the beginning then shrinks according to the curing reaction.
- Finally, since the cure shrinkage is suppressed with a binder, it converges at a shrinkage rate of about 3%.
- If the binder is not contained, shrinkage is about 5 to 8%.

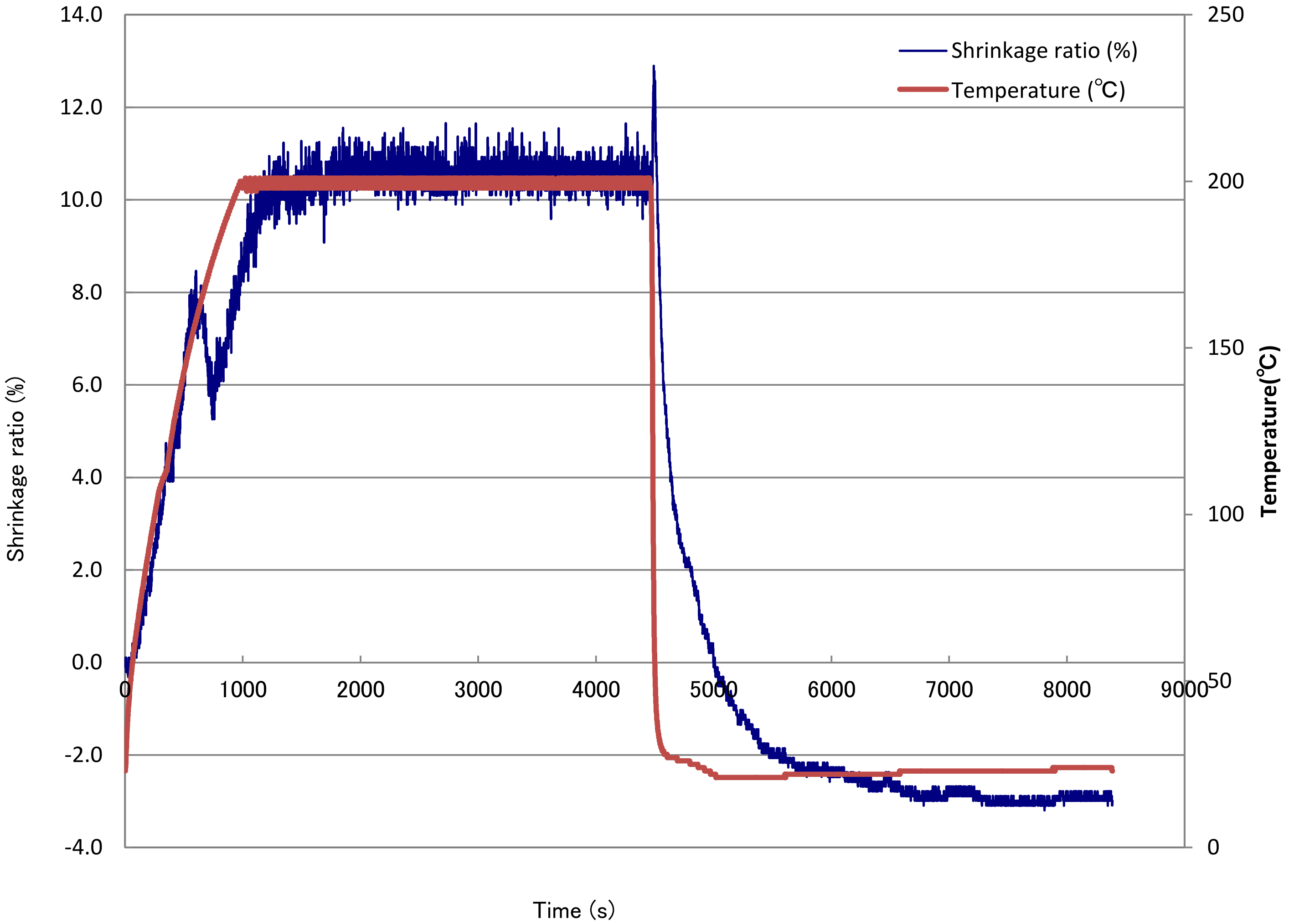
The relationship between the amount of binder added and the rate of shrinkage can also be easily compared with actual measured values.

Shrinkage ratio



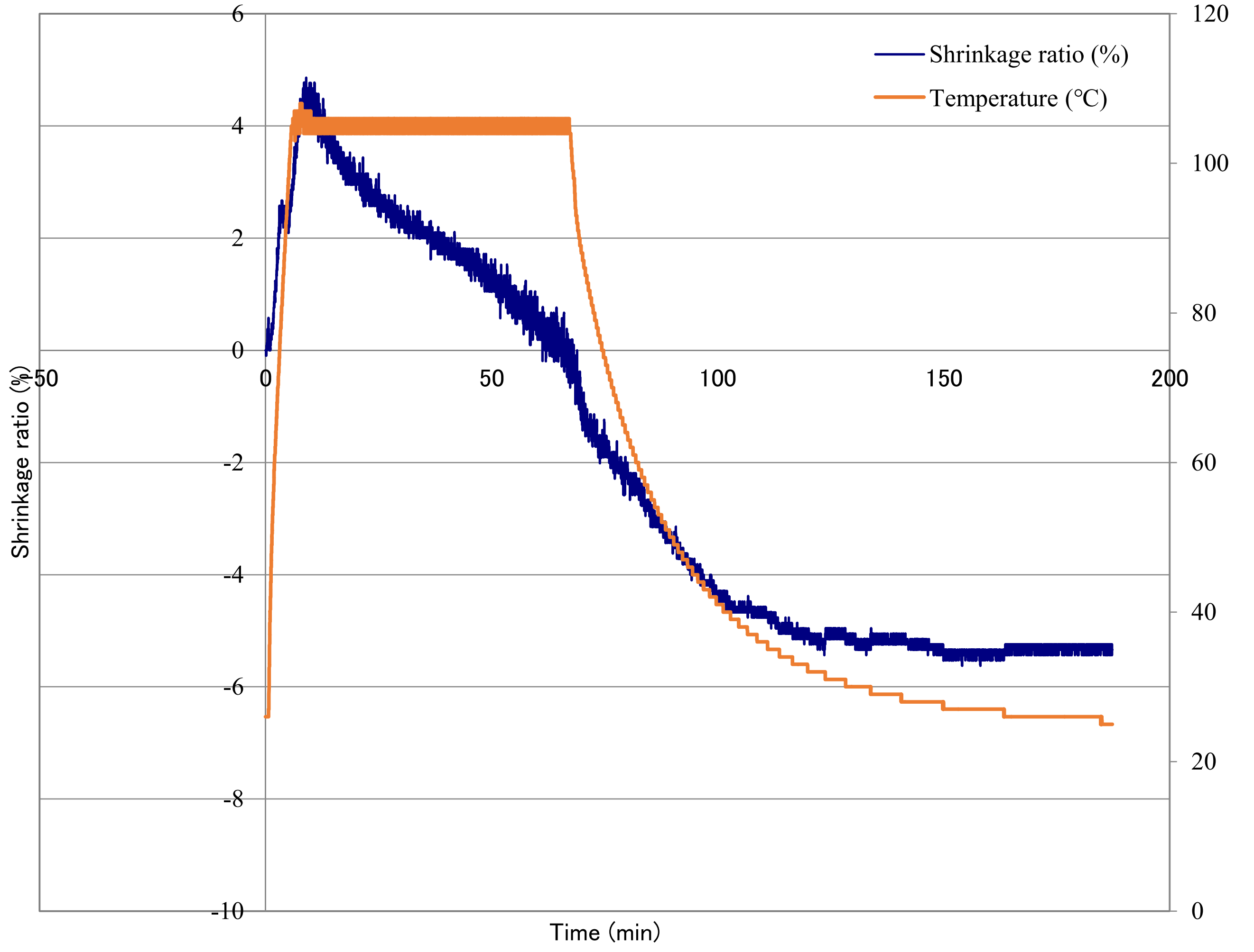
Shrinkage ratio



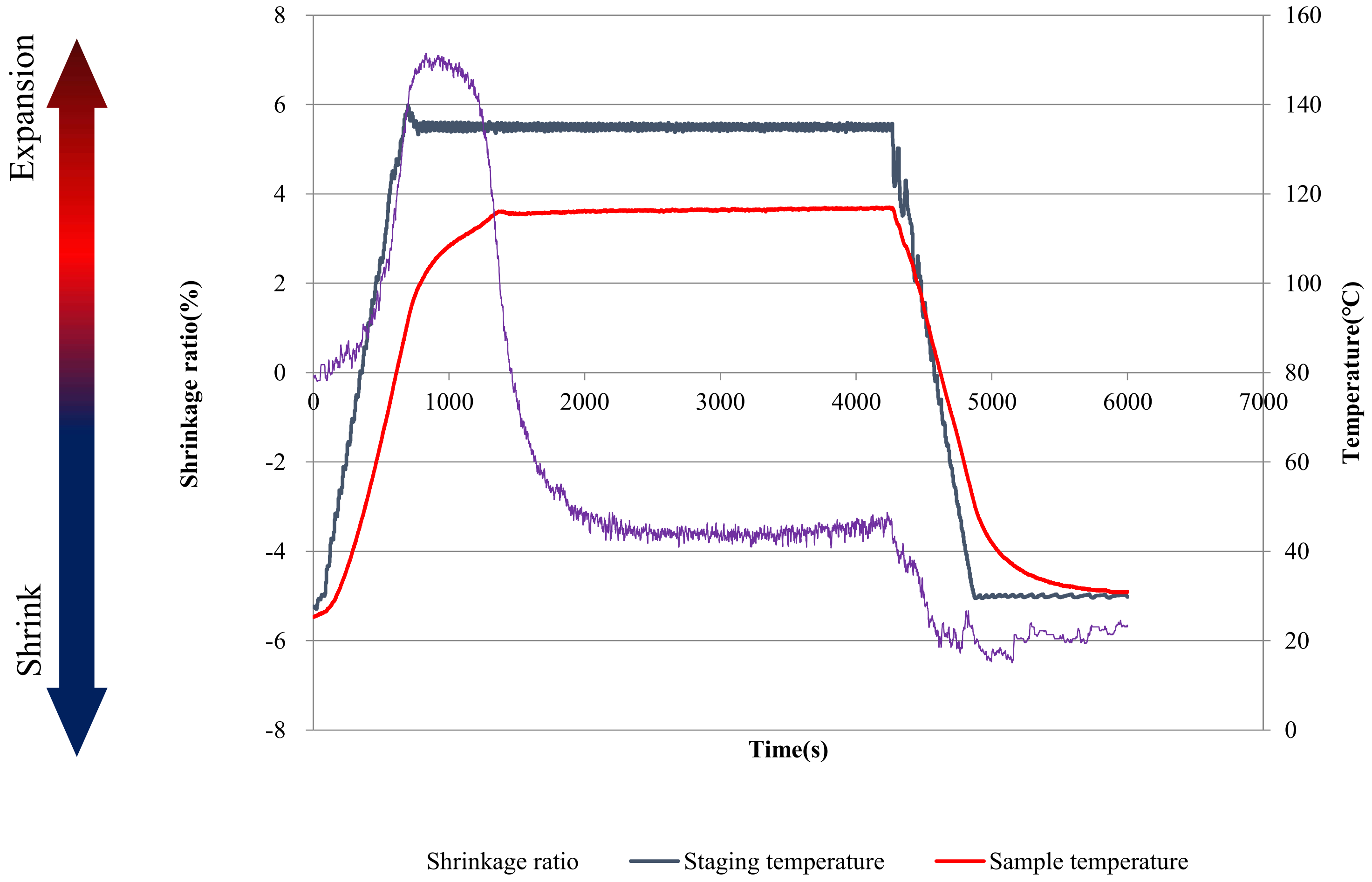


Shrinkage ratio (%)
Temperature (℃)
14.0
12.0
10.0
8.0
6.0
4.0
2.0
0.0
-2.0
-4.0
0
1000
2000
3000
4000
5000
6000
7000
8000
9000
250
200
150
100
50
0
Shrinkage ratio (%)
Temperature(℃)
Time (s)

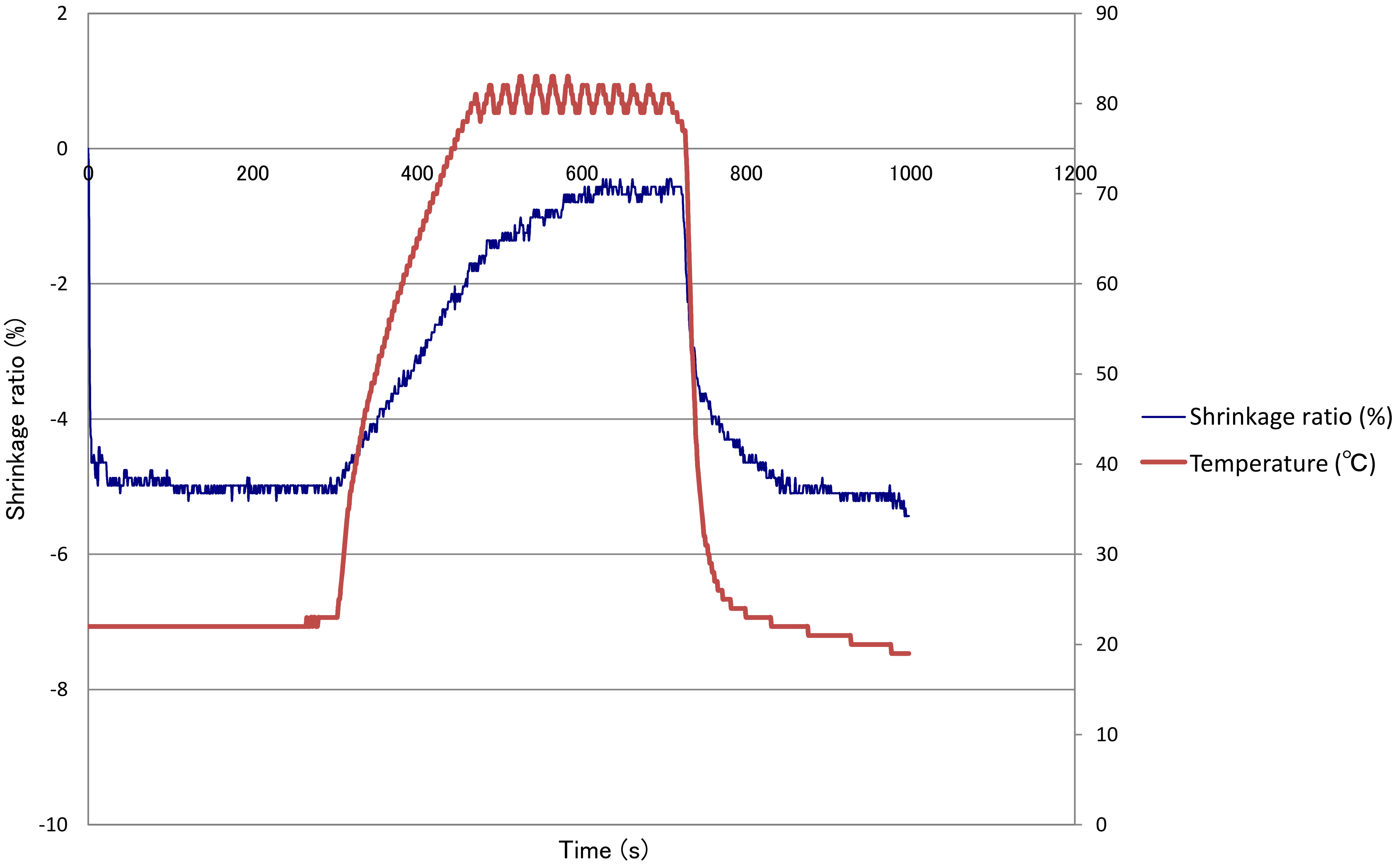
Measurement data: thermosetting epoxy resin shrinkage rate



Measurement data: thermosetting resin shrinkage rate

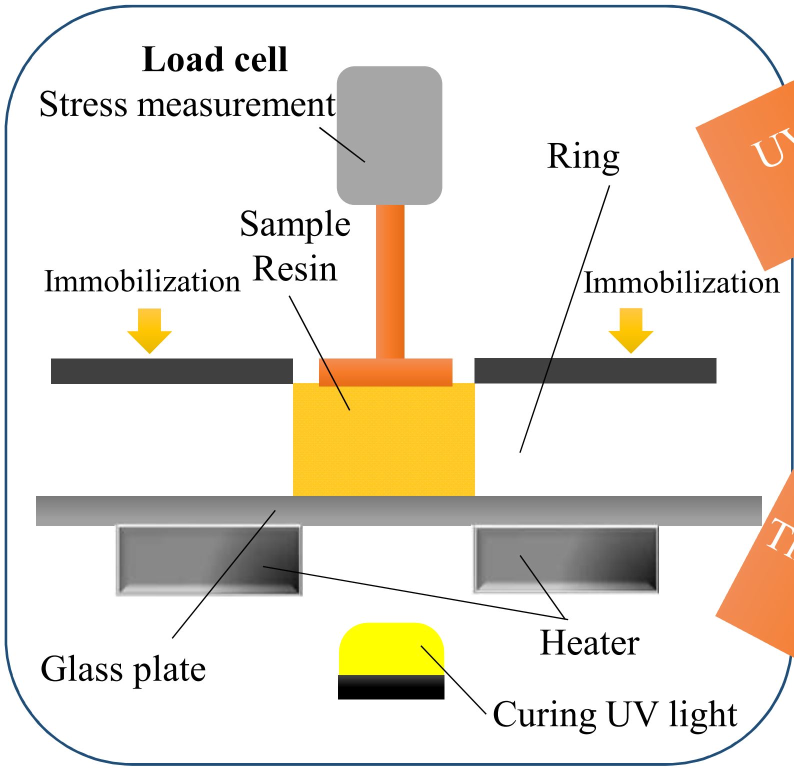


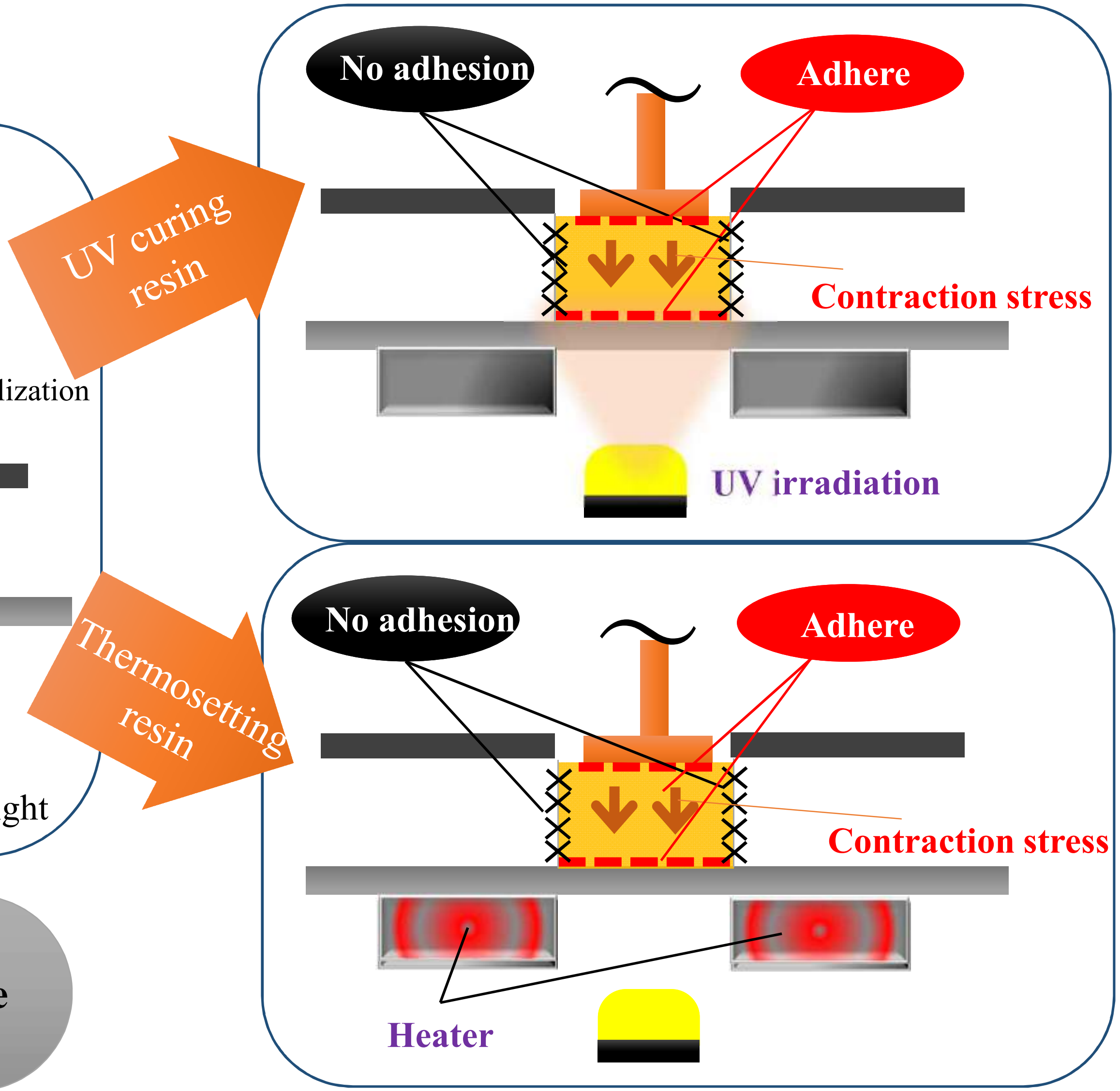
UV curing + Thermosetting



Curing shrinkage stress measurement principle

Sample set state



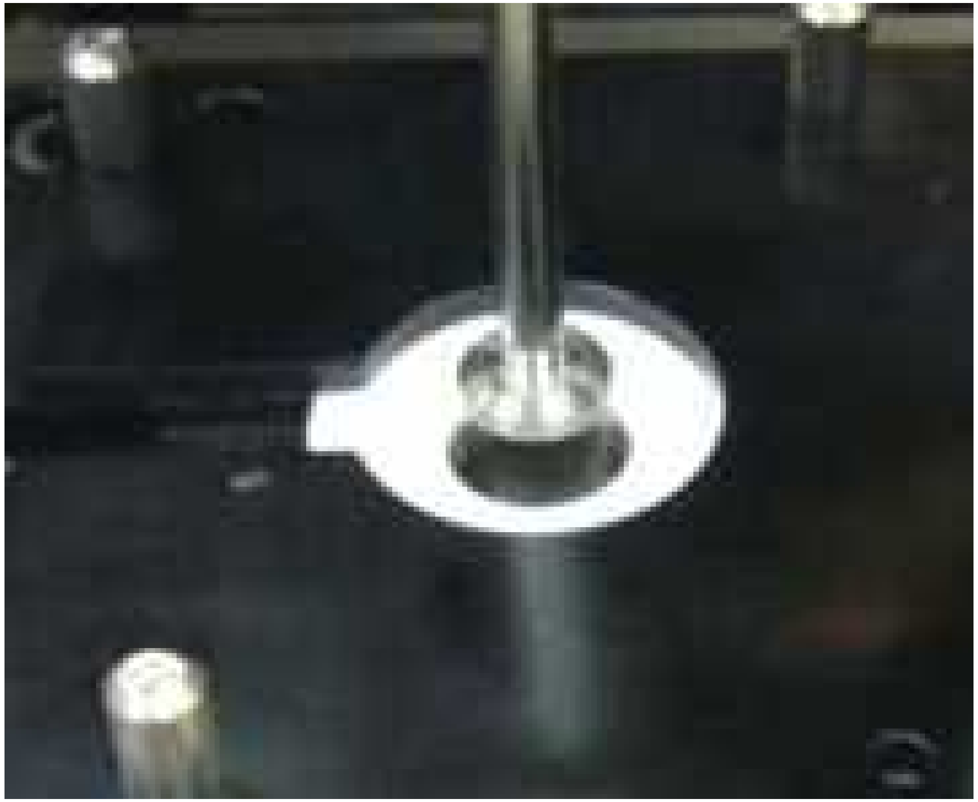


By measuring stress during resin curing, the shrinkage stress of the resin can be known

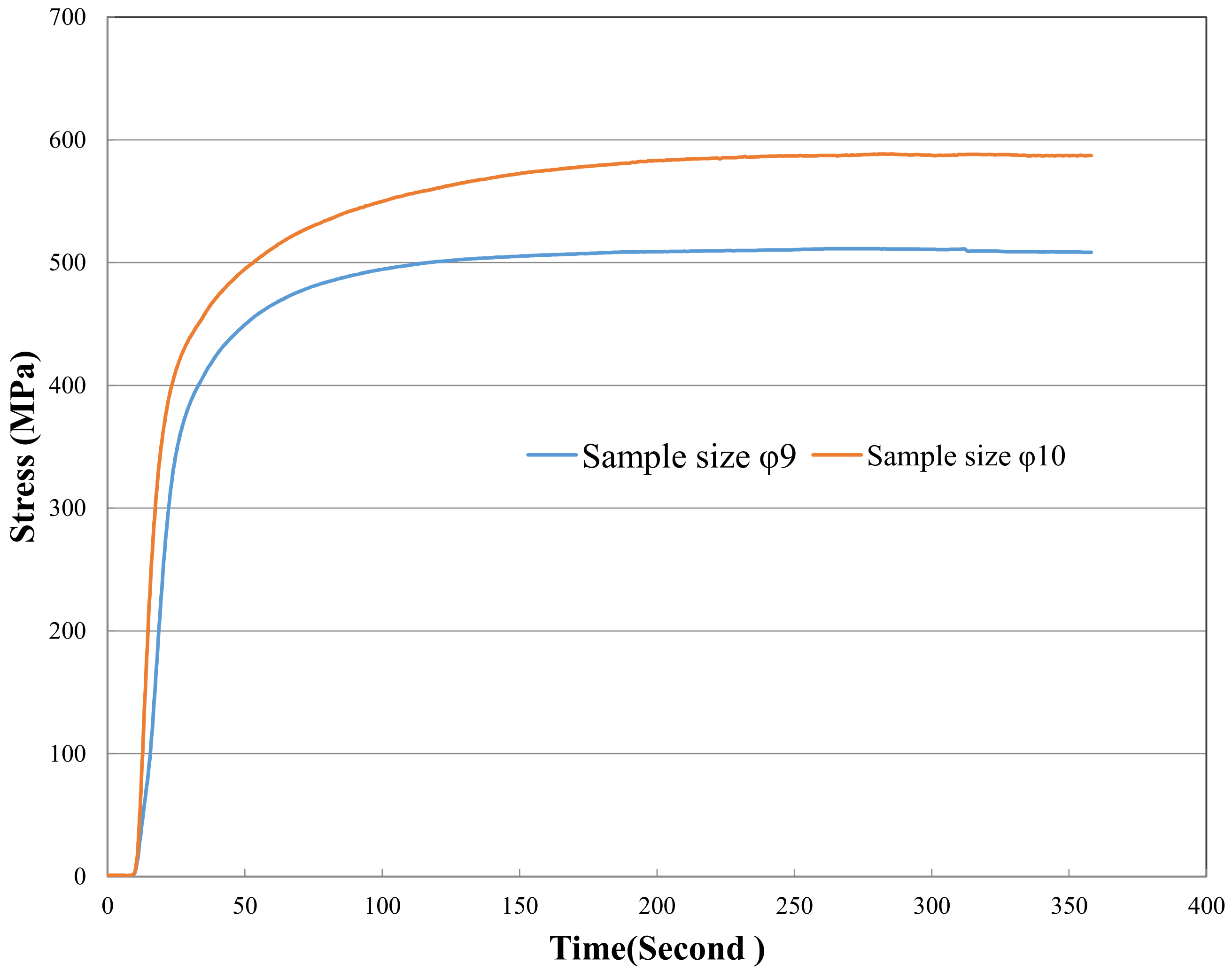
UV irradiation and heater heating can be performed at the same time.

Measurement

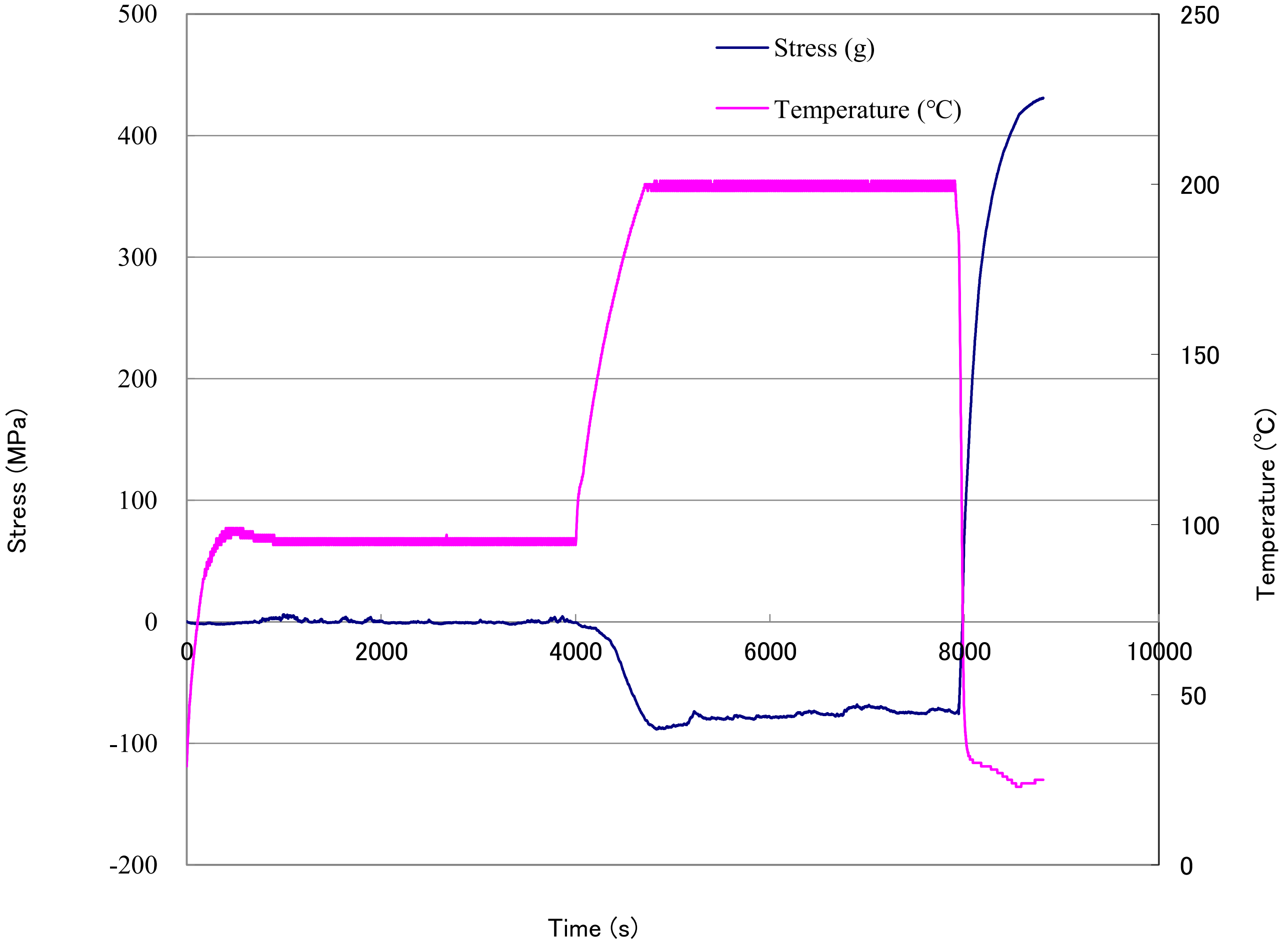
Curing shrinkage stress measurement



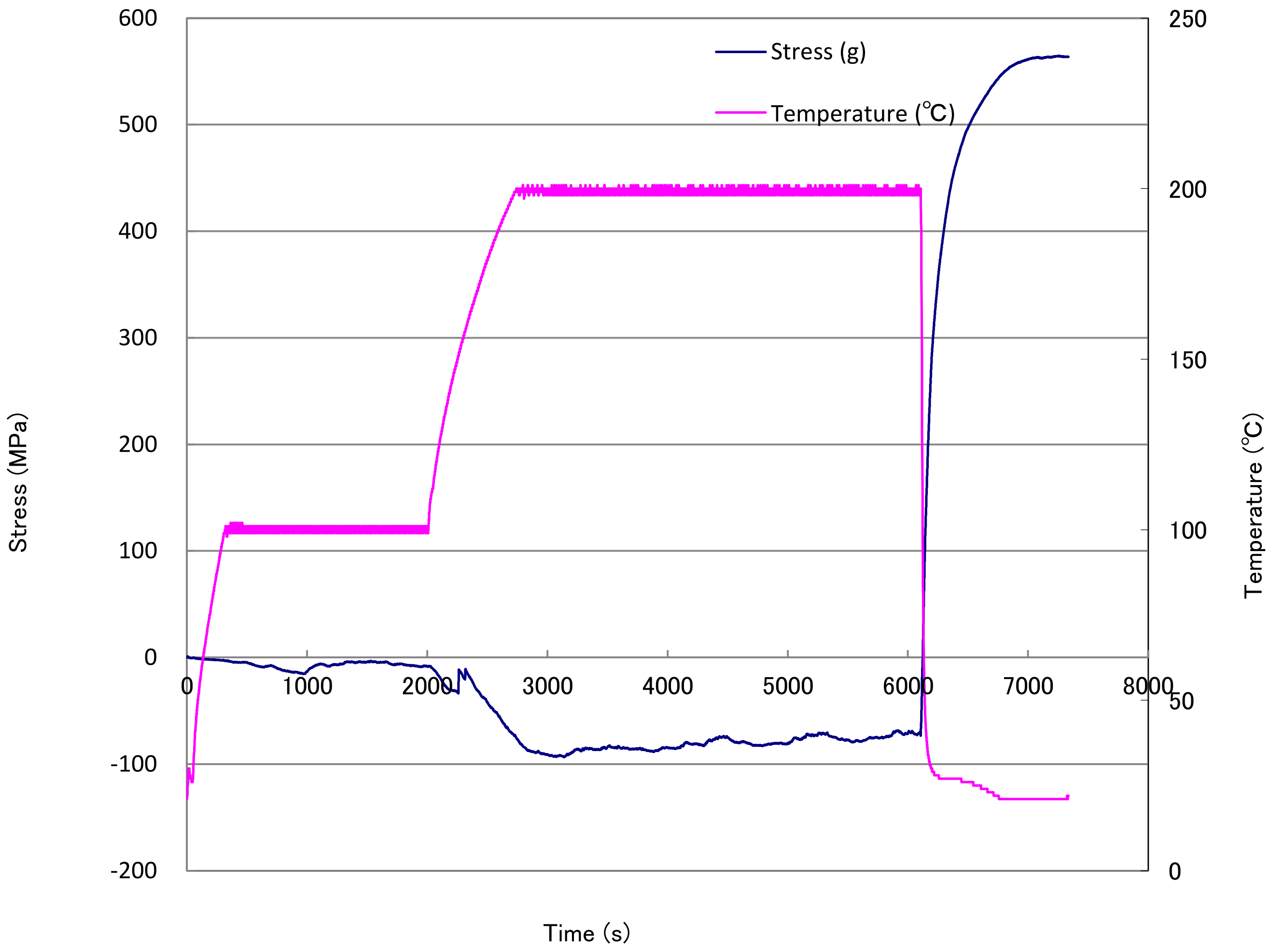
Relation between sample size and stress



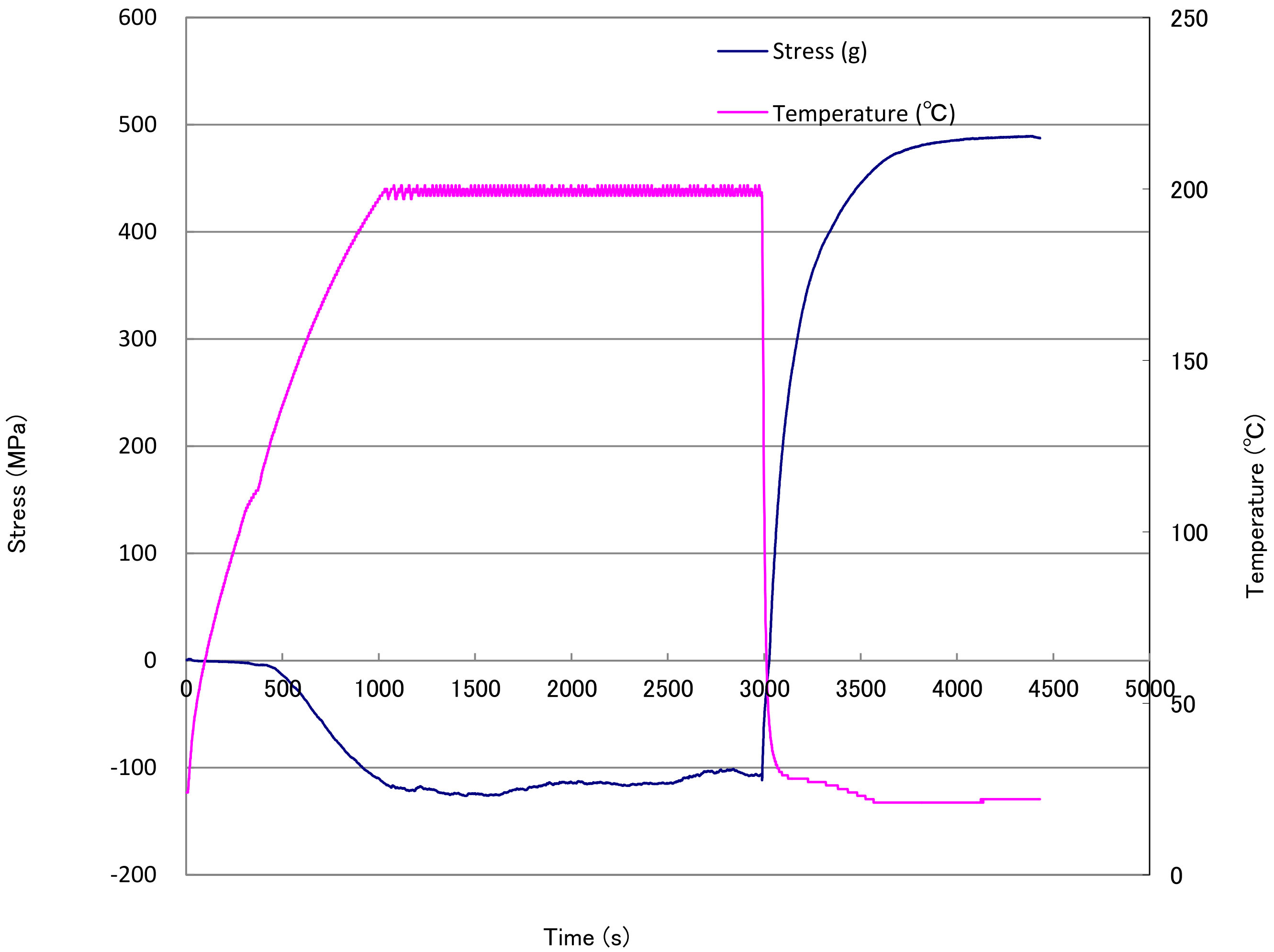
Shrinkage stress



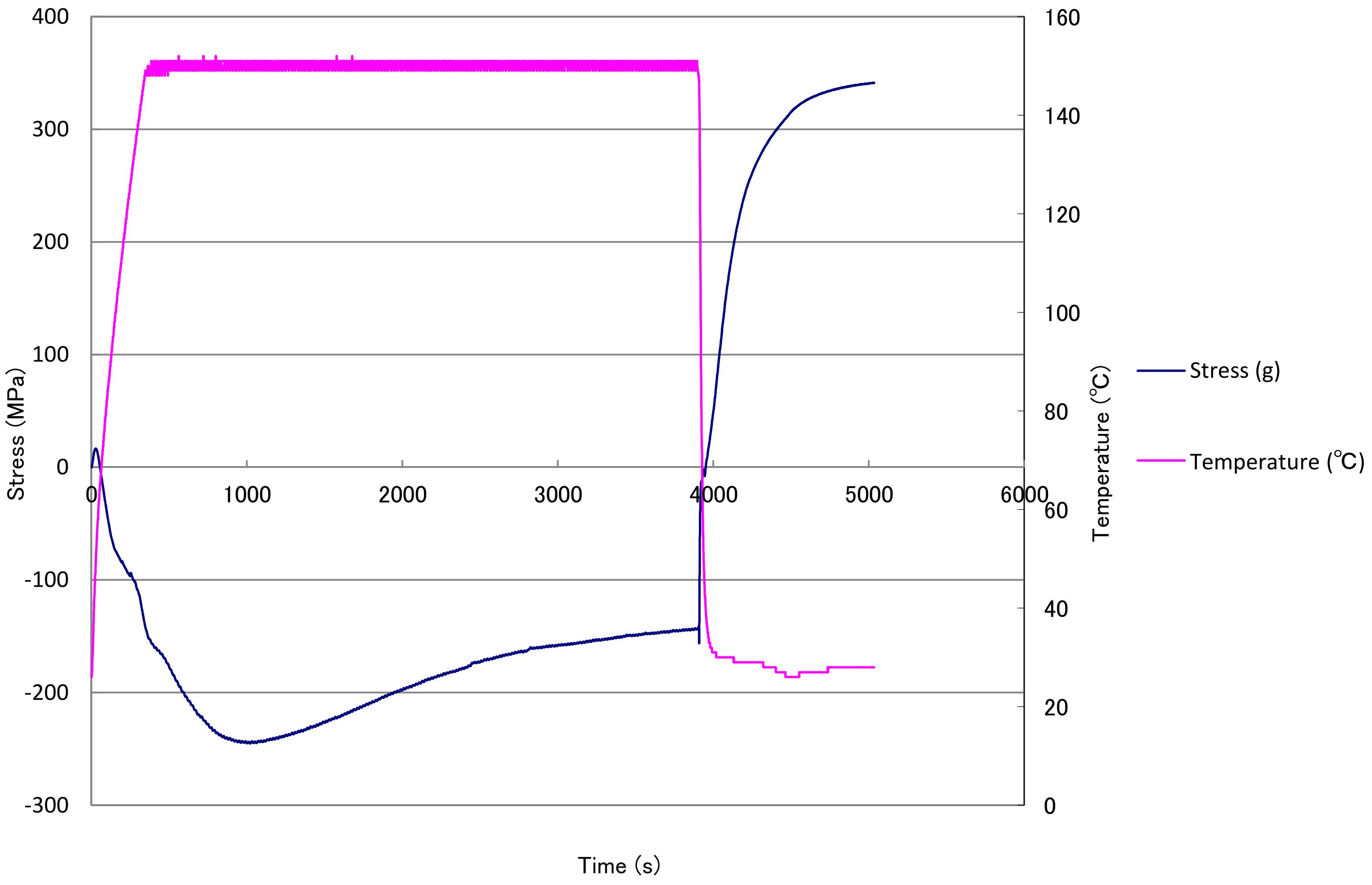
Shrinkage stress



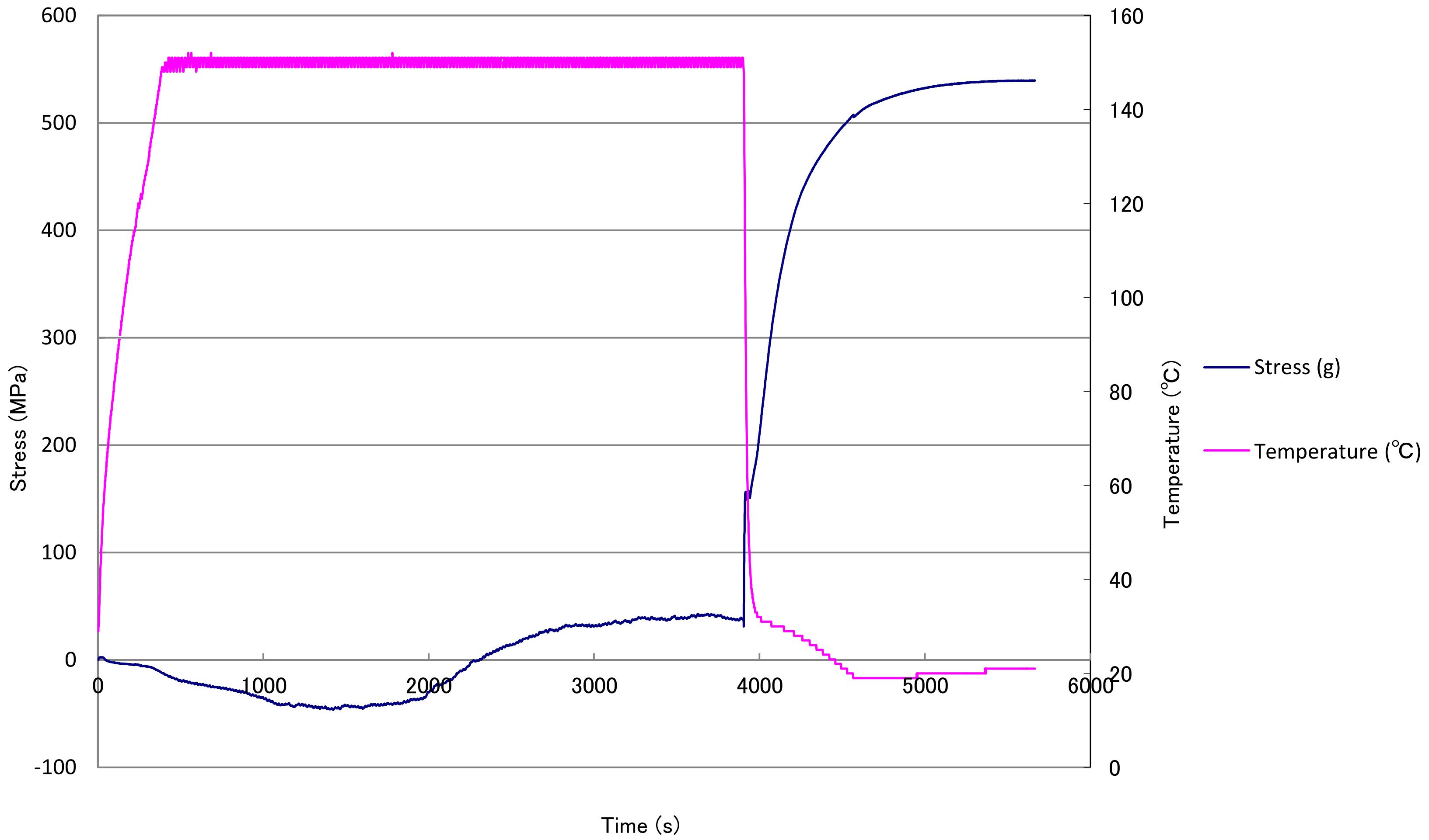
Shrinkage stress



Shrinkage stress



Shrinkage stress



Continuous measurement method of hardened shrinkage rate of UV curing resin and thermosetting resin

Continuous measuring method of curing shrinkage ratio for plastics

The Japan Industry Standardization Committee (a council established under the Industrial Standardization Act) decided to use the "New Market Creative Standardization System" to standardize the three proposals submitted by small and medium-sized enterprises. It is expected that the standardise of excellent technologies and products by small and medium-sized enterprises will lead to the creation of new markets in the future.

1. Overview
Standardization has a significant effect on market creation using new technologies through improved reliability and differentiation in the market. In particular, for small and medium-sized enterprises, it is important to standardise in a competitive fashion.
In order to promote the creation of new markets and the reinforce of industrial competition, ECONOMIC formulated the "Standardise Public-Private War" in May 2014. Based on this battle, in July 2014, the "New Market Creative Standardization System" was established, enabling companies and corporate groups, including small and medium-sized enterprises, to product standardize (JIS) and propose international standards (ISO/IEC) without obtaining consensus from previous industry organizations.

Proposed Theme Proposer [Address]
(1)Standardise of hardened shrinkage continuous measurement method for curing resin

Acro Edge Co., Ltd., Osaka Prefecture
Partner institution: Ikeda Senshu Ginzan Co., Ltd.

2. Future schedule
In the future, the Japanese Standards Association will make up the drafting committee, including the proposed companies, and the drafting of the standardise will be prepare. After drafting, it will be deliberated by the JISC and become a national standard (JIS).
In charge
International Standard Section, Industrial Technology and Environment Bureau
Announcement date
Tuesday, October 11, 2010

THANK YOU

AcroEdge Co., Ltd.
https://www.acroedge.co.jp
〒573-0164 Osaka Prefecture, Hirakata City, Nagaotanimachi 1-70-1
TEL: 072-836-0031 FAX: 072-836-0033 E-mail:office@acroedge.co.jp