TORAY
Innovation by Chemistry

Overcoming the Limits of Conventional Analysis: Advanced Approaches for Semiconductor Packaging and Energy-Related Materials

Part 1. The Attractiveness of Toray Research Center (5 min.)

Part 2. Latest Innovative Material Detective Work

- Thermoset resin analysis (25 min.) & Metal-complex analysis (15 min.)

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Part 1: The Attractiveness of Toray Research Center

Toray Research Center

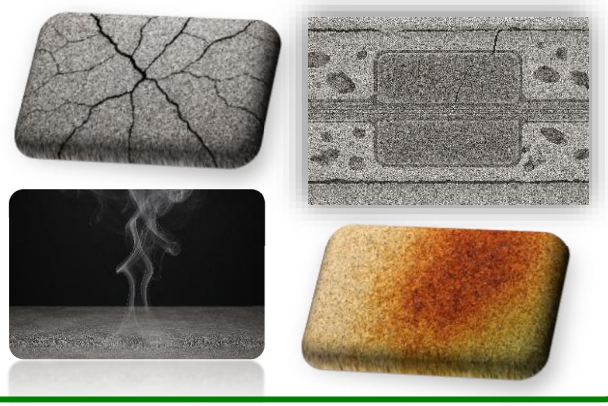
Establish : 1978
400 Researchers (20% PhD expert)

Most Trusted and Proven Partner for Advanced Chemical Analysis Outsourcing in Japan

Clients

Demand

Quality Problems
Reverse Engineering



Sample shipment

Problem-solving

Toray Research Center

Supply

Root cause analysis
Troubleshooting

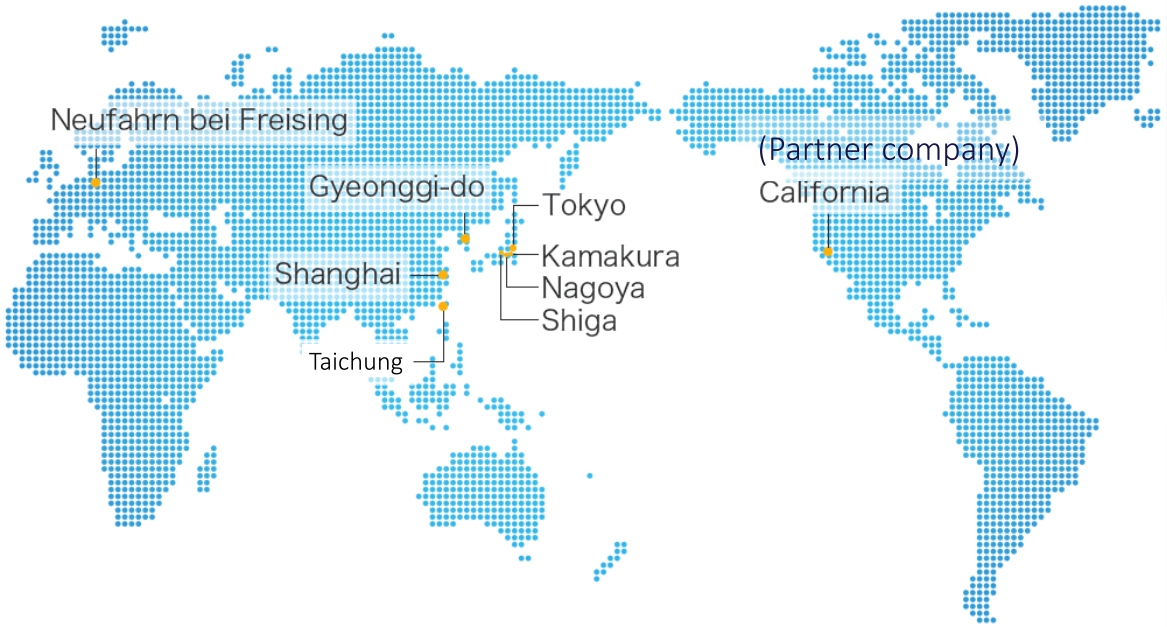
Why We Are Chosen

- Clear Understanding of Your Analytical Needs
- Fast, Tailored Analysis from Design to Insight
- Proven Expertise Built on 45+ Years of Experience

E-mail address:
bunseki.trc.mb@trc.toray

QR code to inquiry form:

Toray Research Center (TRC) / Location



Shiga Main Lab.

Shanghai Lab.

Munich Lab.

Tokyo HQ

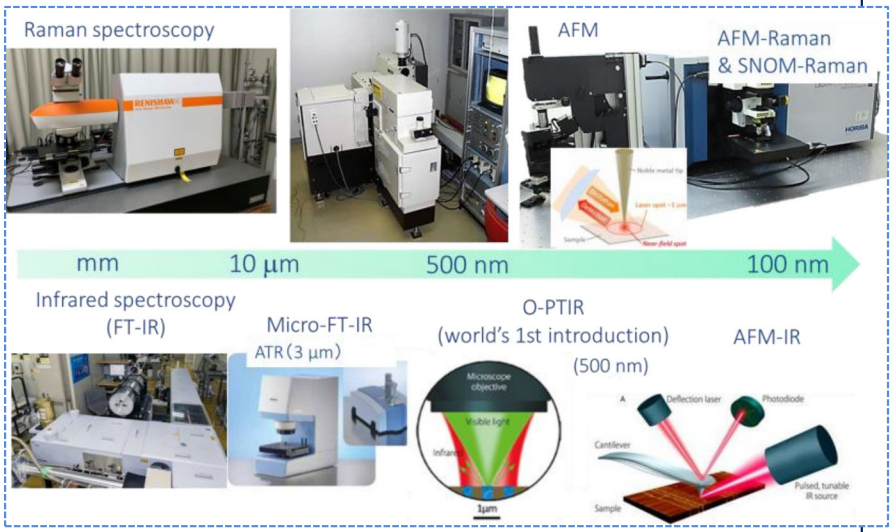
We are a global enterprise with worldwide business operations.

How to achieve problem solving

TRC's competence: Wide variety of analytical instruments (More than 200 instruments)

Representative analytical instruments in Japan's main laboratory

- AAS
- AEM
- CE
- CL
- CLSM
- Composition Analysis
- Cs-corrected STEM
- EA
- EBSD
- EGA
- ELISA
- EPMA
- ESR
- FT-IR
- GC
- GC/MS
- GDMS
- GD-OES
- GPC
- HFS
- Hg Probe
- IC
- ICP-MS
- ICP-OES
- ITC
- LA-ICP-MS
- LC/MS
- LC-NMR
- MALDI-MS
- Mechanical Properties
- Nano-SIMS
- NMR
- NMR (solid-state)
- NRA
- PIXE
- Raman
- RBS
- Rheological Properties
- SEM
- SIMS
- SPM
- SRA
- TD-NMR
- TA
- TEM
- Thermal diffusivity
- TOF-SIMS
- TPD-MS
- UV-VIS
- Vapor Pressure
- XAFS
- XPS
- XRD
- XRF
- XRM, et al.

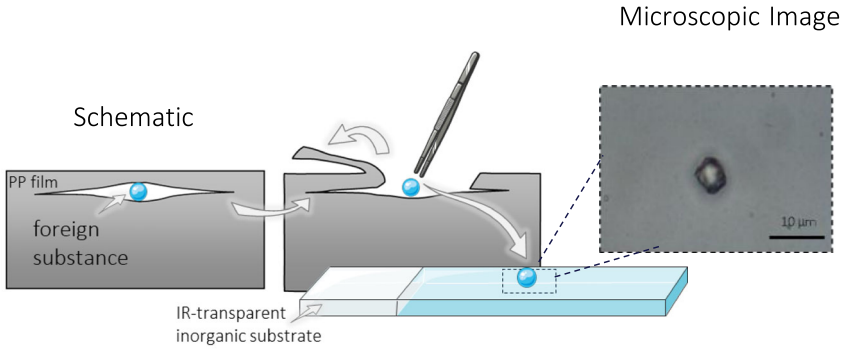


Top-level versatility under one roof!

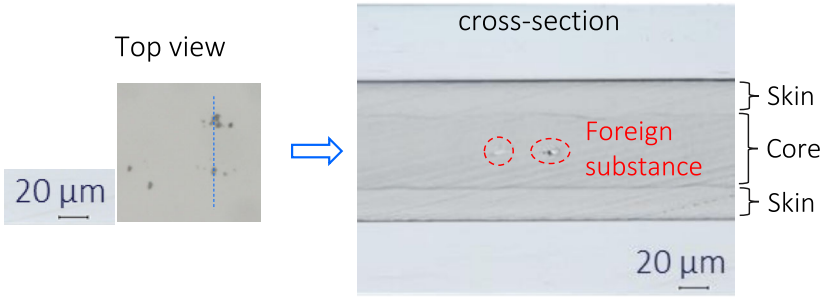
How to achieve problem solving

TRC's competence: Development of sample preparation methodologies

Micro-sampling



Pin-point cross-sectioning



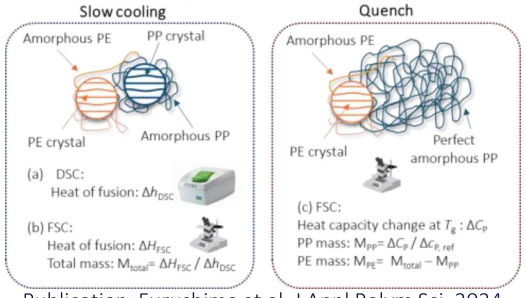
Analysis procedure

How to achieve problem solving

TRC's competence: Development of analytical methodologies

Composition

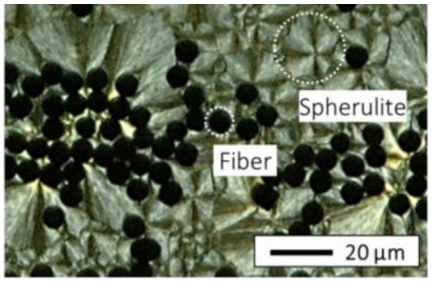
Eco-friendly and rapid determination of PP/PE mass fraction



Publication: Furushima et al. J Appl Polym Sci. 2024

Morphology

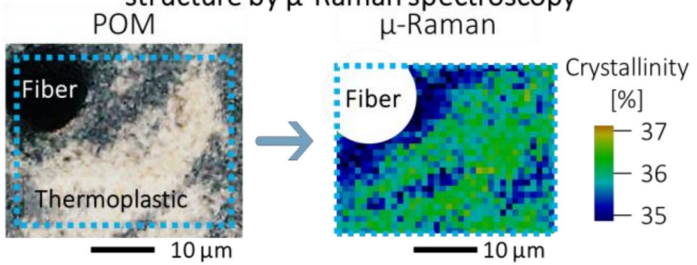
Macroscopic crystalline structure of FRTP observed by POM



Publication: Yoshida et al. Polym Compos. 2024

Chemical structure

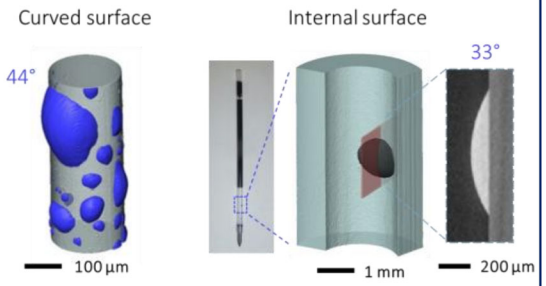
Microscopic distribution of polymer higher-order structure by µ-Raman spectroscopy



Publication: Yoshida et al. Polym Compos. 2025

Surface property

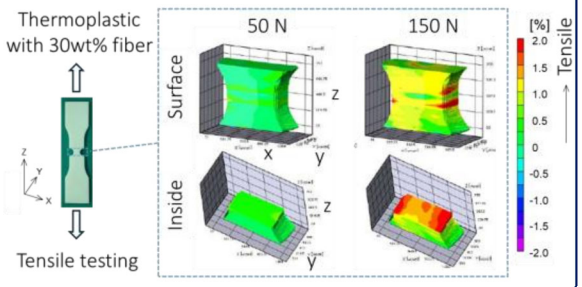
Micro-scale contact angle measurement by Xray-CT



IP right: Patent number; JP7572335, country; Japan

Mechanical property

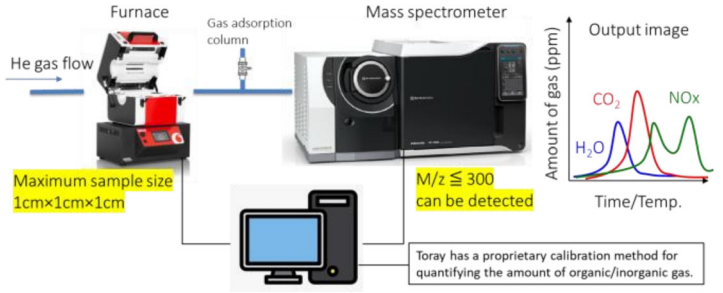
In-situ 3D strain distribution monitoring by Xray-CT with DIC



Funded from Japan's national research institute

Out gas

Temperature Controlled Desorption – Mass Spectroscopy (TPD-MS)

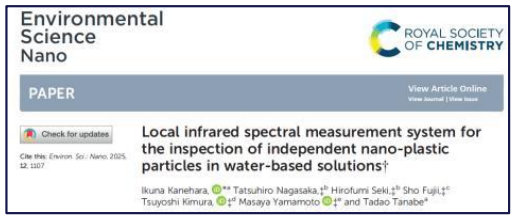


Publication: Furushima et al., Chem. Therm. Therm. Anal.5 (2022) 100029.

How to achieve problem solving

TRC's competence: Advancing analytics via academic collaboration and peer-reviewed research

Publications in 2025 (Materials science)


Environmental Science Nano

PAPER

Local infrared spectral measurement system for the inspection of independent nano-plastic particles in water-based solutions†


Analyst

PAPER

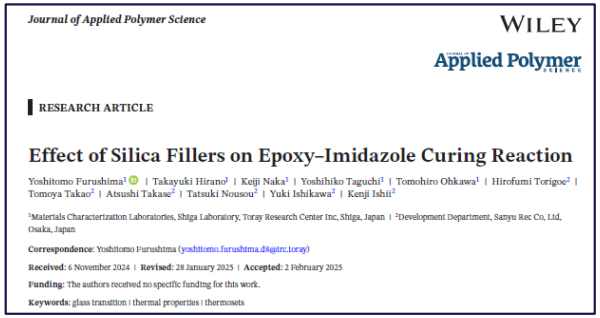
Establishing a universal dry etching methodology to unveil the nanoscale crystalline structure of fiber reinforced thermoplastic composites *via* scanning electron microscopy


Thermochimica Acta

The evolution of the cooperative feature under the curing process of an epoxy resin elucidated by fast scanning calorimetry

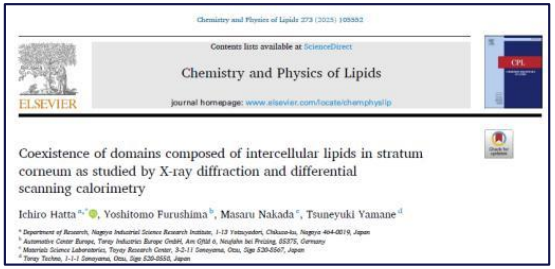

Thermochimica Acta

Thermal Gibbs–Thomson and Hoffman-Weeks analysis for non-isothermal condition of polyethylene glycol


Journal of Applied Polymer Science

RESEARCH ARTICLE

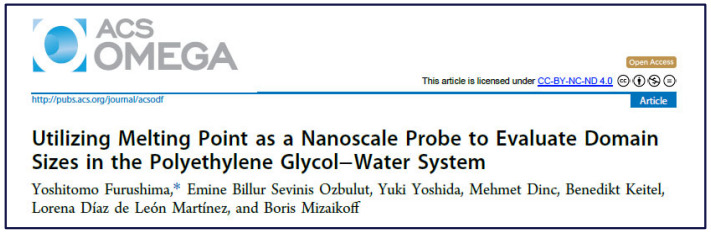
Effect of Silica Fillers on Epoxy–Imidazole Curing Reaction


Chemistry and Physics of Lipids

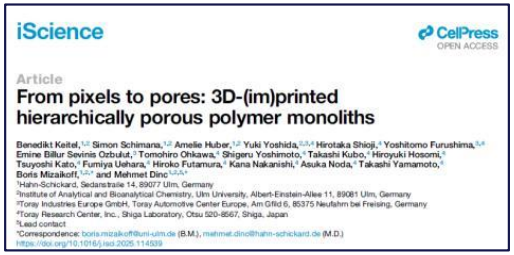
Coexistence of domains composed of intercellular lipids in stratum corneum as studied by X-ray diffraction and differential scanning calorimetry


Polymer

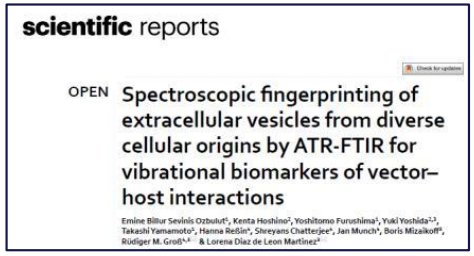
Oxygen-dependent non-isothermal degradation kinetics of polypropylene: a predictive model


ACS OMEGA

Utilizing Melting Point as a Nanoscale Probe to Evaluate Domain Sizes in the Polyethylene Glycol–Water System


iScience

From pixels to pores: 3D-(im)printed hierarchically porous polymer monoliths


scientific reports

OPEN Spectroscopic fingerprinting of extracellular vesicles from diverse cellular origins by ATR-FTIR for vibrational biomarkers of vector–host interactions

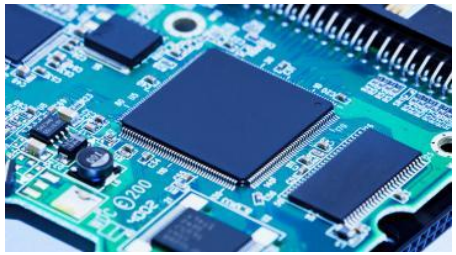
Part 2: Latest Innovative Material Detective Work

Topic:

- Thermoset resin analysis
- Metal-complex analysis

Thermoset resins

Widely used in various industries



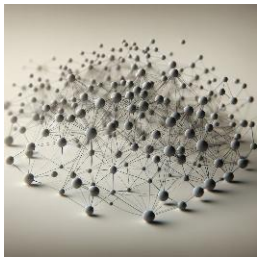
Semiconductor

Devices

Automotive

Aerospace

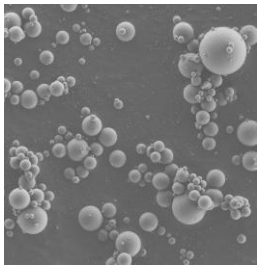
3D network gives various functions



- High strength
- Superior thermal properties
- Chemical resistance
- Lightweight

+

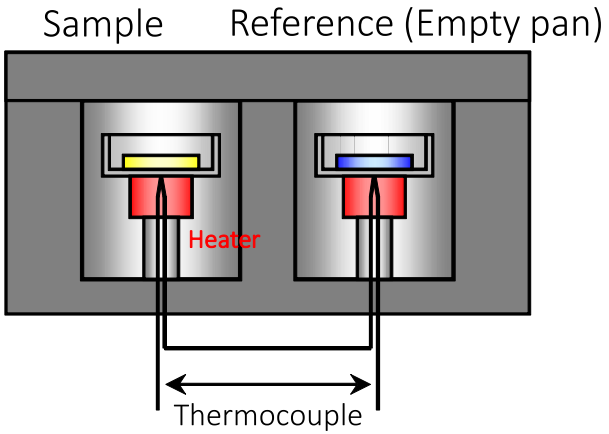
Adding filler or fibers



- Improved mechanical properties
- Enhanced thermal properties
- Modified electrical properties
- Cost reduction

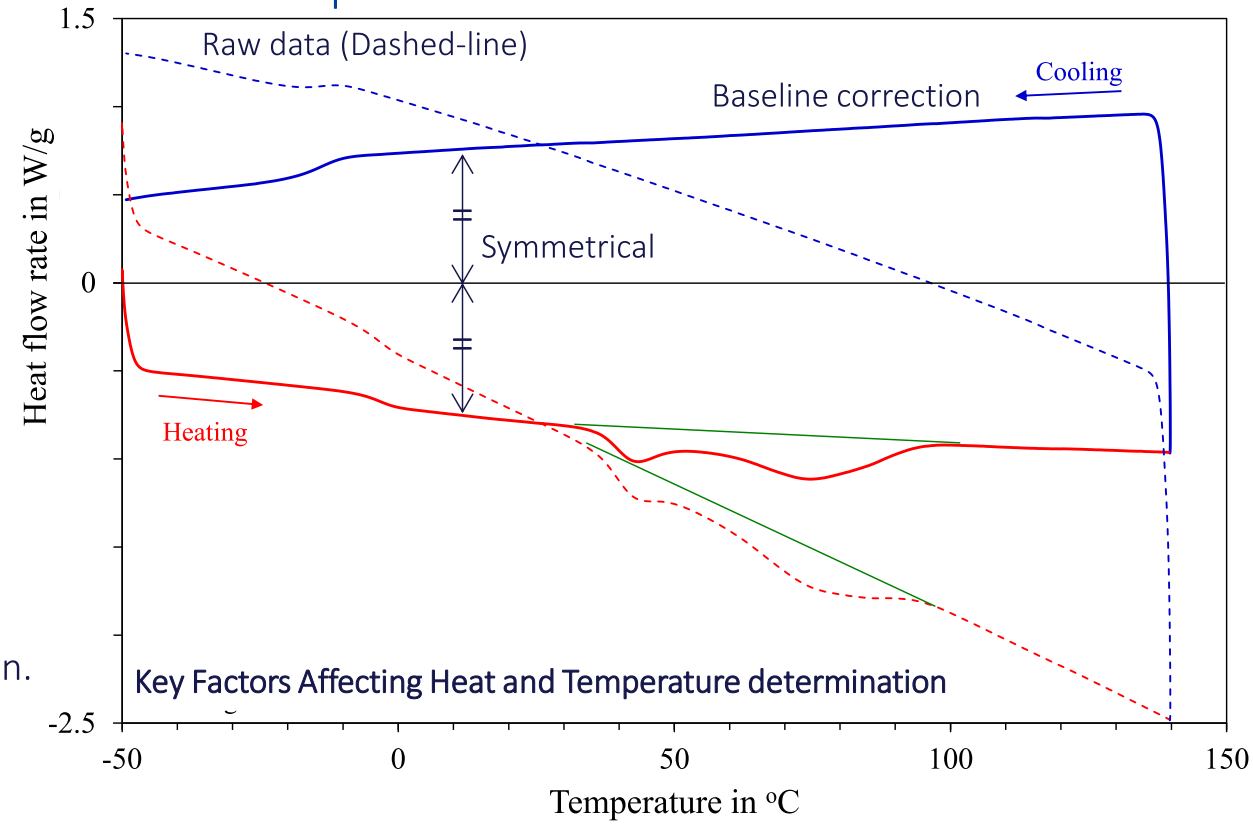
Countless Combinations of Resins, Hardener, Additives, and Fillers Require Analytical Expertise

Differential Scanning Calorimetry (DSC)—Standard Method for Thermoset Resin Analysis



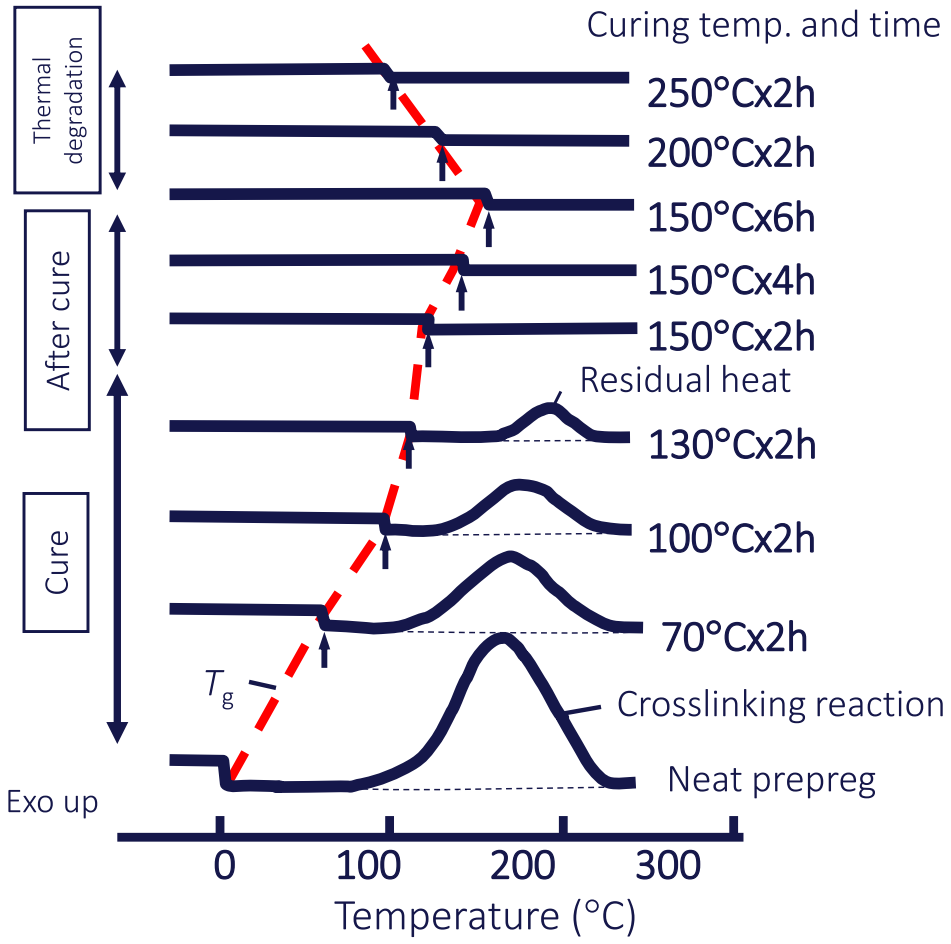
Measure the heat flow rate (W = J/s)
during heating/cooling at a rate of ca.10 °C/min.

TRC's competence



TRC incorporates a high-precision correction method beyond the instrument's standard software

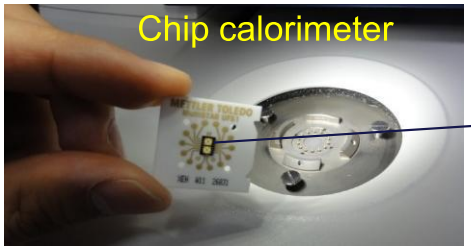
Schematic image of DSC curves of epoxy resins

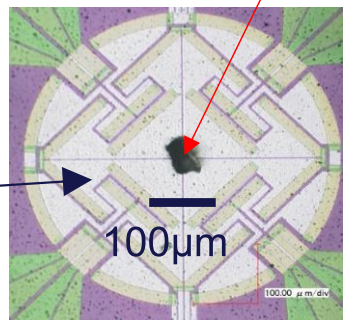


M.Todoki, Shikizai 296,79,2006

Fast Scanning Calorimetry (FSC)

Mettler Toledo FlashDSC1

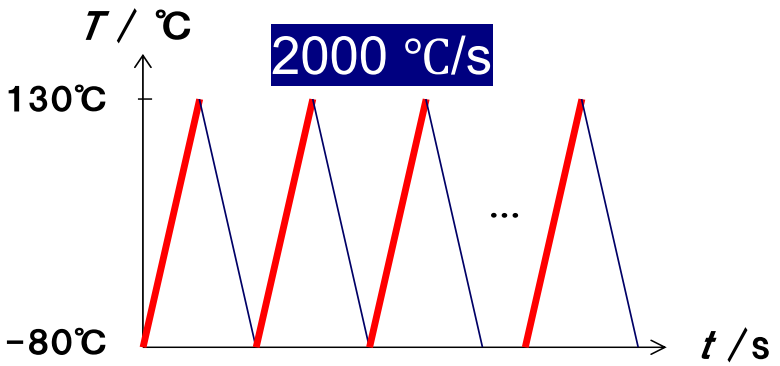




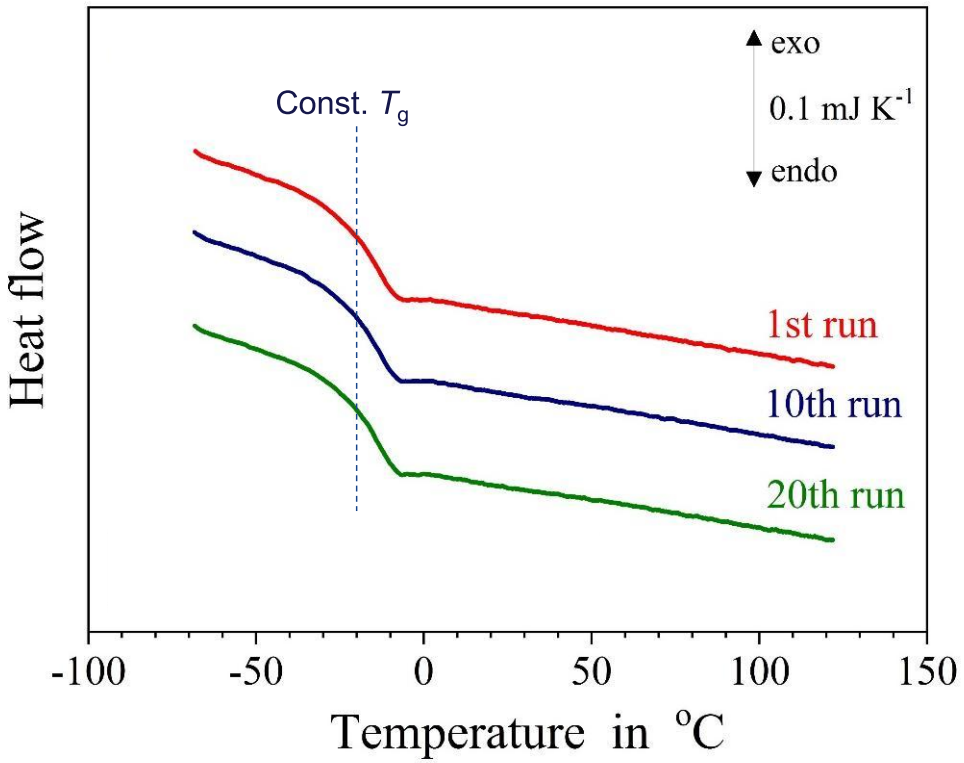
Maximum	FSC(FlashDSC1)	DSC
Heating rate	20,000 °C/s	5 °C/s
Cooling rate	5,000 °C/s	1 °C/s

Quasi-real-time change in T_g of a thermoset resin under cure

<FSC profile>



FSC heating traces of epoxy resin

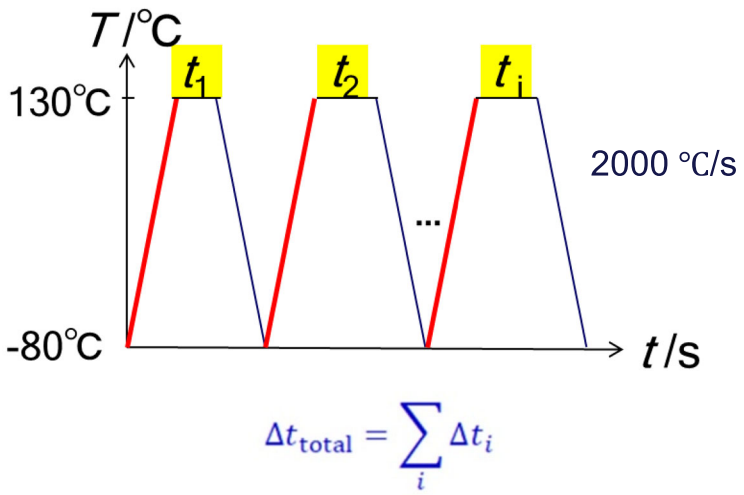


<Key findings>
The chemical reaction of epoxy resin can be suppressed by fast-scan.

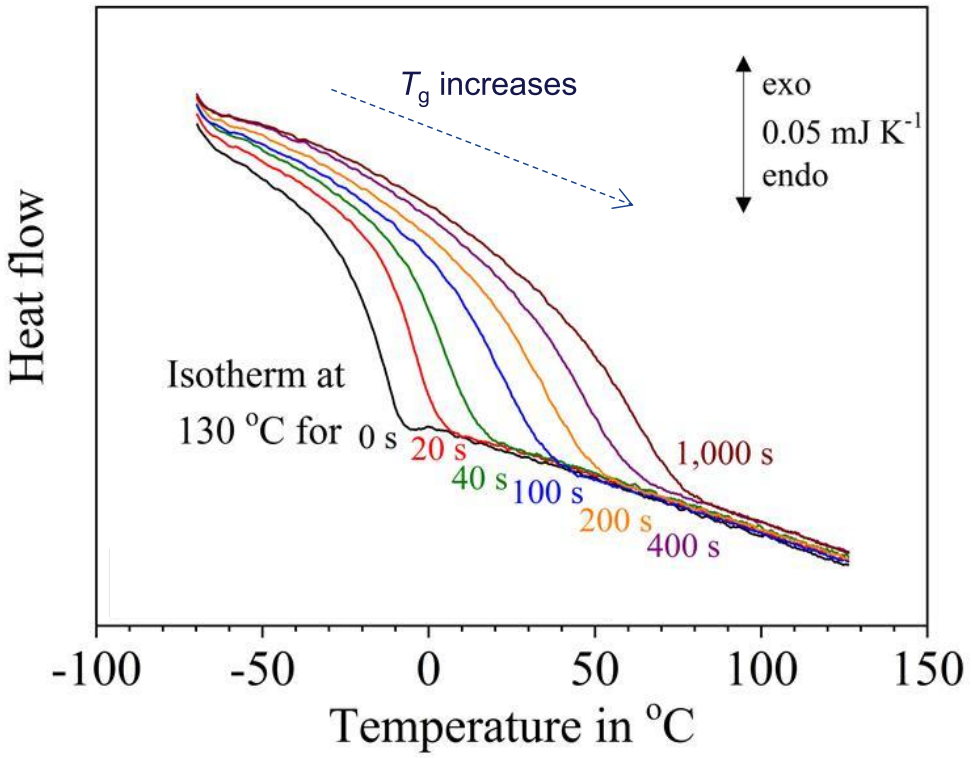
Y. Furushima, Thermochimica Acta 677 (2019) 79-84.

Quasi-real-time change in T_g of a thermoset resin under cure

<FSC profile>

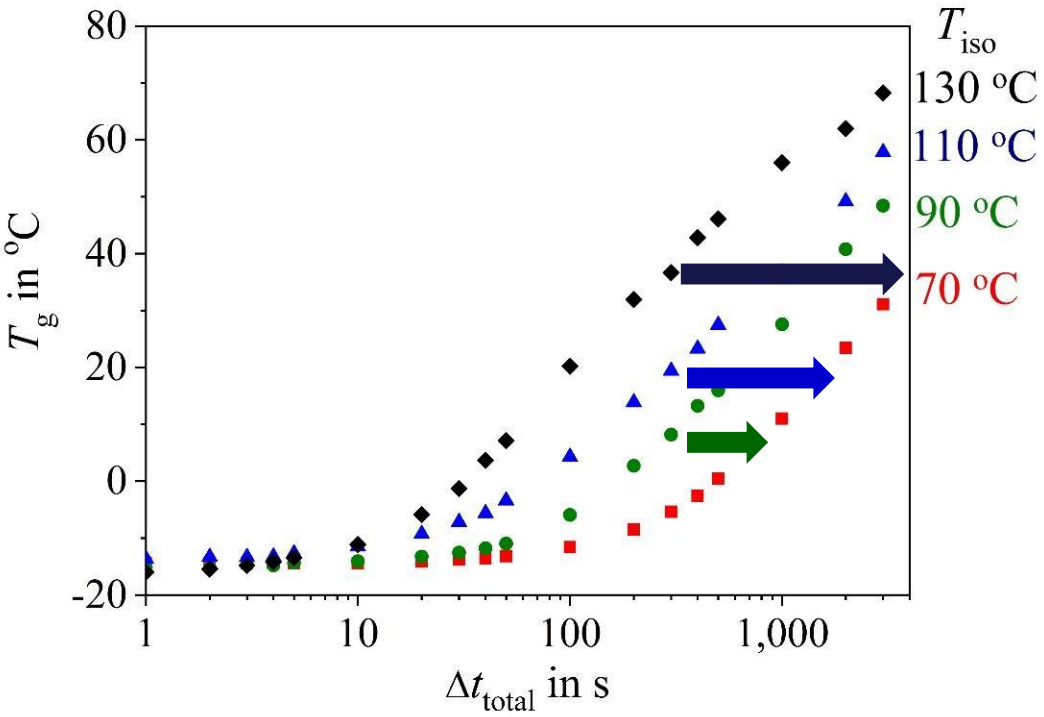


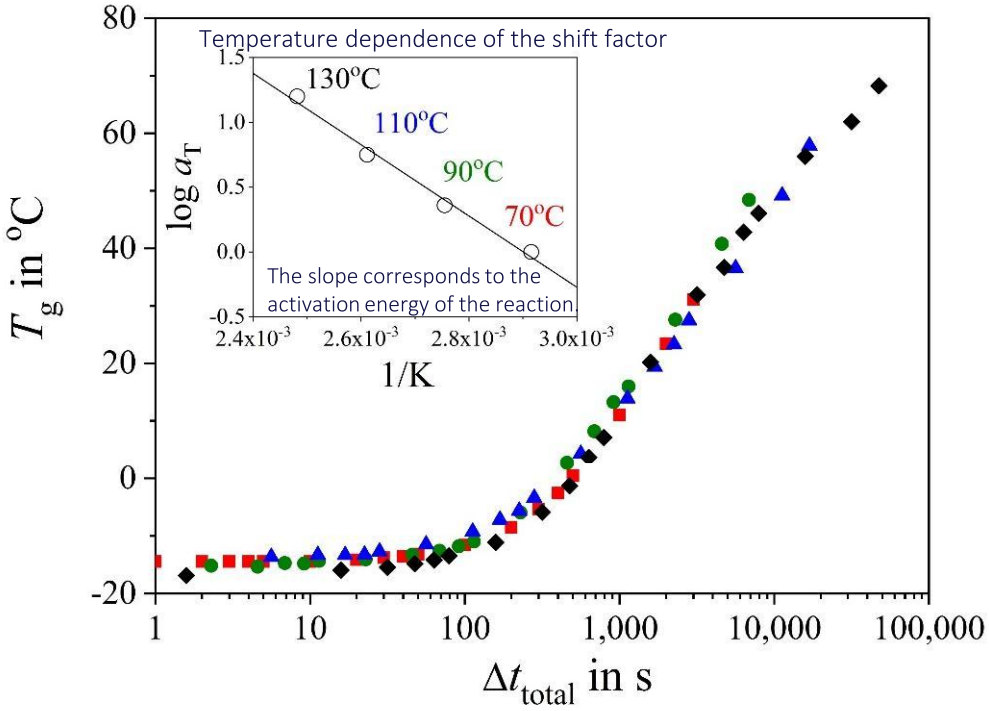
FSC heating traces of epoxy resin



Y. Furushima, Thermochimica Acta 677 (2019) 79-84.

The relation between T_g and curing and a master curve analysis



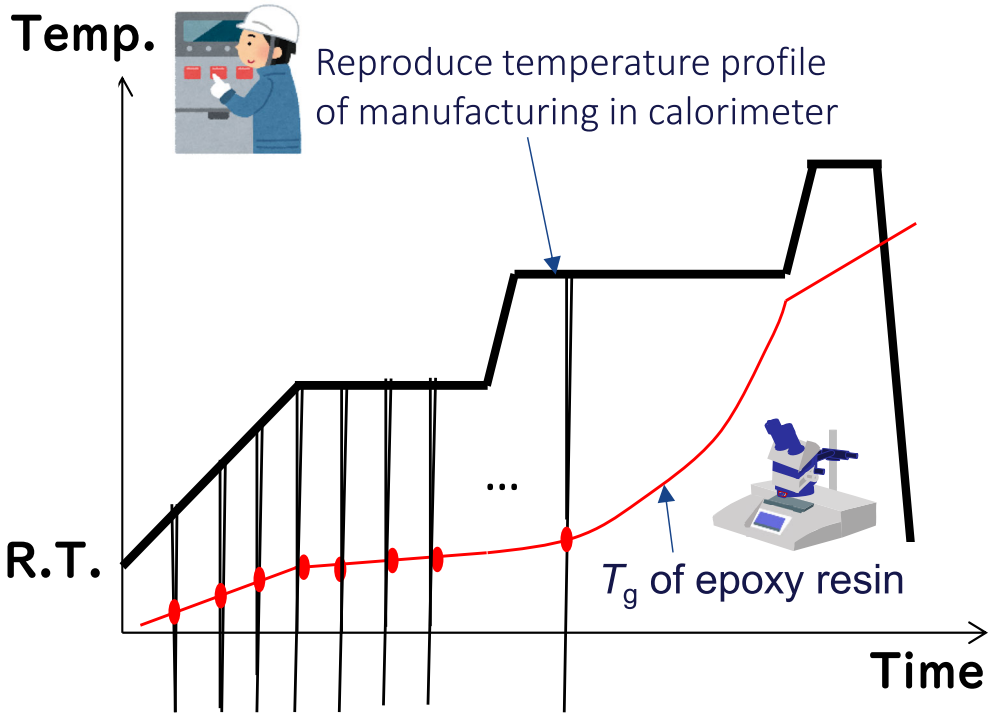


It also enables the prediction of T_g after long-term holding

Y. Furushima, Thermochimica Acta 677 (2019) 79-84.

How can our method be used in industry?

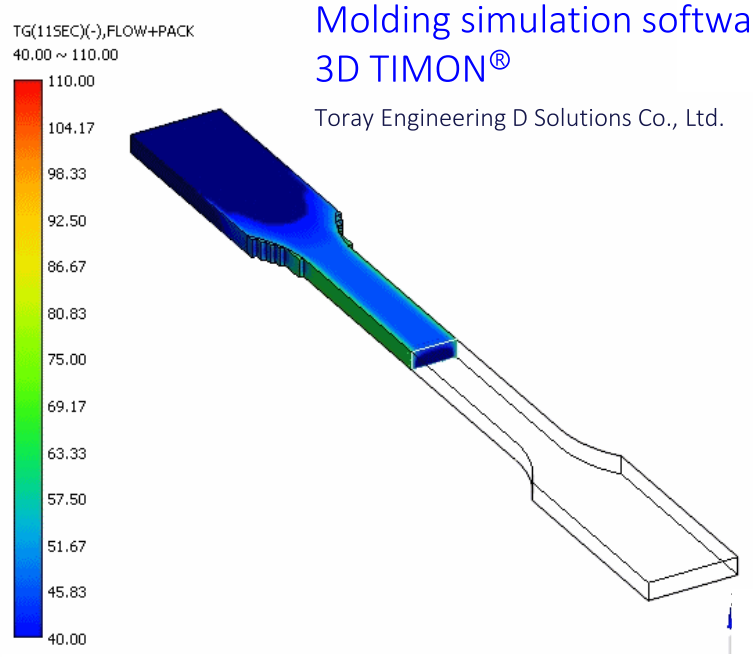
Novel analytical method*



* Y. Furushima, Thermochimica Acta 677 (2019) 79.

Input

CAE (Computer-aided engineering)



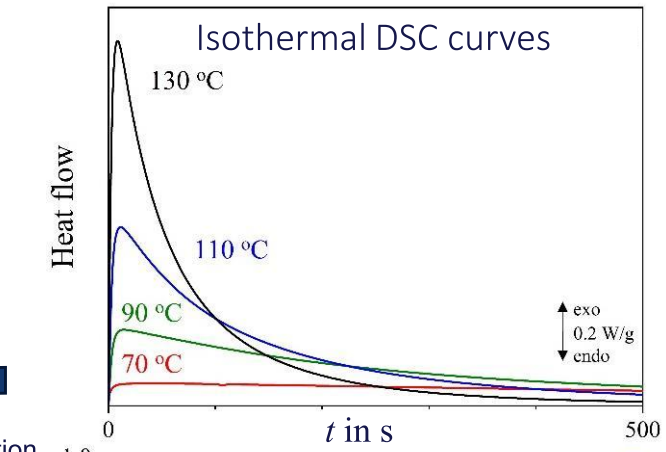
Molding simulation software
3D TIMON®

Toray Engineering D Solutions Co., Ltd.

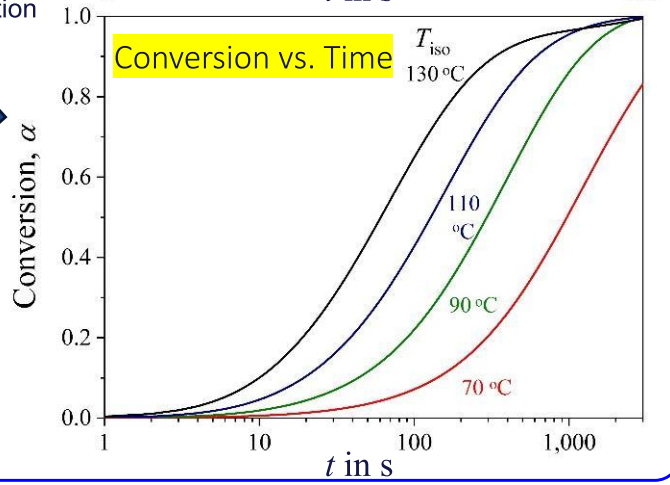
Visualizing T_g during cure

Advanced analytical applications combining DSC and FSC

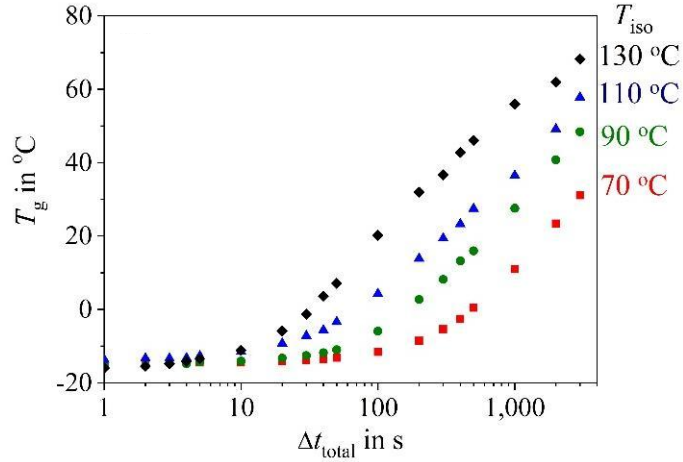
DSC



Time integration of heat flow



FSC



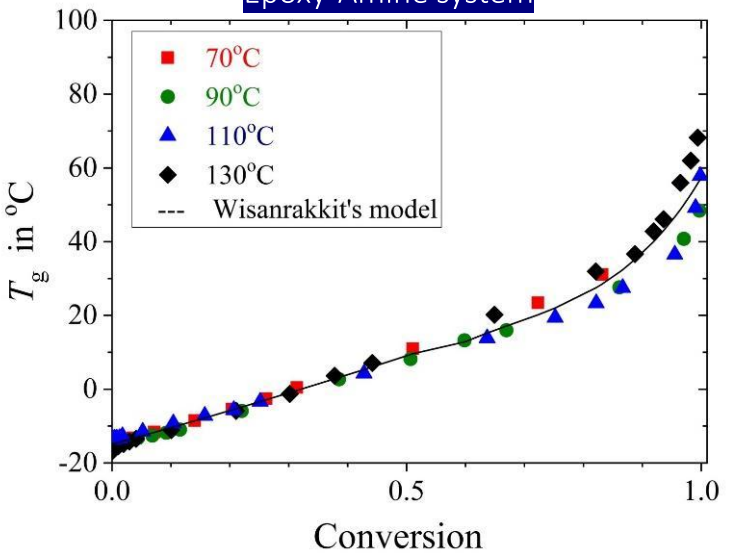
T_g vs. Time

By combining the two datasets, "Conversion vs. T_g" plots can be accurately obtained.

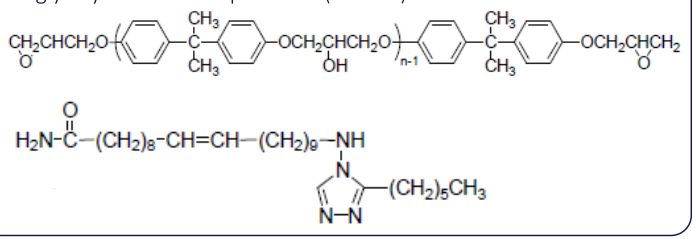
Y. Furushima, Thermochimica Acta 677 (2019) 79.

Relation between conversion and T_g

Epoxy-Amine system



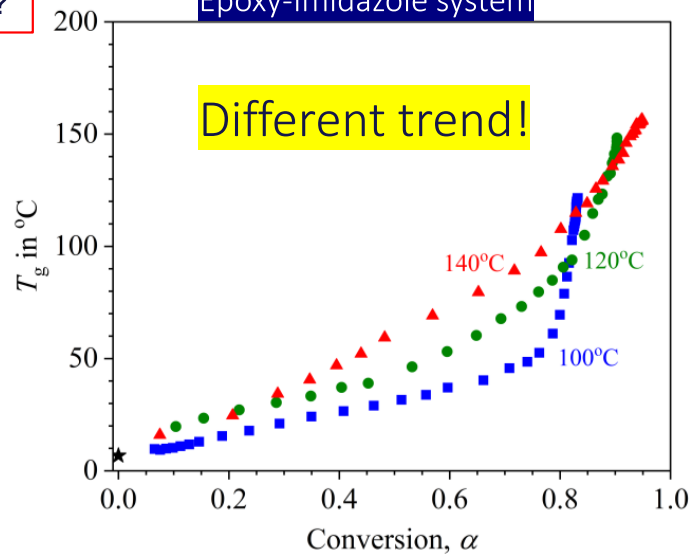
Diglycidyl ether of bis phenol-A (DGEBA)



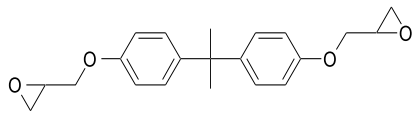
Y. Furushima, Thermochim. Acta 677 (2019) 79-84.
G. Wisanrakkit, J. K. Gillham, J. Appl. Polym. Sci., 41 (1990) 2885.

What's new?

Epoxy-Imidazole system



Epoxy(monomer)



Y. Furushima et al., Polymer 293 (2024) 126685.

Research on Curing Behavior of Epoxy–Imidazole System

Y. Furushima et al., Polymer, 293 (2024) 126685.

Epoxy-imidazole reaction mechanism

e.g. Underfill materials for semiconductors etc.

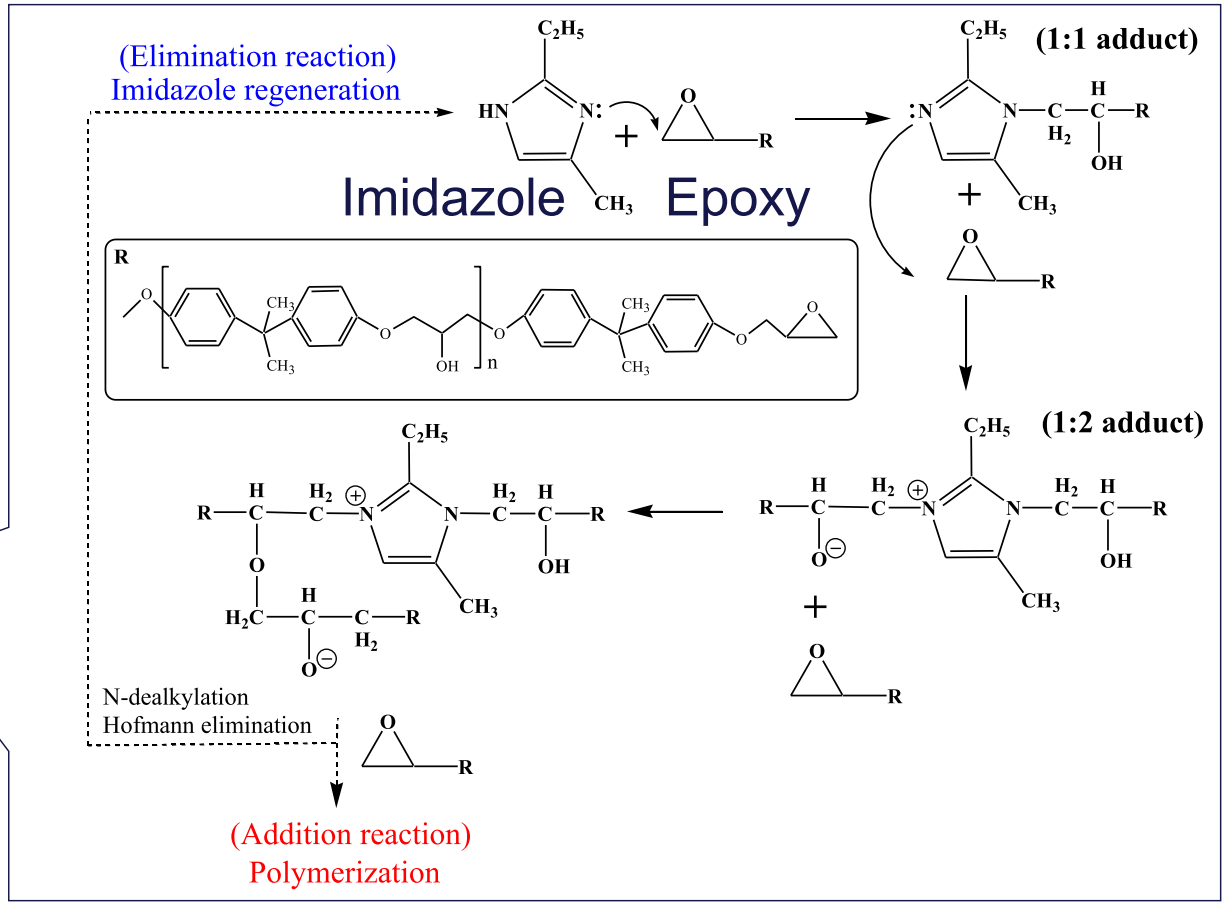
✓ **Sample**

Epoxy : imidazole = 100 : 3 (wt%)

✓ **Complex reaction**

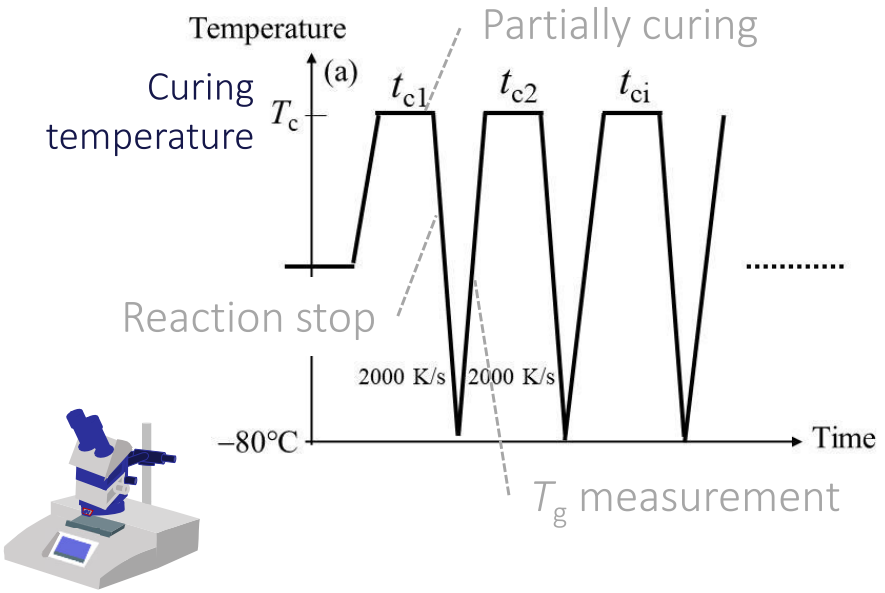
Imidazole regeneration

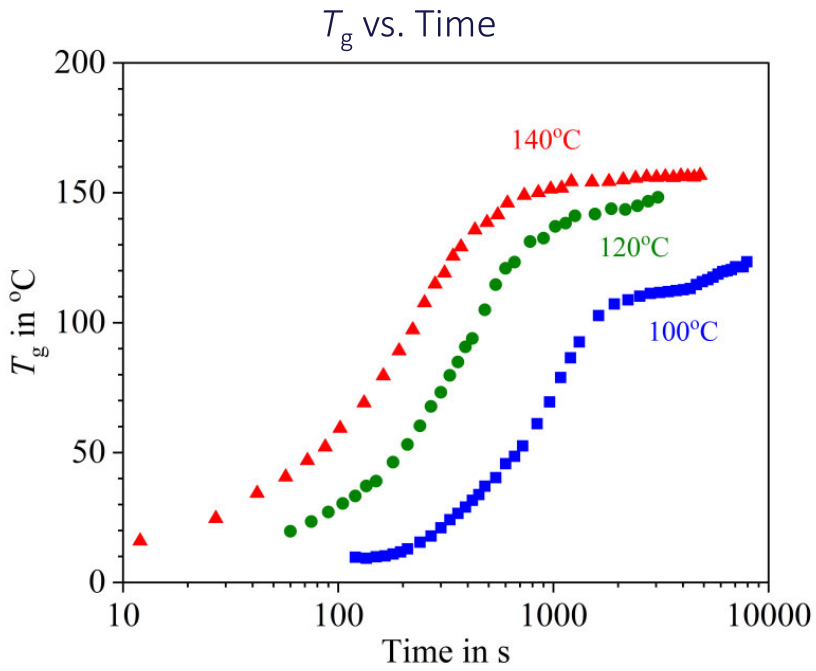
Polymerization



Tracking T_g during isothermal curing

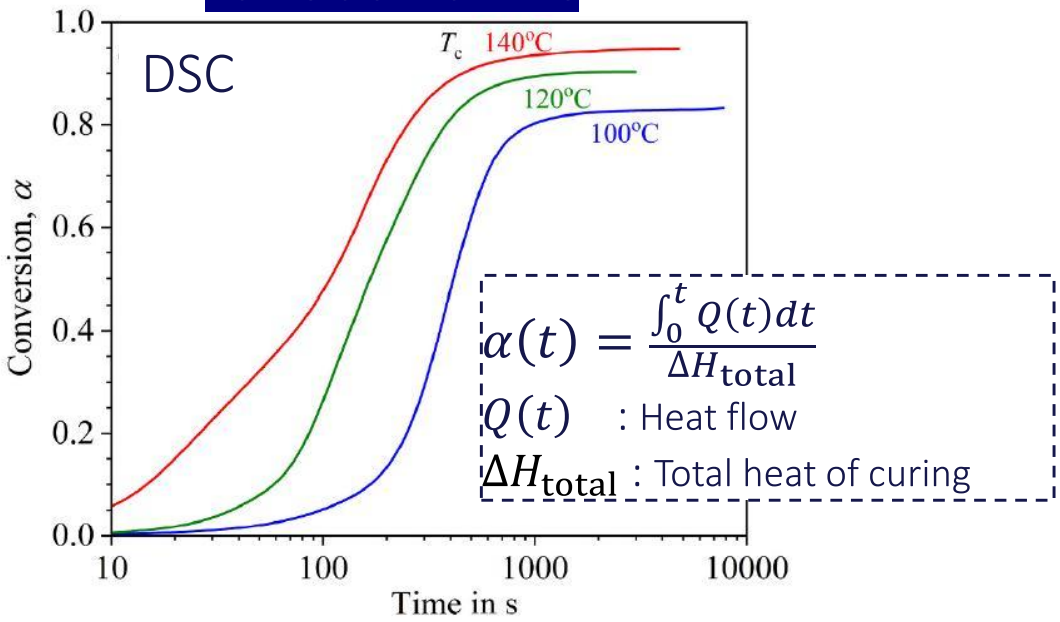
<FSC profile>





Relationship between T_g and conversion

Conversion vs. Time

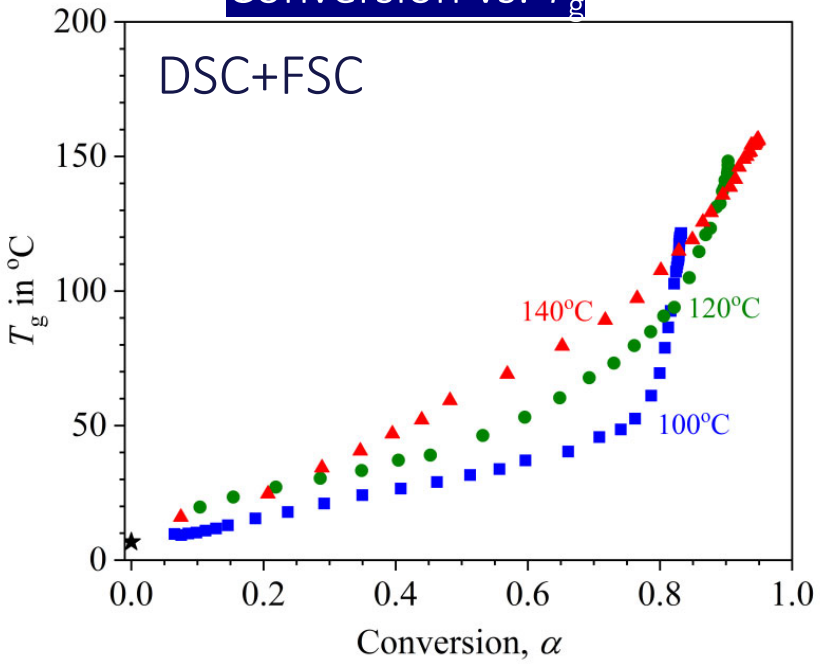


$$\alpha(t) = \frac{\int_0^t Q(t)dt}{\Delta H_{\text{total}}}$$

$Q(t)$: Heat flow

ΔH_{total} : Total heat of curing

Conversion vs. T_g

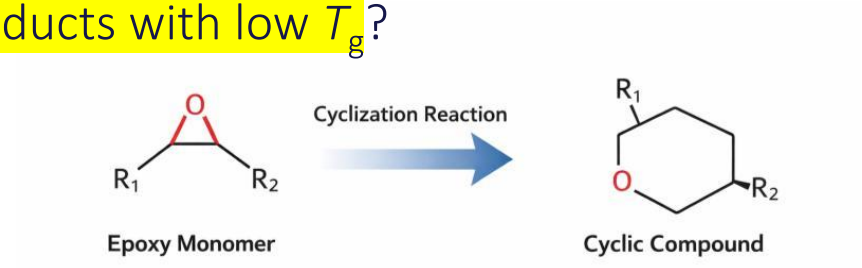


The conversion–T_g plot exhibits a dependence on the curing temperature.
(Different from typical epoxy–amine systems)

Why does the epoxy–imidazole system show a different trend in conversion–T_g plot?

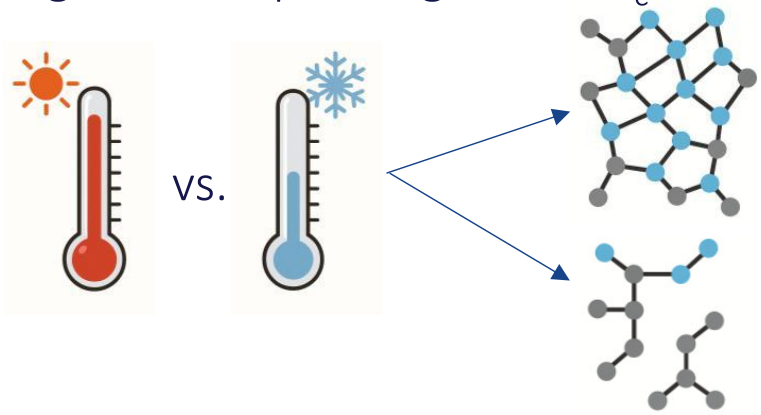
Possibility

1. Low-temperature curing generated low-molecular weight cyclic products with low T_g?



(?)

2. The competition between exothermic and endothermic reactions results in different curing states depending on the T_c ?



(?)

Possibility 1. Do cyclic products form?

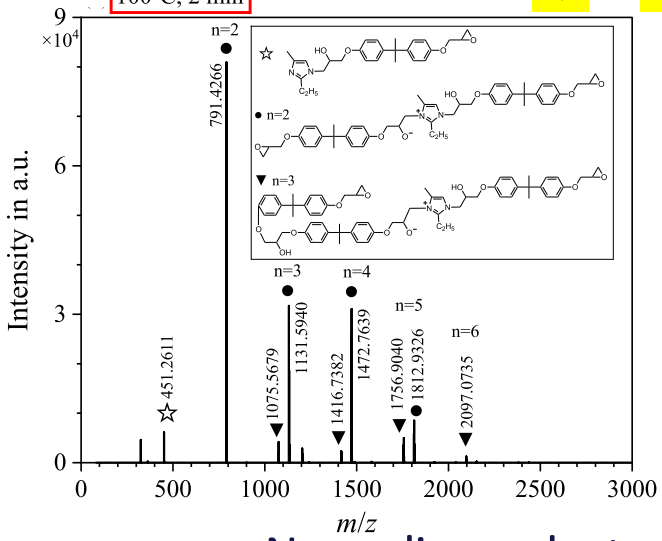
Several studies suggest that terminal epoxides could react with each other to form cyclic products. (without experimental evidence)

S.K. Ooi et al., *Polymer*, **2000**, 41, 3639.

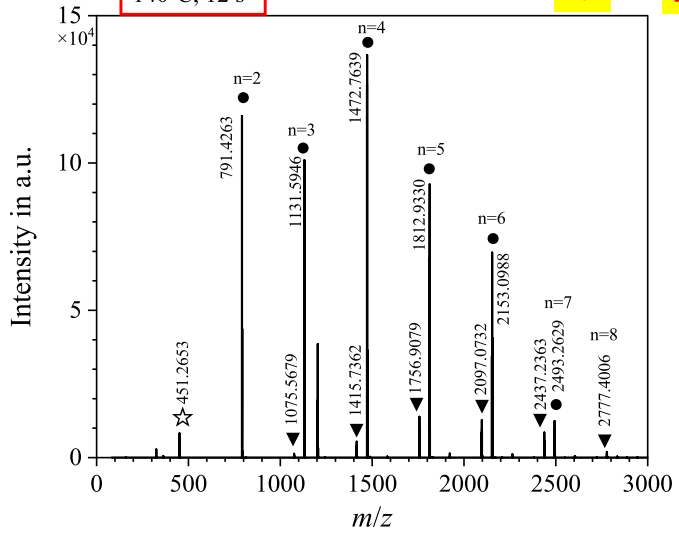
✓ Compositional analysis (MALDI-MS*)

*Matrix Assisted Laser Desorption/Ionization – Mass Spectrometry

Curing condition: 100°C, 2 min — Conversion: 7% — T_g=−10°C



Curing condition: 140°C, 12 s — Conversion: 8% — T_g=−16°C



No cyclic products were detected (Linear product only)

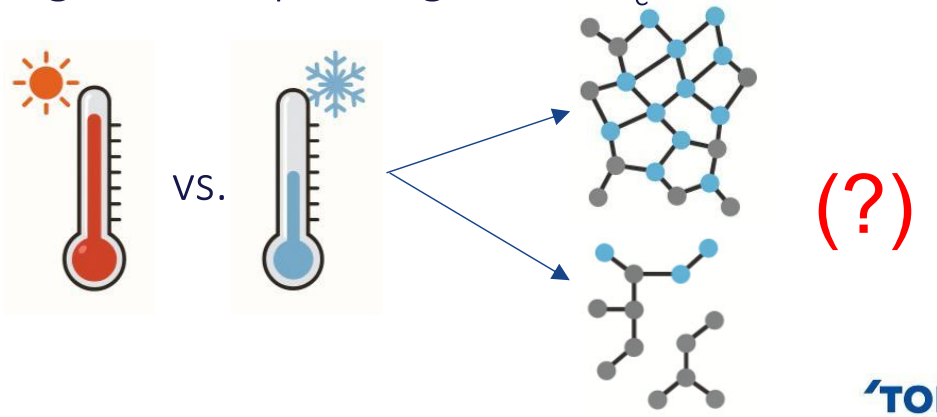
⇒ Difference in T_g is not due to plasticization by cyclic products

Why does the epoxy–imidazole system show a different trend in conversion–T_g plot?

Possibility

1. Low-temperature curing generated low-molecular weight cyclic products with low T_g?

2. The competition between exothermic and endothermic reactions results in different curing states depending on the T_c ?



Possibility 2. Existence of both endothermic and exothermic reactions

Assumption: Both endothermic and exothermic reactions exist.

$$\Delta H_{\mathrm{obs}} = \alpha_{\mathrm{obs}} \Delta H_{\mathrm{total}} = \alpha_{\mathrm{endo}}\, \Delta H_{\mathrm{endo}} + (\alpha_{\mathrm{obs}} - \alpha_{\mathrm{endo}}) \Delta H_{\mathrm{exo}}$$

$$(\Delta H_{\mathrm{total}} = \Delta H_{\mathrm{endo}} + \Delta H_{\mathrm{exo}},\ \alpha_{\mathrm{obs}} = \alpha_{\mathrm{endo}} + \alpha_{\mathrm{endo}})$$

Verification:

By applying ΔH_{obs}, α_{obs}, $\Delta H_{\mathrm{total}}$ at 100℃, 120℃, and 140℃

$$381.9 = \alpha_{100℃,\mathrm{endo}}\, \Delta H_{\mathrm{endo}} + (0.83 - \alpha_{100℃\,\mathrm{endo}})(458.7 - \Delta H_{\mathrm{endo}})$$
$$414.2 = \alpha_{120℃,\mathrm{endo}}\, \Delta H_{\mathrm{endo}} + (0.90 - \alpha_{100℃\,\mathrm{endo}})(458.7 - \Delta H_{\mathrm{endo}})$$
$$435.2 = \alpha_{140℃,\mathrm{endo}}\, \Delta H_{\mathrm{endo}} + (0.94 - \alpha_{100℃\,\mathrm{endo}})(458.7 - \Delta H_{\mathrm{endo}})$$

$\rightarrow \Delta H_{\mathrm{endo}} = -94.3$ J/g (Imidazole regeneration),
$\Delta H_{\mathrm{exo}} = 553.1$ J/g (Polymerization)

$\alpha_{100℃\,\mathrm{endo}}$ =0.119
$\alpha_{120℃\,\mathrm{endo}}$ =0.129
$\alpha_{140℃\,\mathrm{endo}}$ =0.131

Since each reaction rate exhibits different temperature dependence,
the curing state varies with the curing temperature even at the same conversion, α_{obs}.

Summary of epoxy-imidazole system

DSC and FSC showed phenomena specific to epoxy-imidazole:

- ✓ Curing temperature (T_c) dependence of T_g – conversion

Findings

- Plasticization by cyclic products was not occurred. (Pointing out errors in previous studies)
- Both endothermic and exothermic reactions proceed during curing

  Imidazole regeneration Polymerization

⇒ Each reactions progresses depending on T_c

Epoxy-imidazole curing behavior (with filler)

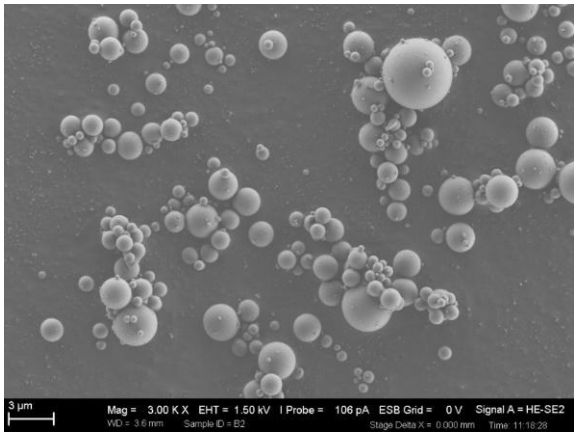
Y. Furushima et al., Journal of Applied Polymer Science, 142(20) (2025) e56895.

Silica Filler identification

Sample･･･Epoxy / imidazole = 100 / 3 + 50 mass% silica filler

✓ Shape

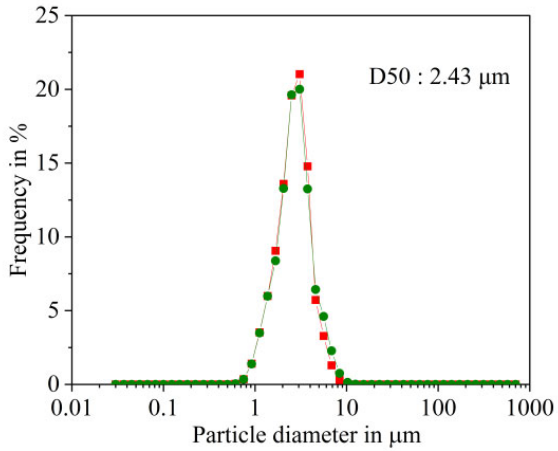
(SEM)



Spherical shape

✓ Size distribution

(Laser Light Scattering)

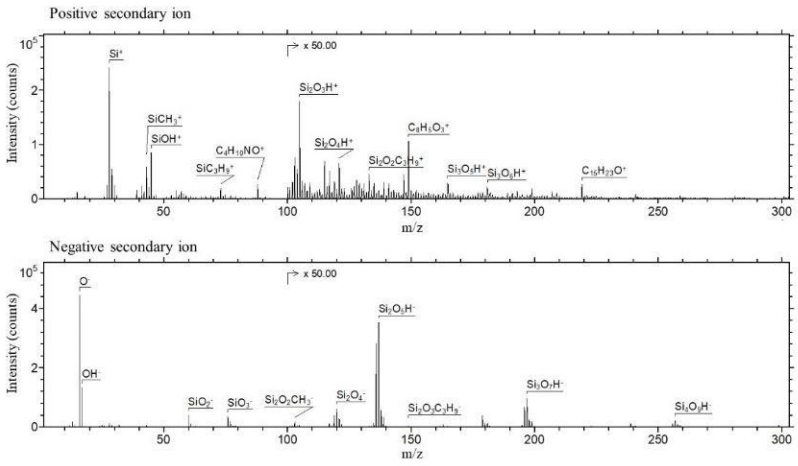


Ave.diameter: 2 µm

✓ Surface functional group

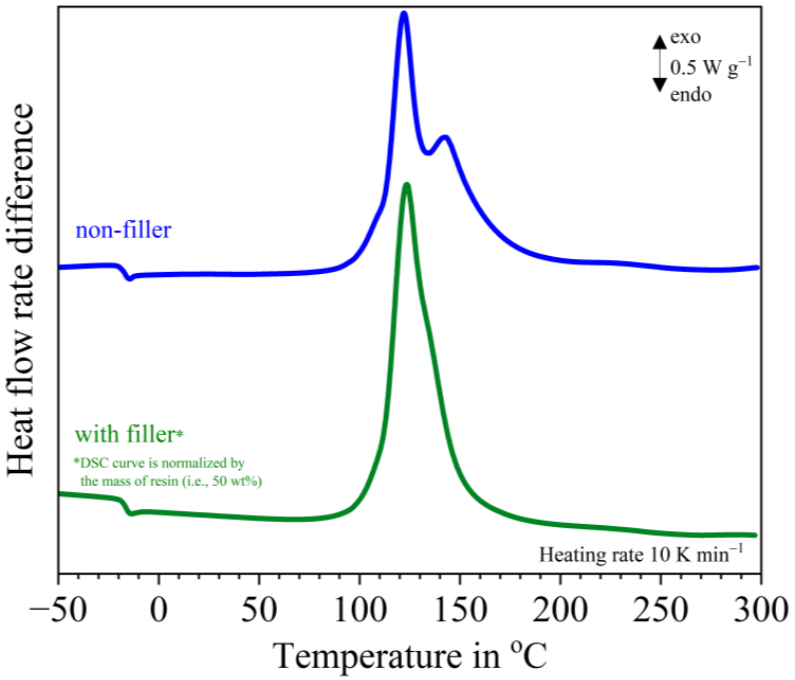
(TOF-SIMS*)

*Time-of-Flight Secondary Ion - Mass Spectrometry



OH groups on surface

Curing behavior of uncured resin during heating (DSC)



✓ Total heat of cure

non-filler	with filler
459	460–470

in J/g

No significant change due to addition of filler

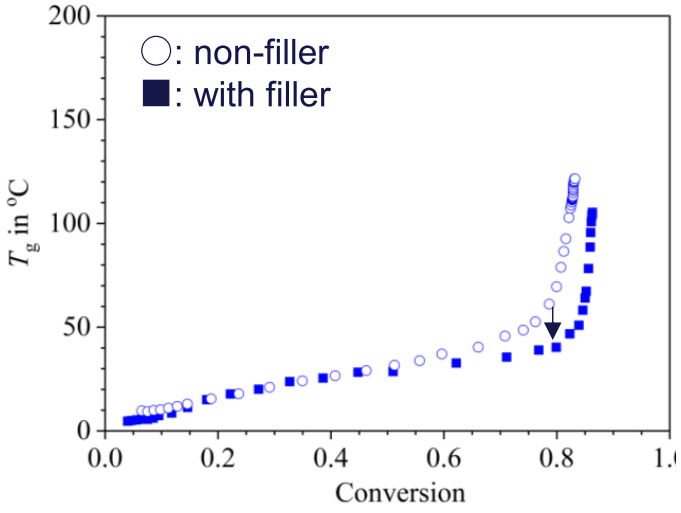
✓ Peak shape

Double peaks were observed only in non-filler

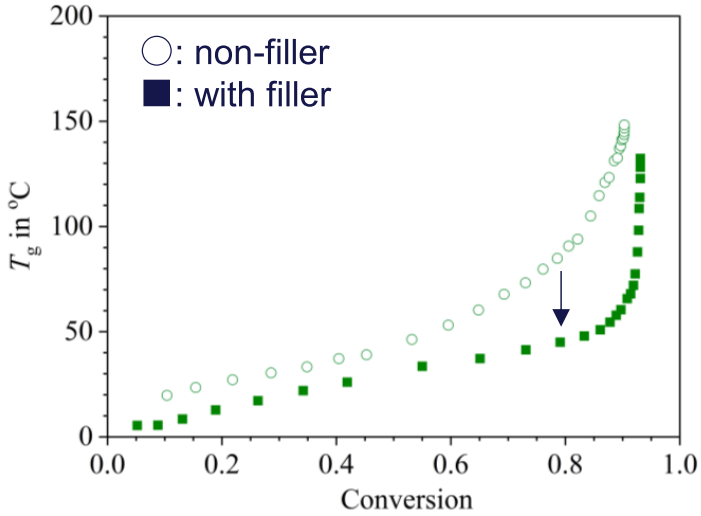
The filler affects the progression of the curing reaction.

Relationship between conversion and T_g (DSC+FSC)

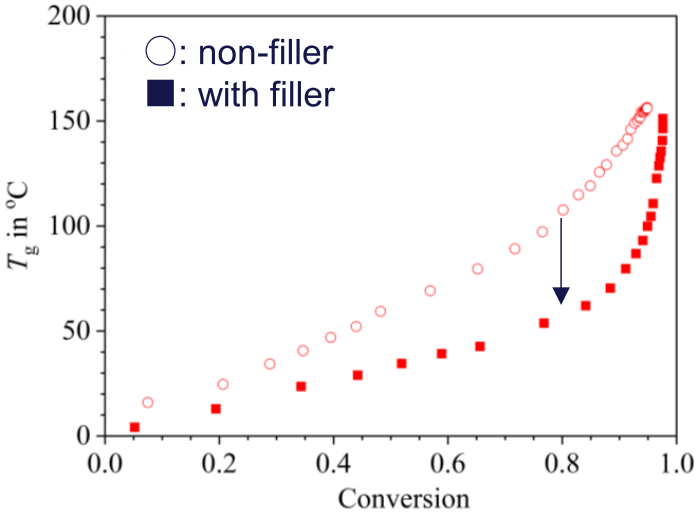
Isotherm 100 °C



Isotherm 120 °C



Isotherm 140 °C

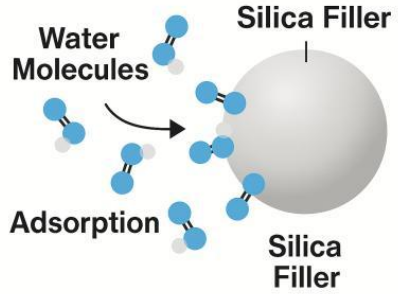


Addition of fillers decreased T_g at same conversion (e.g. Delay of curing reaction)

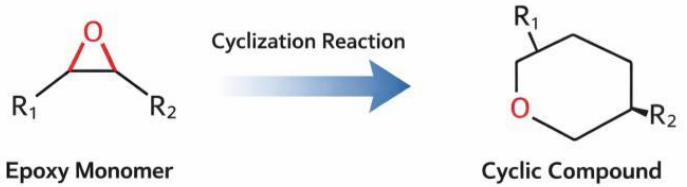
Why does adding filler slow down the curing reaction and lowers T_g?

Possibility

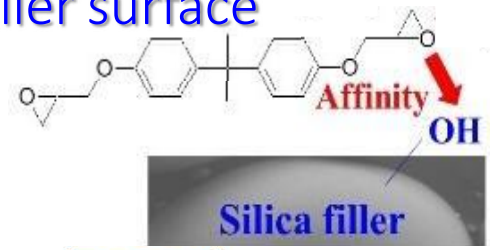
1. Adsorbed water on filler lowers T_g via plasticizing effect



2. Change of curing reaction mechanism



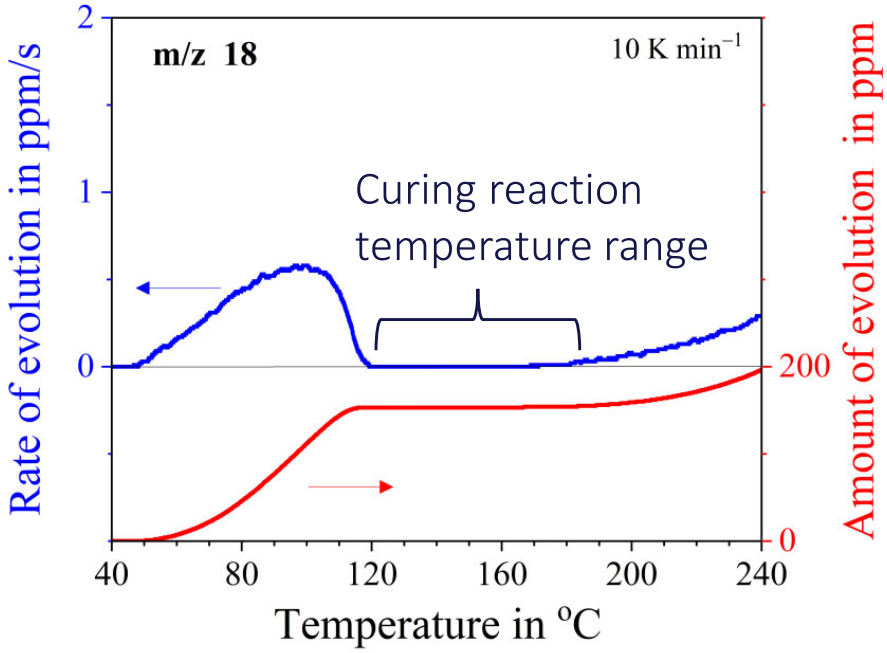
3. Suppression of curing by chemical interaction with filler surface



Possibility 1. Decrease of T_g by water

Plasticization of resin by dehydration of filler surface OH groups?

✓ Adsorbed water analysis (TG-MS)



No dehydration of filler surface OH groups in curing reaction temperature range

Amount of total adsorbed water (0.02 %)
⇒Little effect on T_g of resin

Plasticization by water cannot explain 60 ℃ decrease in T_g with filler

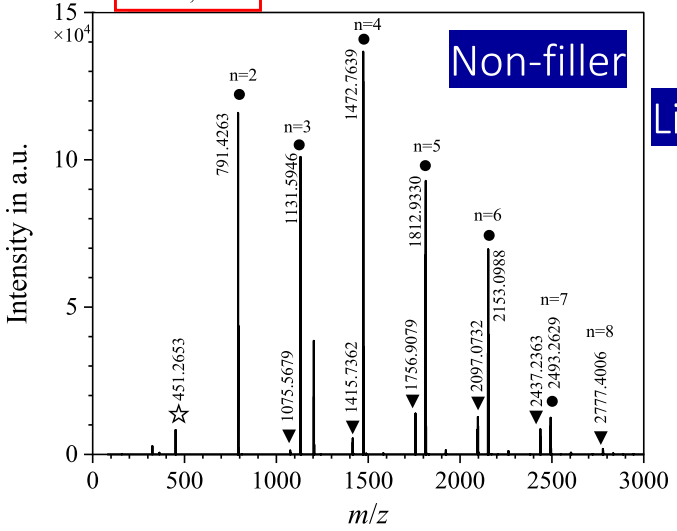
Possibility 2. Change of curing reaction mechanism

Cyclic products generated in curing?

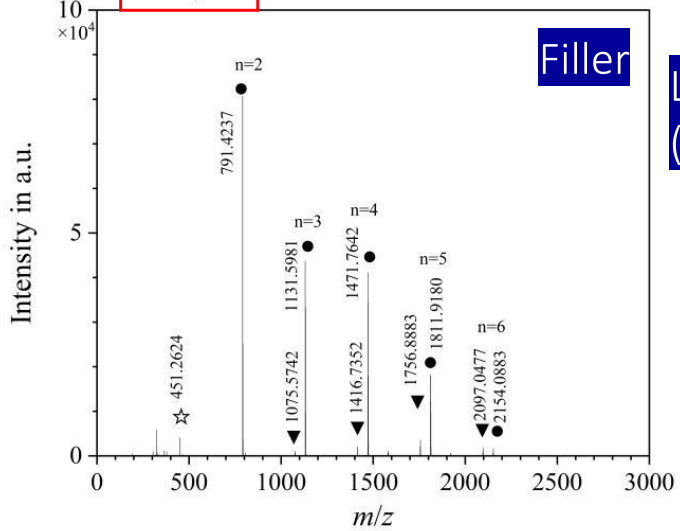
⋯ Cyclic products (conventional hypothesis) vs. linear products (our previous study)

✓ Reaction products analysis (MALDI-MS)

Curing condition: 140°C, 12 s — Conversion: **8%**



Curing condition: 140°C, 6 s — Conversion: **7%**

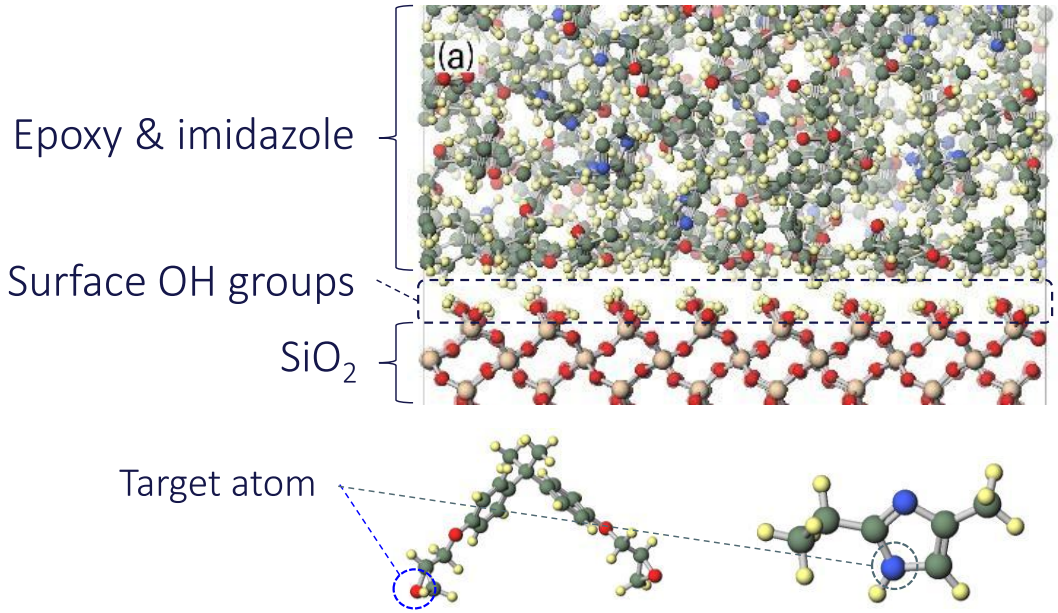


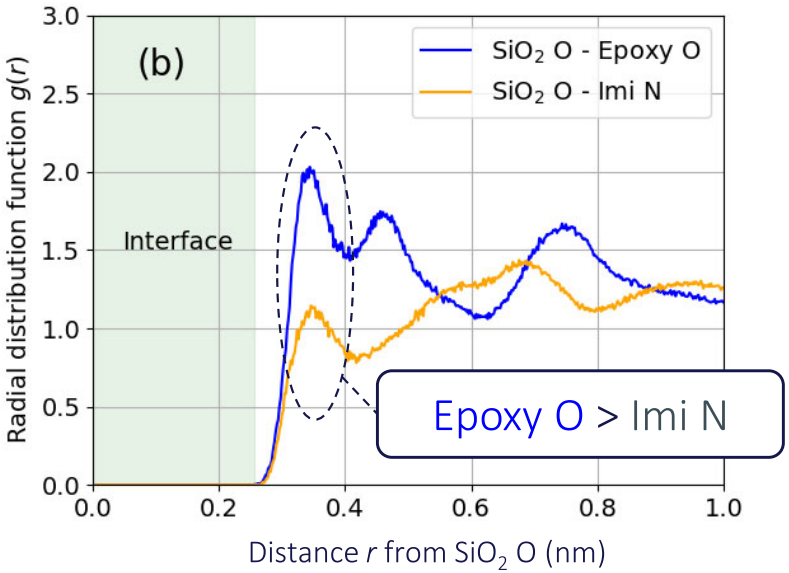
Mechanism was same, but addition of filler delayed reaction progression

Possibility 3. Suppression of curing by chemical interaction with silica filler

Localization of epoxy or imidazole on filler due to difference of interaction with filler

✓ Interaction with filler (MD simulation)





OH groups on SiO_2 surface were more strongly interacted with epoxy than imidazole

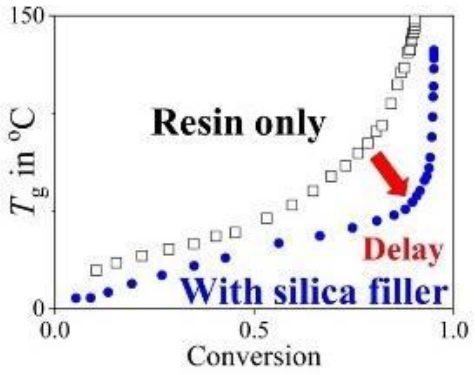
⇒Reaction between epoxy and imidazole was suppressed

Summary of epoxy-imidazole with filler

✓ Addition of filler

Observation

- Delay of curing reaction
- Decrease of T_g at same conversion



Findings

- Plasticization by adsorbed water was not occurred
- Reaction mechanism was same as non-filler
- Interaction OH(silica)-epoxy suppressed the reaction of epoxy-imidazole ⇒ Delayed curing reaction

Closing Remarks

1. Toray Research Center (TRC) has developed a method to track the T_g-change of thermosetting resins in quasi-real time.

2. In epoxy–imidazole systems, TRC discovered that the conversion–T_g curve depends on the curing temperature. This is due to the combined effects of imidazole regeneration (endothermic reaction) and polymerization (exothermic reaction).

3. Adding fillers delays the reaction in epoxy–imidazole systems. This is because the OH groups on the filler surface have high affinity for epoxy-function, which interferes with the epoxy–imidazole reaction.

The techniques —DSC, FSC, TG-MS, MALDI-MS, TOF-SIMS, and MD simulation— are all available as outsourced analysis at TRC. We hope that our technology and expertise can support your research and development of resin systems.

Part 2: Latest Innovative Material Detective Work

Topic:

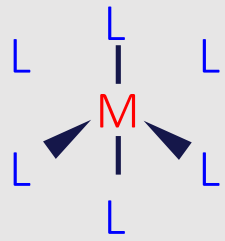
- Thermoset resin analysis
- Metal-complex analysis

An Innovative Methodology for Direct Structural Identification of Metal-Organic Complexes in Liquid Phase

Masahiro Kunisu

Metal Organic Complex in Liquid

✓ Metal-Organic Complex



M: Metal ion
L: Ligand

✓ Wet process with Complex

- Catalytic Reaction
- Metal Plating
- Pigment
- Crosslinking Agent
- Anticancer Drug etc.

Reaction, Decomposition, and Metal Aggregation Properties depend on the complex structure.

✓ Structure Identification of Complex

- Solid Single Crystal (Only)
  - Conventional X-ray Diffraction analysis

- Liquid Solution

very difficult, but …

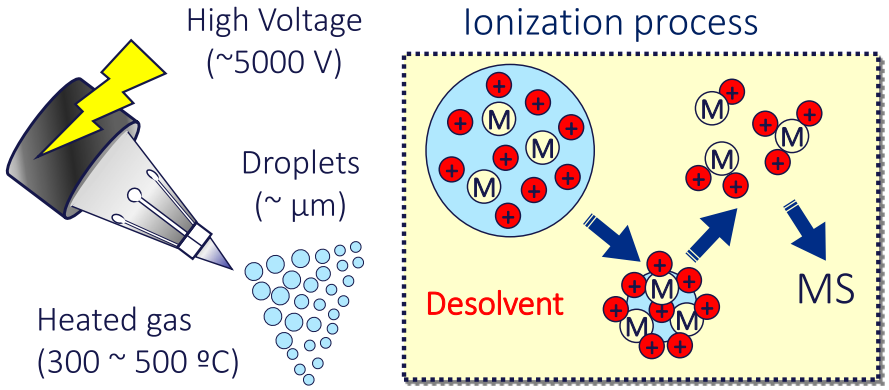
We can suggest new approach for identification!

- (1) nanoESI-MS
  (Mass Spectroscopy)
- (2) XAFS
  (X-ray Absorption Spectroscopy)

(1) nanoESI-MS

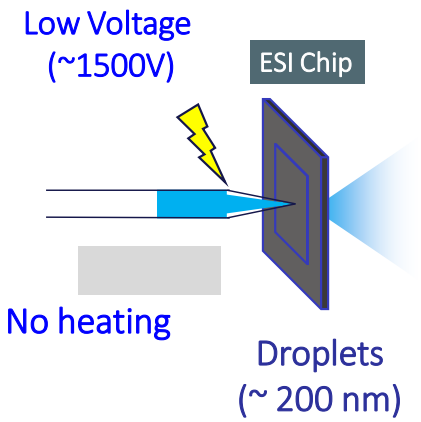
Conventional ESI

(ESI: electrospray ionization)

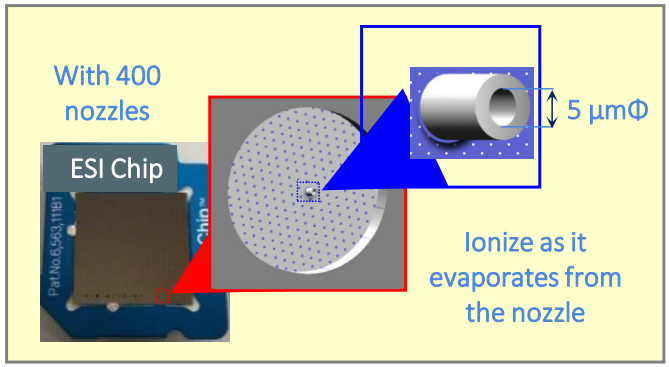


- ✓ Ionization method for LC/MS
- ✓ Fragmentation occurs occasionally during ionization process.

NanoESI



Details of the ESI chip

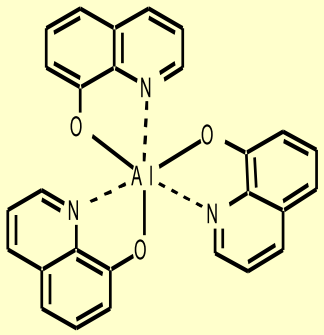


- ✓ Softer ionization
  Decomposition of complex can be suppressed!

(1) nanoESI-MS / Alq_3

OLED material

Alq_3

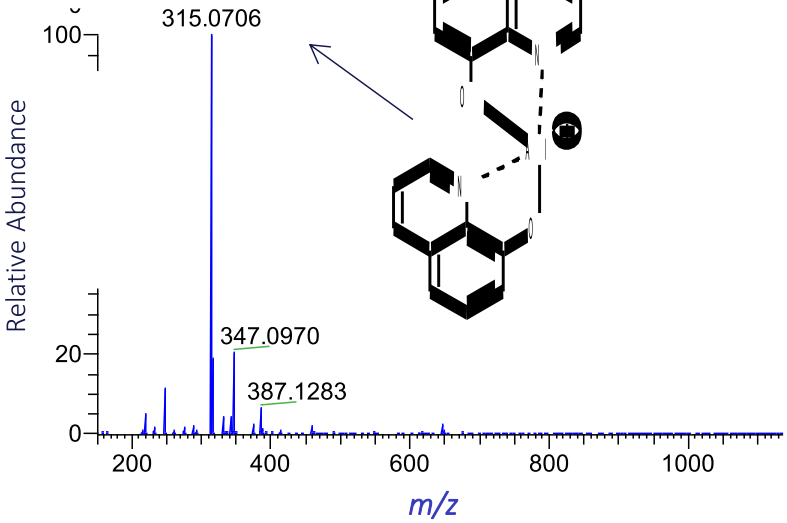


tris(8-hydroxyquinolinato) aluminum

$C_{27}H_{18}N_3O_3Al$
Mass: **459.1164**

Conventional ESI-MS (Positive)

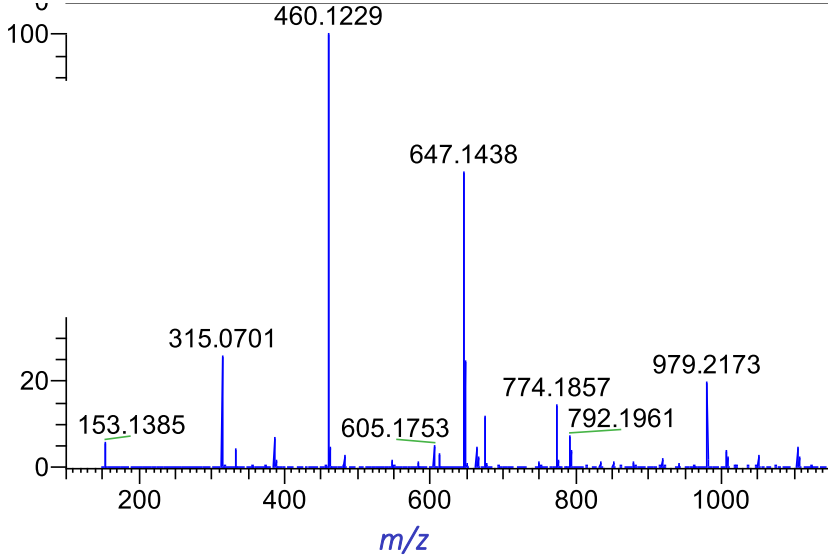
$[Alq_2+H]^+$
$C_{18}H_{12}N_2O_2Al$



✓ Ligand was partially removed during ionization.

NanoESI-MS (Positive)

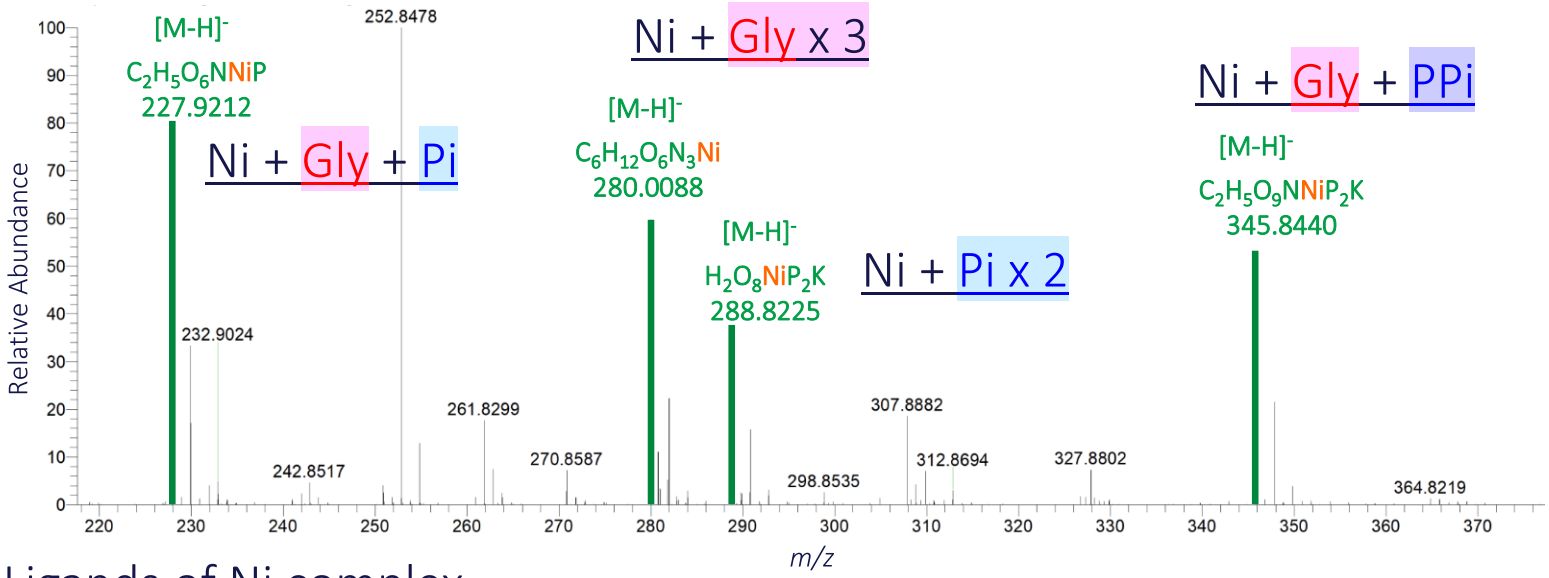
$[Alq_3+H]^+$
$C_{27}H_{19}N_3O_3Al$



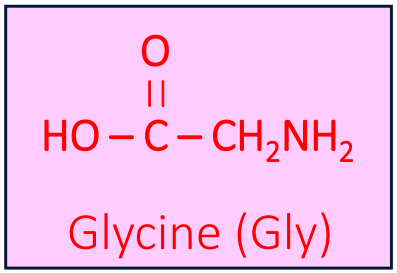
✓ Alq_3 molecule including all ligands can be detected!

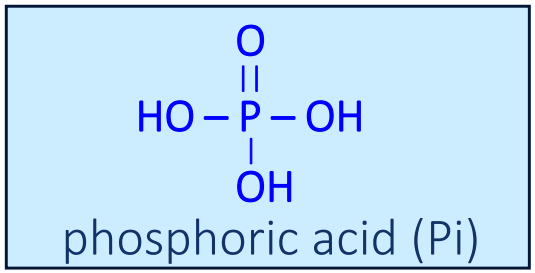
(1) nanoESI-MS / Ni complex

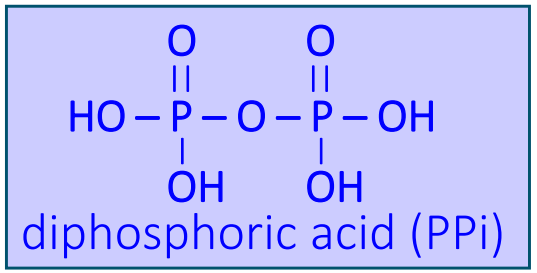
Ni plating solution



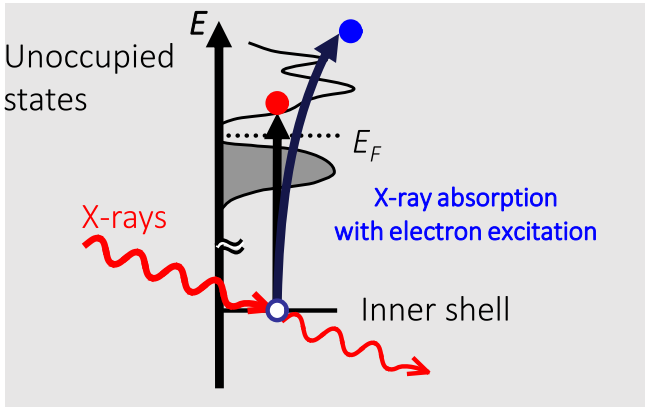
Ligands of Ni complex



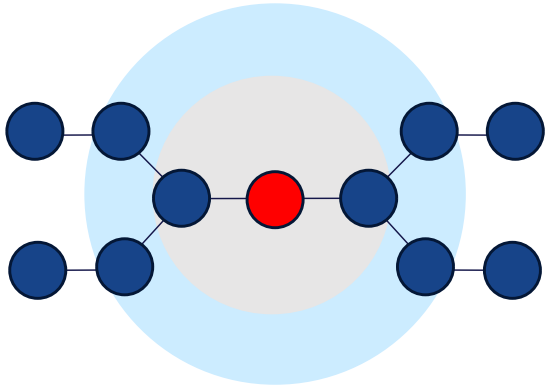


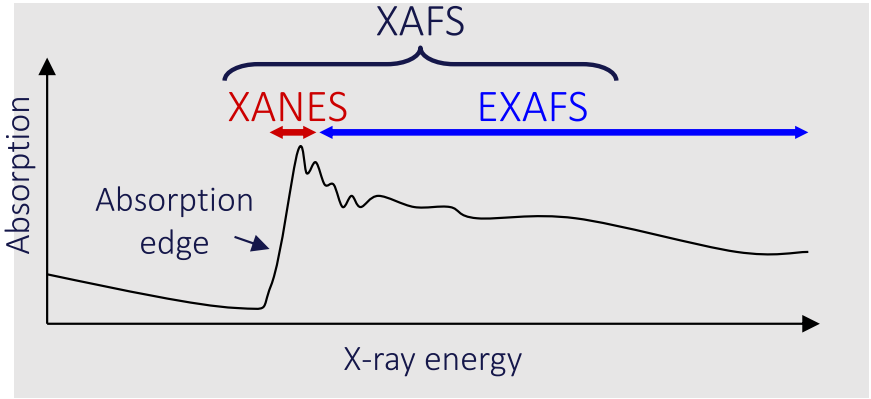


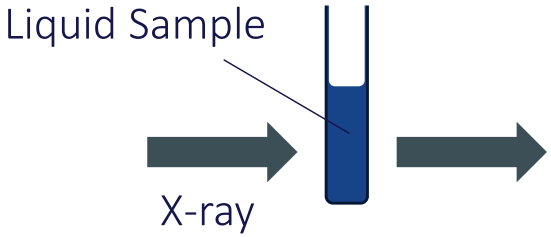
(2) XAFS (X-ray Absorption Fine Structure)



- ✓ Chemical state of metal element
- ✓ Bonding between metal element and 1st, 2nd nearest neighbor atoms





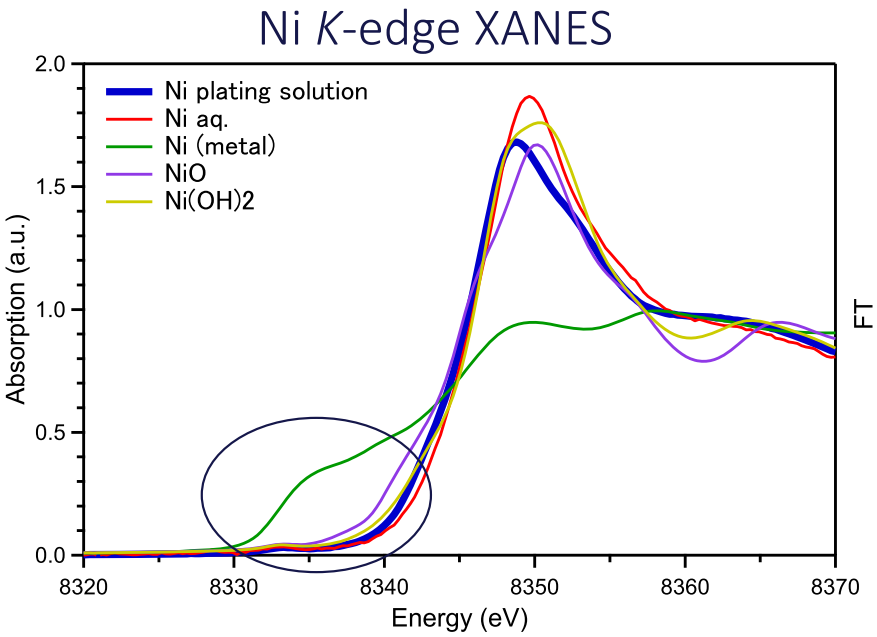


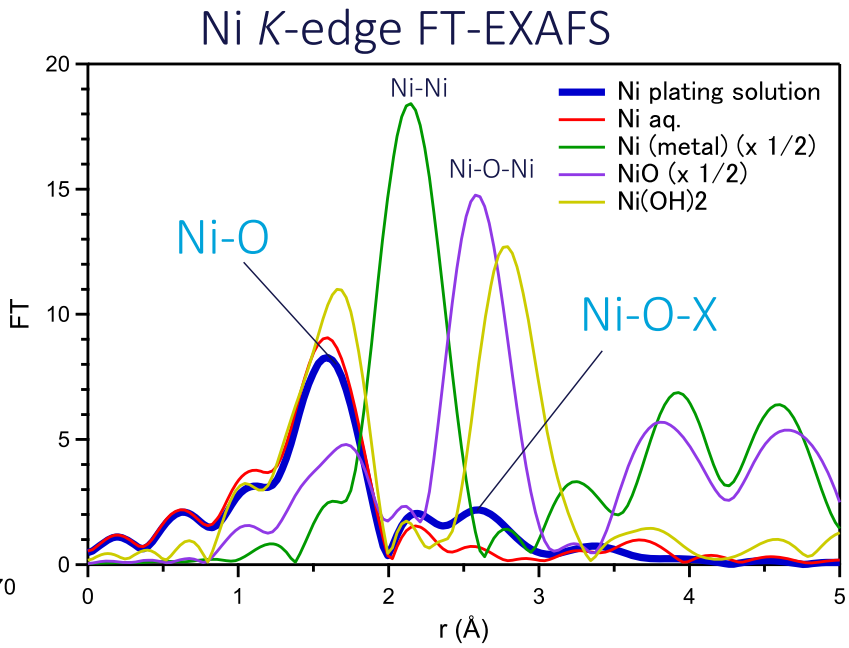
- ✓ Liquids sample can be analyzed without concentration or dilution.

(2) XAFS / Ni complex

Ni aq. :$Ni(NO_3)$ aq. (in HNO_3)
without ligand molecule

Ni plating solution





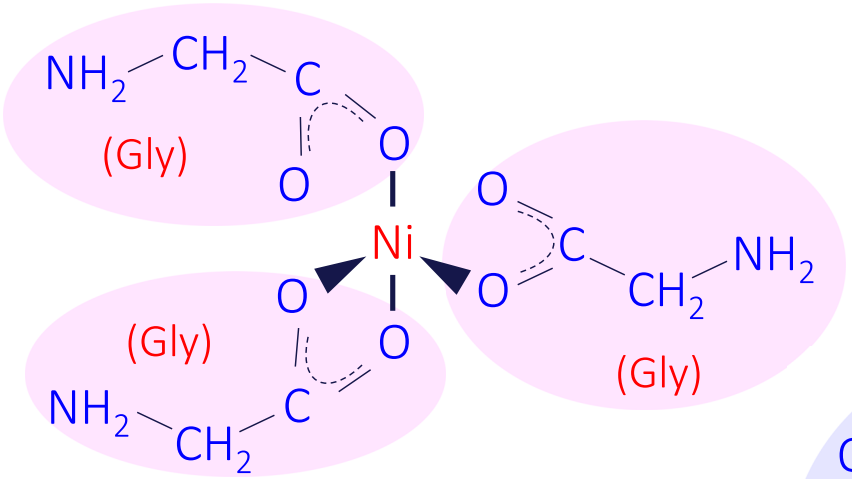
- ✓ Chemical state: Ni^{2+}
- ✓ Coordination: 6-folded

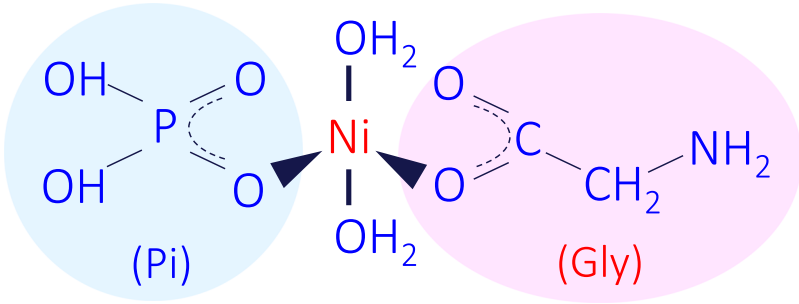
- ✓ Ni-O and Ni-O-X bonding
- ✓ multiple coordination (chelate)
  -> The bonding in Ni complex

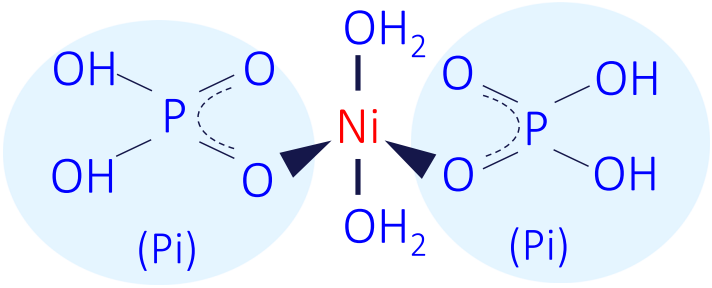
The structure of Ni complex in plating solution

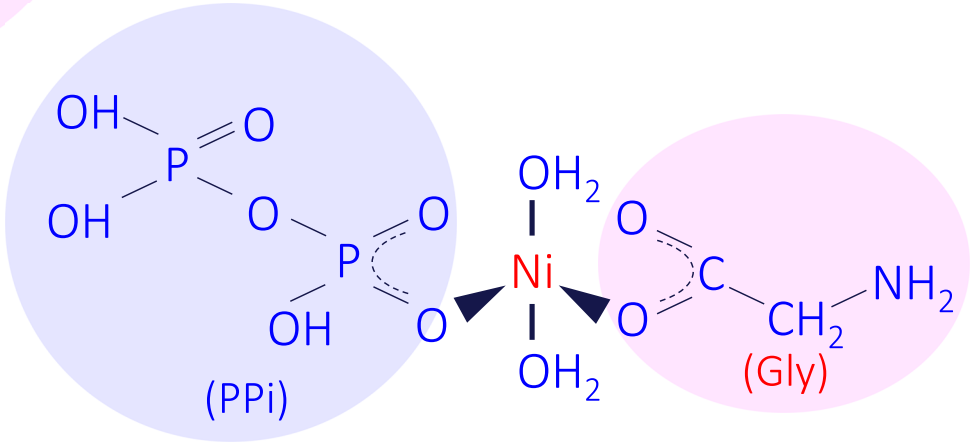
nanoESI-MS: Ni + Gly + Pi, Ni + Gly x 3, Ni + Pi x 2, Ni + Gly + PPi

XAFS: Ni^{2+}, 6 folded Ni, multiple coordination









Advantage and Disadvantage

	nanoESI-MS	XAFS
Advantage	• Mass number of the entire complex molecule • Detail of Ligands	• Chemical state and coordination number of metal • Possible to detect inorganic component (metal ion, nano particle) as well as complex
Disadvantage	• m/z : 50～6000 (Impossible to detect single ion or polymer components) • Only low-viscosity liquids	• Information only around metal ion • The detail of ligands cannot be identified.

Complementary evaluation for metal complex by both nanoESI and XAFS!

Summary

We can suggest new approach for identification of Metal Complex in Liquid materials.

nanoESI-MS

✓ Mass spectroscopy for metal complex in liquid can be performed without decomposition.

XAFS

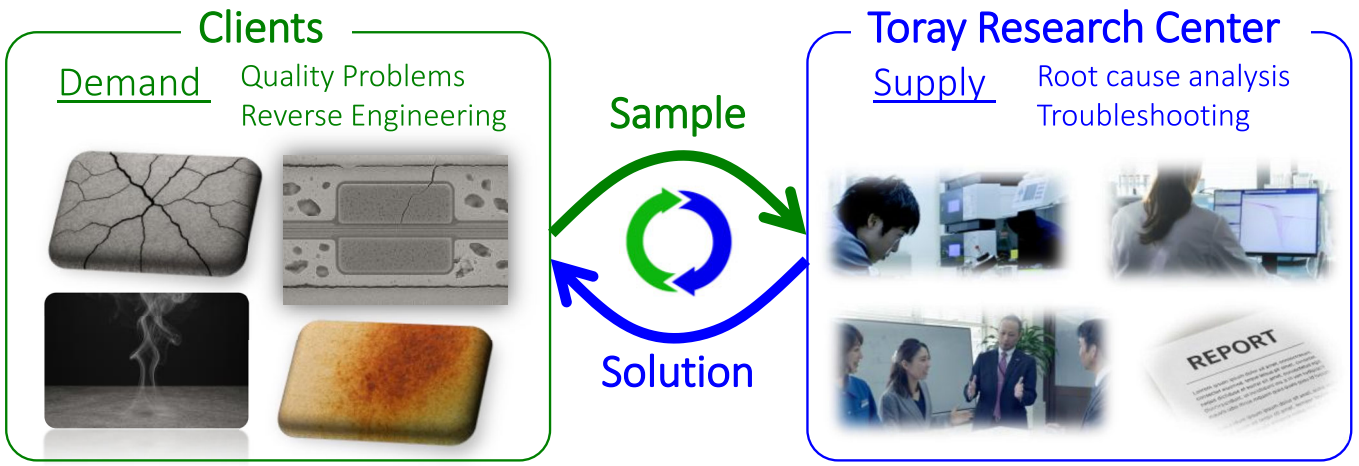
✓ Chemical state and coordination bonding between metal ion and ligands can be analyzed.

➔ Complementary evaluation for metal complex using both nanoESI-MS and XAFS.

For Contact/Quote

QR code link to inquiry form:

E-mail address for inquiry:
bunseki.trc.mb@trc.toray

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