Measurement technique of shrinkage ratio and stress value of epoxy resin

（Continuous measurement of shrinkage rate of thermosetting resin）

Introduction

Several electronic components mounted on semiconductor packages are used for communication devices such as mobile phones and laptop computers. In these semiconductor packages, an epoxy resin, which is a thermosetting resin, is used to seal the integrated circuit (IC) chip. Filling and curing the epoxy resin between the IC chip and the printed circuit board plays an important role in securing the strength and reliability of the electronic components. Epoxy resins are generally accompanied by changes such as crosslinking density and volumetric shrinkage due to chemical reaction during the process of curing from a viscous fluid, and occurrence of residual stress and strain inside the material after curing. These changes may cause defects such as strength reduction and deformation of the semiconductor package, therefore, it is important to characterize the mechanism of thermal stress and deformation behavior generated in the curing process. Widely used curing process of various functional adhesives involves hybrid products combining UV curing and thermal curing.

It is not an exaggeration to say that all industries such as electricity, devices, automobiles, building construction benefits from coating film formation, such as the mentioned curing processes various functional adhesives. In order to maintain international competitiveness and continue to supply high quality products, it is necessary to reduce yield, stabilize production efficiency, and lower product cost. In line with this, it is necessary to accurately establish the shrinkage rate, shrinkage stress and change over time of resin coating the thin film. Conventional methods use viscoelasticity measuring device to measure the shrinkage ratio from the volumetric change before and after shrinkage of the resin (i.e., underwater displacement method described in JIS K 7112, etc.). There has never been a method to simply and substantially measure a trace amount of highly functional resin continuously. A device called Custron (Cure Shrinkage and Stress Analysis System) is a device that can continuously measure the curing shrinkage rate and stress of a resin in a trace amount. In this article, we describe the basic principle of resin shrinkage, cure shrinkage of epoxy resin, and stress measurement method by analysis of data measured by Custron. Also note that during the year of 2018 it is a method accredited in JIS.

１． Cure shrinkage model of epoxy resin

The model diagram of epoxy resin curing is shown in Fig.1. The liquid state A at room temperature is heated which triggers reaction which is meaintained at the curing temperature B. The curing temperature at the end of reaction is defined as C at which point the sample is allowed to cool, reaching the glass transition temperature, Tg, which is defined as D, and finally reaching room temperature E. Shrinkage due to curing reaction occurs between B and C in this model drawing, and contraction due to cooling after curing is indicated by CDE. However, since D corresponds to the Tg of this system, shrinkage in the glassy region (<Tg) corresponds to D - E, shrinkage in the rubbery region (> Tg) occurs between C - D. For further explanation, the contraction between A and E is referred to as total contraction, and the contraction between B and E as maximum contraction. The shrinkage ratio of ordinary thermosetting epoxy resin will be measured between A and E. In the substitution density measurement examples of Kansai University and Yamaoka et al., Etallenediamine has a total maximum shrinkage (A – of 5.1% Max shrinkage B - E of 10.5%. In *Tetrametylenediamine*, total maximum shrinkage at A - E is 4.8% and maximum shrinkage at B - E is 10.1%.

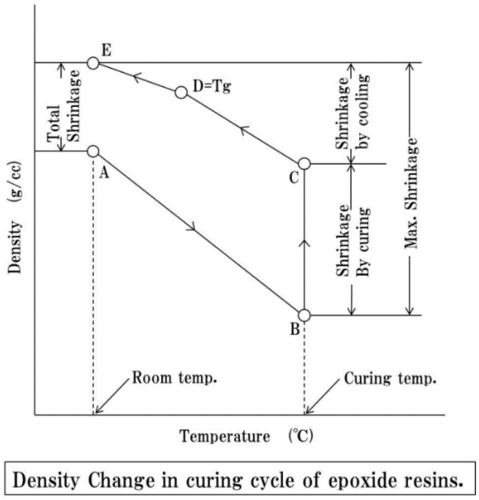

Fig.1 Cure shrinkage model

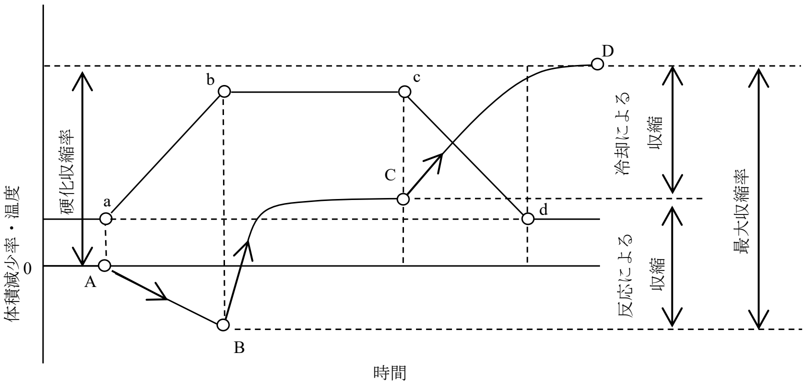

Fig.2 Hardening behavior of thermosetting resin

２． Measurement device outline

Custron was originally developed with the measurement of UV curable resin as a target, but with the diversification of market needs, the demand for application to thermosetting resin gradually increased, thus improvements were made in response to these needs. At the present time, the device can successfully extend the range of response to curing shrinkage rate and curing stress of various materials such as UV curing resin and thermosetting resin. The principle/method is patented on January 27, 2016. The thermosetting resin is often heated and cured to 80℃～300℃ and simultaneous precision control in swelling of the casing by heat and shift of sensor sensitivity are done. This process is repeatedly improved and currently, Custron makes it possible to measure the curing shrinkage rate and curing stress of a high-performance thermosetting resin by eliminating factors that affect the measurement accuracy.

For the measurement procedure, the curing shrinkage displacement of the resin is measured using laser irradiation while cooling system simultaneously maintains uniform temperature at the base of the resin. It is also possible to set the UV light power, thermal profile (normal temperature to 300℃), and not only continuously measure the shrinkage rate and curing stress in that state, but most specially the surface temperature. Furthermore, the upper and lower temperature settings can also be programmed. The curing reaction requires particular temperature in the reaction of the epoxy resin where greater or lesser exothermicity may affect the adherence, thus it is important to measure the reaction heat emitted from the resin itself.

３． Device configuration

Custron consists of a control section, a measuring section, PC, and a chiller. The measurement section is composed of a stage that controls the heating of the material, a measurement laser, a load cell, a radiation thermometer, UVLED, a high pressure mercury lamp, and the like. The basic specifications are as follows.

(1) Continuous measurement of shrinkage ratio, expansion coefficient and stress before reaction, during reaction, reaction
(2) Measurement of resin surface temperature
(3) Approximately 1 cc of measured resin
(4) heating、ＵＶ Irradiation（High pressure mercury lamp、ＵＶＬＥＤ）
(5) Program control

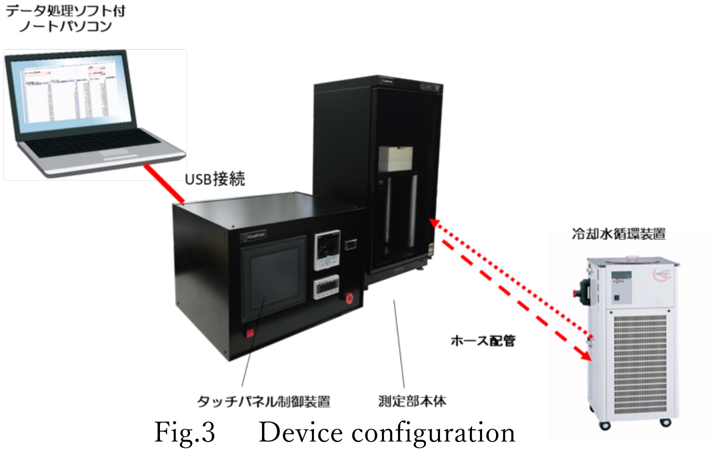

Fig.3　Device configuration

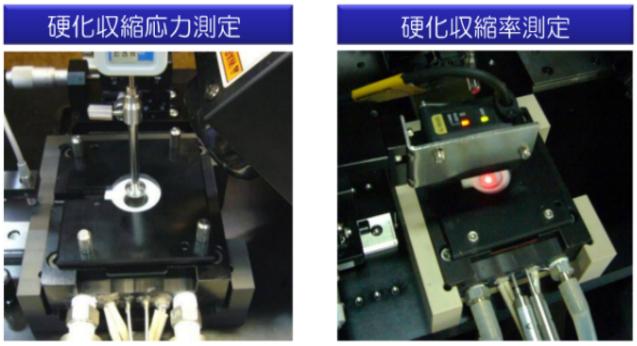

Fig.4　Measuring part

A remarkable feature of this device is that the temperature profile can be set up to 20 temperature conditions identical to an actual production site where the heat for curing the resin has various kinds of heating conditions. Various temperature conditions in the entire production process causes expansion and shrinkage of the resin and greatly affects the quality of the product. This device can reproduce these varied temperature conditions.

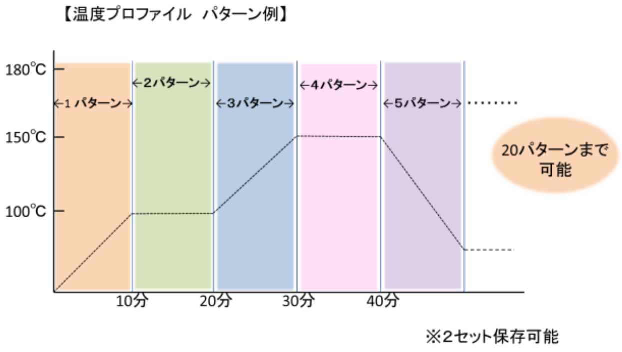

Fig.5　The temperature profile

4． Shrinkage factor calculation formula

Since the shrinkage progresses in accordance with the shape of the container in the fluid sample, assuming that the cross-sectional area of the resin does not change before and after the start of curing, the volume contraction ratio is calculated by the following formula.

$$A(t) = (V_0 - V(t)) / V_0 \times 100 \ (\%)$$

$$= [T_0 - T(t)] / T_0 \times 100 \ (\%)$$

where、

$A(t)$：Cure shrinkage ratio at time t according to arbitrary curing conditions（%）

t ：Elapsed time after initiation of curing

V_0：$t = 0$ Initial volume,

$V_0 = T_0 \times S$

$V(t)$：Volume at time t,

$V(t) = T(t) \times S$

S：Sample cross section

T_0 ：$t = 0$ Initial film thickness（Fig.6 reference）

$T(t)$：The film thickness at the time t under arbitrary curing conditions（Fig.7 reference ）

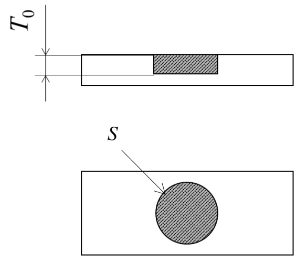

Fig.6 Initial film thickness and sample cross section

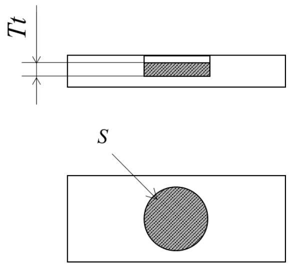

Fig.7 Film thickness and sample cross-sectional area at time t

5. Measurement example

5 - 1 Measurement of shrinkage rate

An example of cure shrinkage ratio measurements of thermosetting resin which is heated to 125℃ and maintained at room temperature is shown in Fig.8. The thermosetting resin expands during heating, then starts shrinking after reaching the curing temperature, and further shrinks when it reaches the normal temperature.

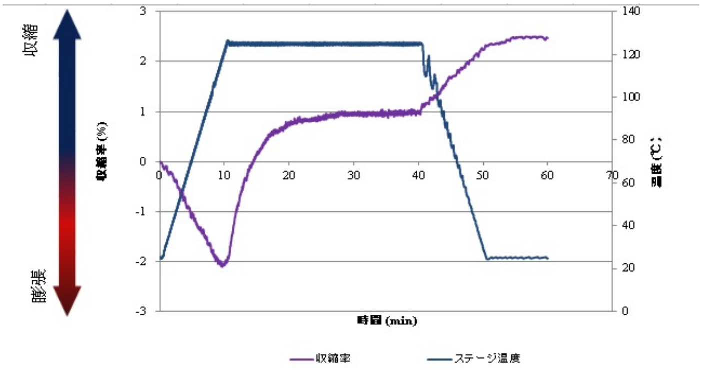

Fig.8 Thermosetting resin shrinkage factor measurement result

Note The measurements before and after curing can be compared with the conventional heat shrinkage ratio according to the conditions specified in **JIS K 6911** (48 h or 168 h) and temperature (80°C or 110°C).

5 - 2 Ultraviolet ray curing - Example of thermal shrink shrinkage measurement

Figure 9 shows an example of measurement results of the cure shrinkage ratio of resin initially irradiated with ultraviolet rays, then warmed and maintained to room temperature. The resin shrinks immediately after irradiation with ultraviolet rays, then it begins to expand again when heating begins, shrinkage starts again when it reaches the curing temperature, and further shrinkage progresses when the temperature is lowered to ordinary temperature.

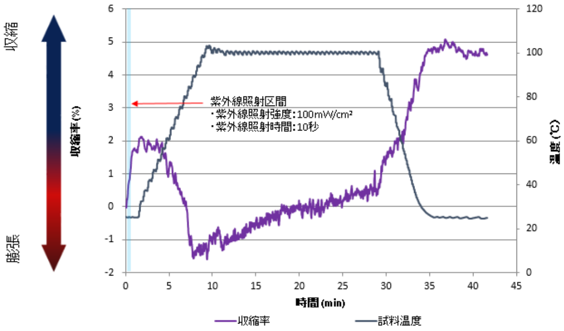

Fig.9 Hybrid thermosetting resin shrinkage measurement example

Figure 10 shows the measurement result of the cure shrinkage ratio when the thermosetting epoxy resin with excessive binder was heated from room temperature to 200°C and then rapidly cooled and maintained to room temperature for 50 minutes. As the temperature rises, the liquid resin begins to expand and is cured by polymerization. However, when the curing reaction is completed at 200°C, expansion due to heat is maintained. However, it contracts with rapid cooling, resulting in shrinkage of about 2%. By continuously measuring the resin surface and the resin measuring plate with two lasers and taking the difference, it is a system that can remove the thermal expansion component of the measurement part and measure the expansion and shrinkage of only the resin in micron order.

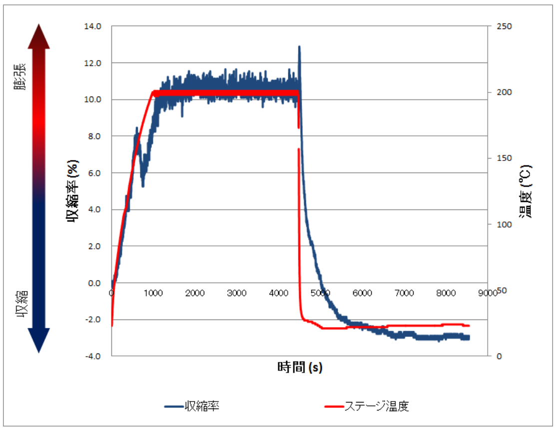

Fig.10 Measurement example of thermosetting epoxy resin shrinkage factor

5 - 3 Example of contraction stress measurement

Figure 11 below shows an example of measuring the stress generation process when the temperature is raised from room temperature to 200°C, kept for 30 minutes and rapidly cooled to room temperature. As the curing starts from the liquid state, the stress gradually starts to generate. The shrinkage rate reaches maximum at the same time as the shrinkage stress turns maximum when the resin rapid cools from 200°C.

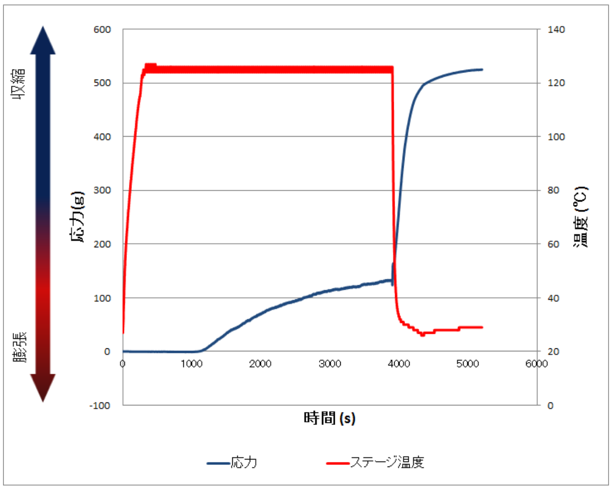

Fig.11　Measurement of shrinkage stress of thermosetting epoxy resin

5 - 4　Two step reaction shrinkage stress measurement example

Fig. 12 below shows the state of stress development in which the temperature is raised from room temperature to 100℃ held for 30 minutes and 200℃ held for 60 minutes. In this case, it can be seen that when the temperature is raised to 200℃. after maintain the temperature at 100℃, the stress has negative value (expanding). After that, stress is rapidly occurring with rapid cooling. In fact, considering the adhesion to the adherend, interface peeling due to rapid strength development can be realized. Also, sudden stress development can also cause factors such as adhesion distortion with an adherend.

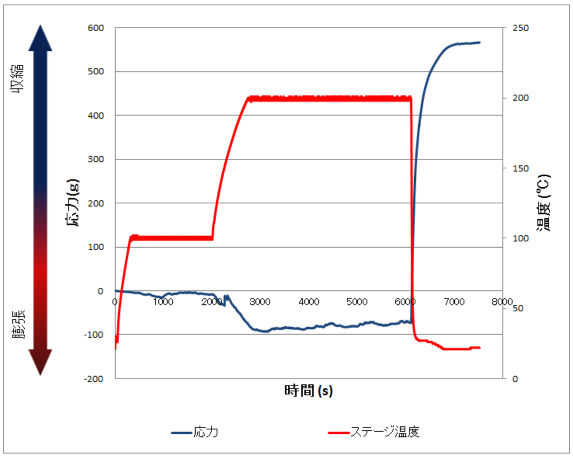

Fig.12　Measurement of shrinkage stress of thermosetting epoxy resin

Conclusion

Continuous measurement method of resin shrinkage ratio is planned to be a Japanese Industrial Standard (JIS) in Financial Year (FY) 2018. This possibility caters to a new market creation type standardization system which is timely in the world of rapidly changing technology such as electronic device’s EV conversion. It may not be cutting-edge, but it supports solutions to fundamental manufacturing problems.

A lot of critical parameters are yet to be answered such as the conditions where the resin will have maximum hardness, conditions where shrinkage of resin is smallest, and conditions for maximum reduction of internal stress.

Despite this, the method is promising in wide range of applications and expects further progress in research and development.

<References>

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（２）電子部材用途におけるエポキシ樹脂　CNC 出版