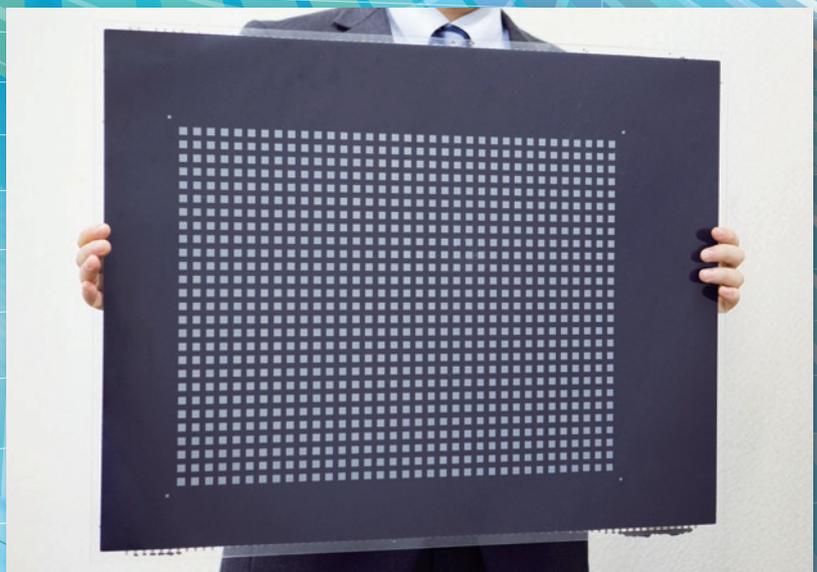
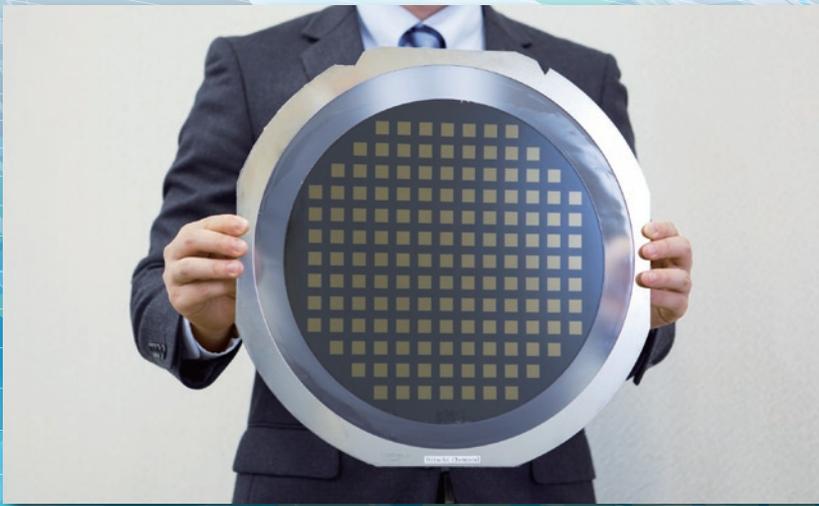


Hitachi Chemical
**Technical
Report**

No.59 / March 2017



CONTENTS

Commentary

- Approaches of Open Innovation to Develop Novel Products and Businesses for Global Market Growth 4
Masato Yoshida

Review

- Open Innovative Activity of Total Solution for Semiconductor Packaging 6
Toshihisa Nonaka · Chuichi Miyazaki

Report

- Low-Temperature Curable Positive-Tone Photosensitive Dielectric Materials 10
Akitoshi Tanimoto · Yu Aoki · Mika Kimura · Sangchul Li · Mamoru Sasaki
- Particle-Aligned Anisotropic Conductive Film (PAL-ACF) for Fine Pitch Interconnection 12
Akiko Iwai · Masaru Tanaka
- Low Transmission Loss/Low CTE Multilayer Material, "MCL-HS100" 14
Tomokazu Shimada
- Reliability Improvement Technologies for Epoxy Molding Compounds on Lead Frame Package 16
Shinya Nakamura
- Insulating Varnish of Motor for Hybrid Vehicle and Electric Vehicle 18
Tatsuhito Fukuhara
- Porous Aluminum for Heat Exchanger 20
Takehiro Shimoyama · Keita Sone
- Hot-melt Adhesive for Automotive Interior 22
Yuzuru Takahashi
- Copper Free Brake Pads with Stable Friction Coefficient 24
Masamichi Mitsumoto
- Demonstration Project of Power System Stabilization with the Hybrid Battery Energy Storage System 26
Yoshikazu Hirose · Shinichi Sano · Hisaki Takeuchi · Shigeo Aone
- New Development of High Heat Resistance and Low Dielectric Thermosetting Resin, "S. F. Resin" 28
Masaki Takeuchi · Eri Yamada
- Shock Absorbing Material 30
Akihiro Yoshida · Naoki Takahara · Takanori Miya
- Exosomal mRNA Analysis kit from plasma and urine, "ExoComplete" 32
Mieko Ogura
- High-density Sintered Sprocket for Silent Chain Made by Die Wall Lubrication Compacting with Liquid Coating 34
Satoshi Onodera



Review : Open Innovative Activity of Total Solution for Semiconductor Packaging (p.9)



Executive Officer
General Manager
Research & Innovation
Promotion Headquarters

Masato Yoshida

Approaches of open innovation to develop novel products and businesses for global market growth

Since its establishment in 1962, Hitachi Chemical has combined “material technology” and “processing technology” to create new state-of-the-art products. These technologies were cultivated through the development and manufacturing of original products such as insulating varnishes, industrial laminates, porcelain insulators and carbon brushes. Based on these technologies, Hitachi Chemical has made efforts to enhance its competitiveness as an enterprise focusing on research and development and to anticipate market needs.

Our common approach has been to conduct research and development within our own departments to realize ideas for products. However, as a result of factors such as the diversification of customer needs, the shortening of product life cycles, and the change in the competitive structure due to market globalization, we have reached the limits of what can be achieved through internal research and development. Although we have collaborated with the Hitachi Group, domestic and overseas universities, and research institutes for the purpose of enhancing basic and conventional technologies, we have decided to introduce a new strategy called “open innovation”. This strategy will allow us to create new businesses that use technology found outside of existing networks.

Open innovation, proposed in 2003 by Professor Henry Chesbrough of Harvard University, is an important concept wherein a company proactively cooperates with other companies to create innovative value and accelerate the creation of new businesses. In addition to incorporating innovative technology, open innovation involves securing the appropriate resources (management resources) at the appropriate times and from the required areas. These resources include distribution routes, manufacturing sites, and others necessary for commercialization. Although we are still in an early phase, I describe our efforts to implement open innovation in the next.



Open Laboratory

Regarding the development of semiconductor packaging materials, it is important to develop and provide packaging materials in a short period to accommodate reduced product cycles. For this reason, in June 2014, we established an open laboratory for the following purposes: to enhance the technology of semiconductor packaging materials; to shorten the development period; and to anticipate future needs. At this open laboratory, we engage in open innovation by collaborating with the manufacturers of semiconductor packaging materials as well as equipment manufacturers and the manufacturers of packaging materials.

Furthermore, we will establish the innovation center to connect the various our technologies with the future market. The center will serve as a place for collaborative creation where we discover future needs by working with customers, set manufacturers, equipment manufacturers, and the stakeholders involved in our businesses. We will prepare a comfortable space for promoting ideas, hold an interactive exhibition of our core technology, and establish a program where people from different fields to meet and discuss various topics. We look forward to creating novel products and businesses through these activities with customers.

External Agencies

We use external agencies, such as venture capital companies that invest in unlisted growth companies and agencies that match enterprises having needs and seeds. With these agencies, we work proactively to acquire technical licenses, conduct M&As and joint development projects, and engage in mutual sales. Through these activities, we are accelerating the speed of commercialization. In May of last year, we started investing in a venture capital company in the United States and assigned a full-time officer to start technical exploration. In cooperation with Hitachi Chemical America and departments in Japan, we are collecting the latest information on venture enterprises and research institutes, and sending the information to our research and development departments. Last year, we acquired about 2,000 items of information about venture enterprises and began exploring promising technology. We are developing functional films using nanotechnology introduced from the United States as high-performance materials for displays.

Along with promoting the activity of open innovation to establish it as a new culture, we will accelerate the creation of new businesses and products. Through these efforts, we aim to realize a better life and society by providing technology, products, and services that lead us into a new era.

Open Innovative Activity of Total Solution for Semiconductor Packaging

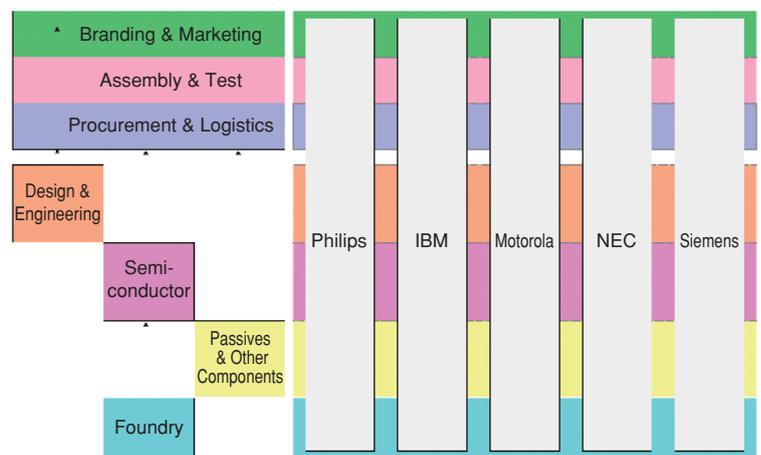
Toshihisa Nonaka Chuichi Miyazaki

Packaging Solution Center, R&D Headquarters

Since the 21st century began, the mainstream of the supply chain of the semiconductor package industry has changed from vertical integration to a horizontal specialization model. The twilight of Moore's law, which has been a driver of the electronics industry for the past half century, is becoming apparent and the barrier of 5 nm coming in several years is convincing. Recently, packaging technology is strongly expected to lead the continued progress of the system performance of electronic devices. In this situation, the strategy of the packaging material business of Hitachi Chemical is dynamically changing. This article describes open innovation through co-creation with other companies and organizations, based on Hitachi Chemical's open laboratory, founded with a state-of-the-art full assembly line in 2014 at the former Tsukuba Research Laboratory (currently the Core Technology Center). It also describes the creation and proposal of a total solution of a brand new semiconductor package, unifying material, equipment and process.

1 Introduction

The supply chains for semiconductors during the period from 1980 to 2000 are shown in **Figure 1**. As shown on the right side of the diagram, vertical integration models by large-scale semiconductor manufacturers (referred to as integrated device manufacturers or IDMs) were typical. However, in the 21st century, horizontal specialization based on functional differentiation began to spread (as indicated on the left of the diagram from "Branding & Marketing" to "Foundry"). IDMs, which had been responsible for both manufacturing semiconductor wafers and assembling semiconductor packaging, transformed into enterprises called foundries and companies that handle OSAT (outsourced assembly and test), respectively. Furthermore, as the latest movement, the largest foundry, Taiwan Semiconductor Manufacturing Co., Ltd. (TSMC), not only manufactures semiconductor wafers, but also handles a part of the package assembly process using the manufactured semiconductor wafers. Although these are the main industry types where companies use packaging materials in manufacturing, design houses (enterprises that design semiconductor packages, outsource the manufacturing, and then sell the finished products) and other enterprises that use this business model (designing and selling the finished products but outsourcing manufacturing) are gaining power. (An example of an enterprise that uses this business model is Apple Inc. in the United States.) As a result of this trend, to propose total solutions for semiconductor packages, we need to approach many different customers from various angles.



(Reference: Prismark Partners LLC, ELECTRONICS SUPPLY CHAIN REPORTER Q3 2016)
Figure 1 Supply chain of semiconductor products in 1980-2000

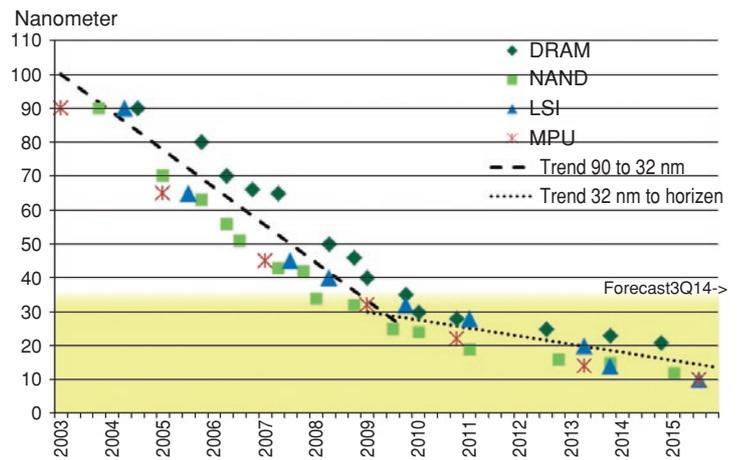
2 Status of Semiconductor Packaging Technology

The changes to technology nodes used in the mass production of semiconductor wafers are summarized in **Figure 2**. From this figure, it is obvious that refinement has been slowing down since 2009. The introduction of the 10 nm mass production process in 2017 and a plan for a 7 nm process have been announced. As such, the 5 nm process, which has long been considered the hurdle for CMOS, is expected to be achieved within the next several years. In the midst of these changes, three-dimensional technology has been rapidly developing for several years, and the actual application of such technology to memory has started.

With respect to NAND flash, the practical application of three-dimensional technology to memory cells has been achieved, allowing for further reduction of the bit unit price and high integration (two factors crucial to memory). On the other hand, with respect to DRAM, at present, three-dimensional technology relies on tip-to-tip or tip-to-wafer lamination using through-silicon electrodes (through-silicon via or TSV). (This type of lamination is referred to as 3D mounting.) As a result, higher integration, higher speed, and lower power consumption have been achieved, but the reduction in the bit unit price is still difficult.

Regarding logic semiconductors, a reduction in wafer yield due to the refinement of technology nodes (from 16 or 14 nm to 10 nm and then to 7 nm) has been predicted by various sources (Figure 3). As a countermeasure, a split-die package has been developed by using 2.5D mounting and silicon interposers.

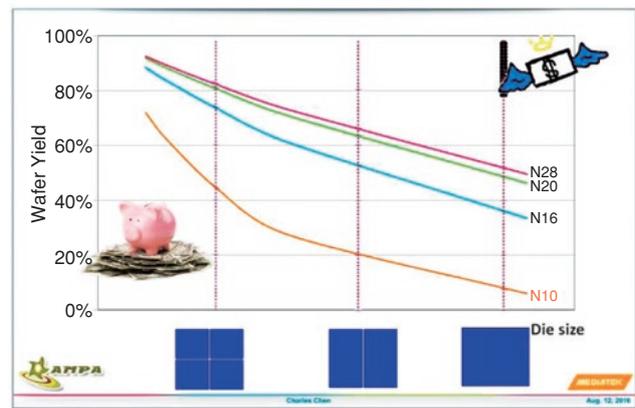
As described previously, the refinement of technology nodes (which has continuously supported the evolution of the system performance of semiconductor products for more than a half century) is slowing down. In light of such circumstances, packaging technology is now expected to play a larger role in the advancement of semiconductor performance, to which end 3D mounting and 2.5D mounting using TSV have been developed. Furthermore, in the past two or three years, the fan-out package has attracted attention for the following reasons: the cost reduction in TSV processing has not progressed, the reduction in the thickness of the package for mobile devices is required in order to address heat radiation from heated chips, and the fan-out package has good high-frequency characteristics due to its short wiring length.



(Reference: <http://www.semi.org/jp/node/18331>)

Figure 2 Volume production technology node transitions

Application: high end logic splits for wafer yield



Source: Dr. Charles Chen, MTK, cited with permission



(Reference: The handout distributed for Dr. Mike Ma's presentation at Semicon Taiwan 2016, SiP Global Summit 2016—2.5D/3D IC Packaging with Optical Technology Forum)

Figure 3 Relationship between technology node and wafer yield

3 Fan-Out Packages

“Fan-out package” is a generic term for a type of package where connecting terminals are arranged in a region larger than that of the chip. There are many types of fan-out packages. Although complicated configurations are sometimes required, for example, in the case of package-on-package (PoP) when connecting the top package to the bottom package, fan-out packages can be categorized into two main types: those created via the RDL-last method where redistribution lines (RDL) for fanning out are created on the semiconductor chip; and those created via the RDL-first method where a semiconductor chip is loaded onto the completed redistribution lines. Note that the RDL last method can be further categorized into face-up and face-down for a total of three fan-out package types (Table 1). In the RDL-last, face-up method, adhesives are applied to the back surface of a chip, which is then secured to the carrier material. Next, molding is performed and then the molding materials are ground to expose the chip terminal, thereby forming the redistribution layer. On the other hand, in the RDL-last, face-down method, adhesives are applied to the active surface of a chip, which is then secured to the carrier material. Next, molding is performed and then the carrier, adhesives, etc., are peeled back to expose the active surface on which the redistribution layer is formed. In the RDL-first method,

wiring layers are first formed such that the area in which each wiring layer is formed is larger than the size of the chip. Next, on the wiring layer, a semiconductor chip is loaded as a flip chip, and then the molding is sealed. The method used for wafers of 8 inches or 12 inches in size is generally referred to as the fan-out wafer level package (FO-WLP). Similarly, the method used for square wafers of 300 mm to 700 mm in size is generally referred to as the fan-out panel level package (FO-PLP). Various approaches to these methods have been proposed and applied depending on the specification of the package concerned, the required characteristics, and other conditions related to the infrastructure and technology of the manufacturer.

Table 1 Method classification of fan-out package

RDL-first	Face-down	×	Wafer level
RDL-last	Face-up		Panel level
	Face-down		

There are various methods for creating fan-out packages. The materials generally consist of carrier materials, temporary fixing materials, RDL insulating materials, wiring-forming photoresists, sealants, etc. Frequently used equipment include coating machines for liquid materials, laminators for film materials, back grinders for wafer processing, dicers, chip loaders, exposure and developing machines for processing photosensitive materials, compression molding machines, etc. Our company's product lineup includes many of these materials and equipment, many of which are installed in our open laboratory (Figure 4). In our packaging solution center, we work with various material-related departments and use the functions of the open laboratory to perform trial manufacturing of FO-WLP test vehicles (Figure 5). We are also working on proposing total solutions to customers and providing feedback to various material-related departments.

Concept of "Open Laboratory"

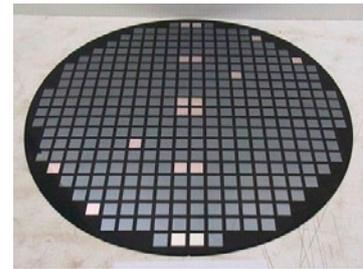
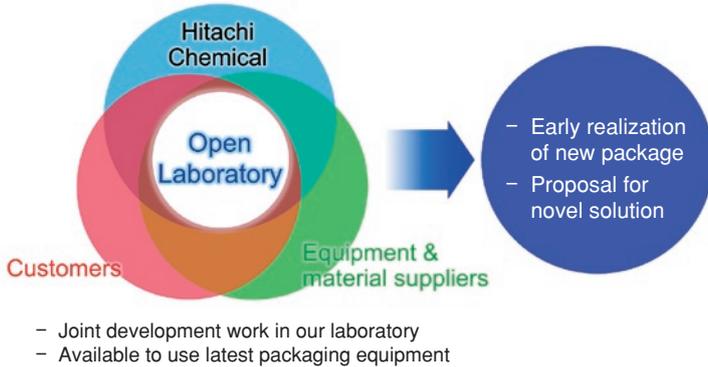


Figure 5 FO-WLP test vehicle made at Open Laboratory

Hitachi Chemical's "Open Laboratory"



Figure 4 Hitachi Chemical Open Laboratory Concept and landscape photo

4 Open Innovation and JOINT Project

Open laboratory was established and functions as a place for collaborative creation with semiconductor packaging-related customers, equipment and material manufacturers, etc. It is also a strategic tool for promoting open innovation. However, if we limit ourselves to using only our open laboratory facilities and our own products, it will be difficult for us to handle all cases (such as fan-out packages) that require novel, diverse, and speedy response. For this reason, in March 2016, we started the Jisso Open

Innovation Network of Tops project (JOINT), using equipment in cooperation with material manufacturers.

The trial manufacturing of test vehicles for fan-out packages of RDL-last, face-up type was carried out by outsourcing the processes of providing, forming, and delamination of temporary fixing materials to Tokyo Ohka Kogyo Co., Ltd.; the process of compression molding to Towa Co.; and the process of grinding molding materials to Disco Co. All other work was performed by our company. Similarly, the FO-PLP test vehicle trial manufacturing was carried out by using carrier glasses provided by Asahi Glass Co., Ltd., and by outsourcing the high-speed loading of a large amount of chips to Fuji Machine MFG. Co., Ltd. Although the project started in March, the quick action of each company made it possible to finish the trial manufacturing by the latter half of April. The actual test vehicles manufactured in both trials were introduced at ICEP 2016 (exhibition held in Sapporo in April 2016) and ECTC 2016 (exhibition held in Las Vegas, USA, in May 2016). These exhibitions are international conferences for packaging-related technology and attracted the attention of participants in the field (Figure 6). The JOINT project has achieved high-level trial manufacturing by assigning each process to a company with excellent skills in each field. Through this trial manufacturing, our final goal is to not only acquire know-how about each process from each company, but to also to work with all companies to propose a total solution for all of Japan. Such a solution would integrate conditions such as materials, equipment, and processes. Regarding semiconductor packaging processes that tend to be monopolized by equipment manufacturers or material manufacturers, it is sometimes difficult for individual companies to obtain general information about all processes of the trial manufacturing of the package. The trial manufacturing of the JOINT project is also expected to address such problems. In addition to the aforementioned companies, several other companies have expressed their intent to participate in the JOINT project. Thus, we hope to enlarge the collaborative network, propose a timely and adequate total solution for semiconductor packaging, and contribute to the expansion of the industry and of our company's business.

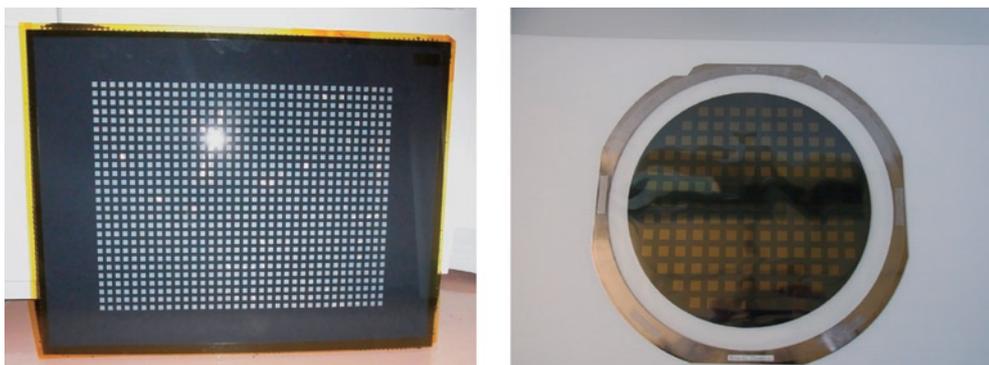


Figure 6 FO-PLP and FO-WLP demonstration samples assembled by JOINT project

5 Conclusion

As a result of the JOINT project, research and development is now performed in places outside of our company. In light of this, we plan to further expand the open laboratory (the key to proposing total solutions) in order to continue contributing to the semiconductor packaging industry, where supply chains and products continue to change. We hope to become the number one manufacturer of mounting materials in the world by implementing a cluster strategy for mounting materials. In FY 2016, we expanded the cleanroom inside a building at the current Tsukuba site and introduced new processing equipment. We are considering expanding or relocating to a place closer to the city in FY 2017 for the following purposes:

- To further promote open innovation
- To improve access from domestic and overseas customers and relevant companies such as JOINT project members
- To further cultivate open-mindedness

We are considering, if we do expand or relocate, to establish a consortium under the initiative of Hitachi Chemical as an advanced form of the JOINT project. In the semiconductor packaging industry, most parts of the supply chain are located overseas. We have already expanded our business overseas, with the current open laboratory acting as the global mother site to both the packaging solution center and open laboratory branches to be established in the future. We plan to enhance the functions of the packaging solution center as described above and, as a first step, we have started participating in the panel-level fan-out consortium held by Fraunhofer IZM in Germany. In the future, we hope to continue contributing to the mounting materials business, and to make our packaging solution center a global hub and an information-sharing base.

Low-Temperature Curable Positive-Tone Photosensitive Dielectric Materials

Akitoshi Tanimoto Yu Aoki Mika Kimura Sangchul Li Mamoru Sasaki

Photosensitive Materials R&D dept.,
Electronics-related Materials Development Center,
R&D Headquarters

1 Abstract

Recently, packages for semiconductors with a redistribution layer (RDL), such as fan-out wafer level packages (FOWLPs), have been developed to achieve downsizing; increasing the pin count and lowering cost. Dielectric materials used for FOWLPs are needing to meet requirements such as low warpage, high reliability and adhesion strength for metals used as RDL. We developed low-temperature curable positive tone dielectric material AH series for FOWLPs. The AH-3000 has low residual stress to reduce substrate warpage, as well as high tensile strength and low CTE for more reliable FOWLPs.

2 Characteristics

- Low residual stress contributes to the reduction in the substrate warpage.
- High resolution is suitable for the refinement of redistributed wiring.
- High thermal-cycle resistance and high-temperature-storage durability improve reliability of devices.

3 Background of the Development

Recently FOWLP (**Figure 1**) has attracted attention with capability of many I/O pins by redistribution of bump position which could expand beyond the chip area. Since redistribution layer is formed after molding, materials for FOWLP are required to have a variety of characteristics, such as low-temperature curability, low residual stress, thermal cycle resistance, and adhesion to copper. We promoted the research and development of positive-tone photosensitive materials as dielectric materials for redistribution layers and launched AH-1170.¹⁾ Since this product shows low stress and has excellent adhesion strength to copper, it is applied as redistribution layer of FOWLP.

In recent years, an increase of the number of redistribution layers to increase more pin counts, even lower stress and more thermal-cycle resistance are required.

We improved thermal stability of the base resin to increase thermal cycle resistance.

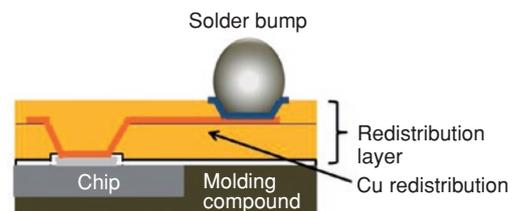


Figure 1 The FOWLP structure

4 Technical Details

The properties of the AH series are shown in **Table 1**. AH-3000 has even lower residual stress and can be expected to relieve warpage in a multilayer redistribution structure. In addition, the resolution of AH-3000 has been improved. **Figure 2** shows the cross-sectional shape of patterns after curing. The pattern shape of the cured AH-3000 can be controlled by ramp-up conditions during cure process. Therefore, AH-3000 can be used for various structures such as through-silicone via and bumps.

Moreover, AH-3000 shows high thermal cycle resistance by its improved tensile strength and reduced CTE. Mechanical properties after thermal cycle testing and high temperature/high humidity tests are shown in **Table 2**. The mechanical properties of AH-3000 were not deteriorated by the thermal cycle test or the high temperature/high humidity test and maintained its initial properties.

Thus, AH-3000 has excellent photosensitive characteristics and high reliability. It is suitable for redistribution layer of FOWLP.

Table 1 General Properties of the AH Series

Item	Unit	AH-1170	AH-3000
Tone	—	Positive	Positive
Film thickness	μm	2~20	2~35
Exposure dose*	mJ/cm ²	400	440
Resolution*	μm	10	3
Curing temperature	°C	180~240	←
Glass transition temperature	°C	> 200	> 200
Young modulus	GPa	2.0	2.3
Elongation	%	50	50
Tensile strength	MPa	115	147
CTE	ppm/K	58	45
Residual stress	MPa	20	16

*Film thickness after curing: 10 μm

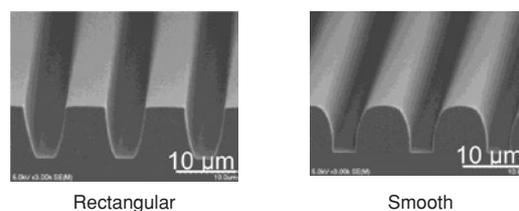


Figure 2 Cross-section of the cured AH-3000 (10μm)

Table 2 Mechanical properties of the AH-3000 after the reliability test

Item	Unit	Initial	After thermal cycle test*	After high temperature/high humidity tests*
Tensile strength	MPa	147	147	147
Elongation	%	50	49	50
Young modulus	GPa	2.3	2.3	2.3

*-65°C to 150°C for 200 cycles

5 Future Business Development

- Development of dielectric materials which is curable at even lower temperatures

[Reference]

- 1) A. Tanimoto, S. Nobe, H. Matsutani, Abstract of 15th The Symposium on Polymers for Microelectronics, 2012, 12.

Particle-Aligned Anisotropic Conductive Film (PAL-ACF) for Fine Pitch Interconnection

Akiko Iwai Masaru Tanaka

Conductive Materials R&D Dept.,
Electronics-related Materials Development Center,
R&D Headquarters

1 Abstract

In recent years, flat panel displays used in smart Phones, tablet PCS, etc. have a larger size and higher image quality. Following this trend, technical solutions for enabling fine-pitch interconnections are required for anisotropic conductive film (ACF) used in the Chip-on Glass (COG) modules of these applications. Hitachi Chemical has developed particle-aligned anisotropic conductive film (PAL-ACF) for fine pitch interconnection utilizing core technologies for designing advanced performance resins and particle dispersion process technology.

2 Characteristics of the New Product

- Enables collective fine-pitch interconnections.
- Enables both conductivity and insulation in fine-pitch interconnections.

3 Background of the Development

In the global market for flat panel displays, the demand for mobile products, such as smartphones and tablet PCs, is rapidly growing. As their built-in panel displays, such products use liquid crystal displays and organic EL displays that use the COG bonding system. In recent years, as liquid crystal displays are rapidly developed to support larger image size and higher image quality, the number of electrode terminals of driver IC chips is steadily increasing and electrode circuits are becoming more fine-pitch interconnected.

In light of this, there is an increasing need for the ACF for the COG bonding system that is used to respond to fine-pitch interconnection. To this end, a function-separated bilayer construction ACF¹⁾ was adopted, the conductive particle size was reduced, and the number of conductive particles was increased. However, the following problems arose: these methods have limitations in insulation between the adjacent circuits, and the variation in the number of conductive particles captured between the counter circuits increased. To solve these problems, we started to develop an ACF for fine-pitch COG bonding system using resin design technology and conductive particle dispersion technology, two of our fundamental technologies.

4 Technical Details

During the development of this product, resin design technology was enhanced to further improve the functionality of the separated bilayer construction ACF¹⁾. The layers include the anisotropic conductive film layer with dispersed conductive particles (ACF layer) and the non-anisotropic conductive particle film layer with adhesives only (NCF layer). For this type of ACF, the fluidity of the adhesive of the ACF layer at bonding was less than that of the NCF layer for restricting the flow of the ACF layer generated by the flow of the NCF layer at bonding. As a result, the efficiency of capturing conductive particles between the counter electrodes was improved. In the ACF we developed, we were improved the ability to capture conductive particles and reduced variation by increasing the difference in the resin flow between the ACF layer and NCF layer by 7.6 times in comparison with the conventional product. The resin flow characteristics of conventional and developed products are shown in **Figure 1**.

A comparison of the structures and characteristics of the conventional and developed products is shown in **Table 1**. During development, we improved the conductive particle dispersion technology to create technology

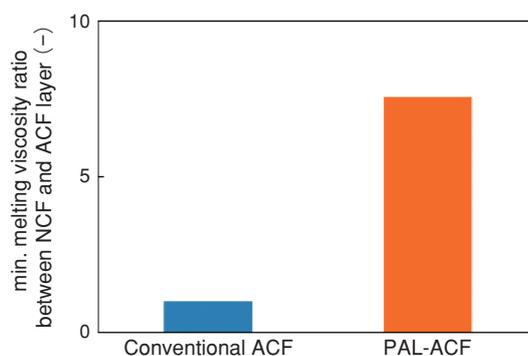
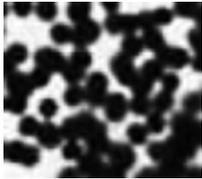
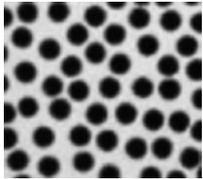
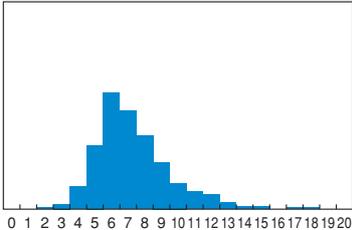
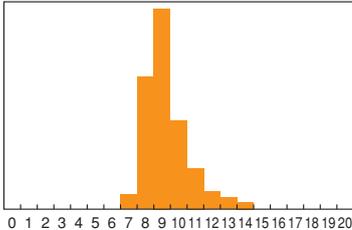
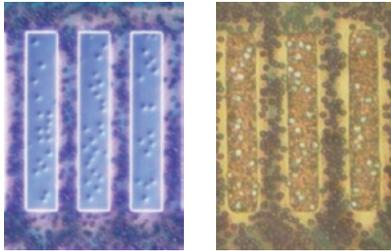
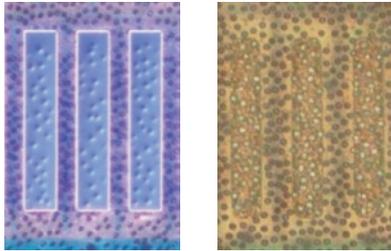


Figure 1 Melting viscosity ratio between NCF and ACF layer

for monodispersion where the conductive particle exists as monodispersed particle without coagulation (a phenomenon that was difficult to achieve with conventional products).

The developed ACF can capture conductive particles efficiently while maintaining the conductive particle monodispersion state before bonding, and without allowing the conductive particles to flow between the counter circuits even after bonding. As a result, we could capture a large number of particles and achieve high insulation resistance while limiting variation in the number of captured conductive particles, thus making possible the fine-pitch interconnection that was difficult to achieve for conventional products.

Table 1 Properties of ACF

Item	Conventional ACF	PAL-ACF
Conductive particle arrangement		
Product structure (cross-sectional schematic diagram)		
Monodisperse ratio of conductive particle (%)	Unmeasurable	≥ 75
Smallest connection circuit	Area* ¹ (μm^2)	500
	Space* ² (μm)	12 / 5
Frequency in number of conductive particles captured [particles] (Connection area: $400 \mu\text{m}^2$)		
Photo of bonded area* ³ Left : Differential interference microscope image Right : Optical microscope image (Connection area: $1,200 \mu\text{m}^2$)		
Insulation resistance (Ω)* ⁴	$8.6\text{E}+10$	$1.7\text{E}+14$

*¹ Actual and minimum bump to bump space / Bump to pad space after bonding.

*² Effective bonding area between bump and electrode on glass after bonding. Calculated value using Hitachi's TEG. Ave-3 $\sigma \geq 5$ pcs.

*³ Bonding conditions: $150^\circ\text{C}/5$ seconds/ 60 MPa

IC chip: $0.9 \text{ mm} \times 20 \text{ mm} \times 0.2 \text{ mm t}$, Au bump, IC bump area size: $12 \mu\text{m} \times 100 \mu\text{m}$ ($1,200 \mu\text{m}^2$),
Glass substrate: Thickness: 0.2 mm , ITO electrode/ITO-Metal electrode

*⁴ Bonding conditions: $150^\circ\text{C}/5$ seconds/ 60 MPa

IC chip: $0.9 \text{ mm} \times 20 \text{ mm} \times 0.2 \text{ mm t}$, Au bump, IC bump area size: $12 \mu\text{m} \times 100 \mu\text{m}$ ($1,200 \mu\text{m}^2$),
Glass substrate: Thickness: 0.2 mm , ITO electrode, Bump-pad distance: $5 \mu\text{m}$
Reliability test: High Temperature and Humidity Test ($85^\circ\text{C}/85\% \text{RH}$, 500 hrs.)

5 Future Business Development

- Sales promotion of the developed product
- Finding new ways to apply the product

[Reference]

1) Nozomu Takano, Tohru Fujinawa, and Toshihiko Kato: Hitachi Chemical Technical Report, No. 55, pp. 21-23 (2013)

Low Transmission Loss/Low CTE Multilayer Material, “MCL-HS100”

Tomokazu Shimada

Laminate Materials R&D Dept.,
Electronics-related Materials Development Center,
R&D Headquarters

1 Abstract

Semiconductor packages for smartphones and other electronic devices are becoming smaller, thinner and denser. Lowering of rigidity due to the thinning of the package substrate increases the warpage and interconnection failures of the package. To reduce this warpage, lower CTE substrate is effective. Meanwhile, with recent advances in high-capacity, high-speed communications, electrical signals used for information communication equipment tend to be higher frequencies each year. However, the higher the signal frequencies are, the more electrical signals are converted into heat in the circuits, and transmission loss is increasing. These issues have led to the demand for substrate materials with low Dk and low Df. So, focusing on the developments of package substrate materials with low CTE, and high-speed network substrate materials with low Dk and low Df, we have developed MCL-HS100.

2 Characteristics of MCL-HS100

- Very low transmission loss and low warpage.
- High heat resistance and high glass transition temperature (T_g) (general characteristics).
- Environmentally friendly material that uses halogen-free flame retardant.

3 Background of the Development

Since the advent of mobile electronic devices (such as smartphones), the size and thickness of semiconductor packages has been decreasing, while the density of semiconductor packages has been increasing. At the same time, rigidity and the thickness of the substrate has been decreasing. This causes increased warpage of the package substrate at mounting, leading to mounting problems. To address these mounting problems, it is effective to reduce the difference in the coefficient of thermal expansion between the chip and the package substrate by reducing the thermal expansion of the substrate. In addition, the higher performance of electronic devices and the dramatic progress in network technology led to a rapid increase in data transmission capacity and speed. The signal frequencies that can be handled by electronic devices have been steadily increasing each year. As a result, the substrate must respond to higher speeds and there is increasing demand for low transmission loss materials.

In light of this, our company has been developing the low thermal expansion material MCL-E-705G, the next-generation package materials characterized by MCL-E-770G, and the next-generation high speed network materials characterized by the low transmission loss material MCL-LW-900G. Using the results of this material development, we successfully developed the material MCL-HS100, which has the properties of both low thermal expansion material and low transmission loss material.

4 Technical Details

1. Design concept of MCL-HS100

Generally, the reduction in the coefficient of thermal expansion of the substrate material can reduce the warpage of the thin-type package substrate. Low thermal expansion is achieved by providing the base resin of the MCL-HS100 with the plane stack structure of the aromatic ring and by introducing hard segments with a strong intermolecular force between the stacks. In addition, low thermal expansion is realized by introducing a low elastic soft segment to allow resin to easily follow the thermal behavior of glass cloth (**Figure 1**). Furthermore, resin that is low dielectric and has high heat resistance was applied to the base resin (a high heat resistant resin), using our unique technology for polymer alloying. Moreover, using a similar resin,

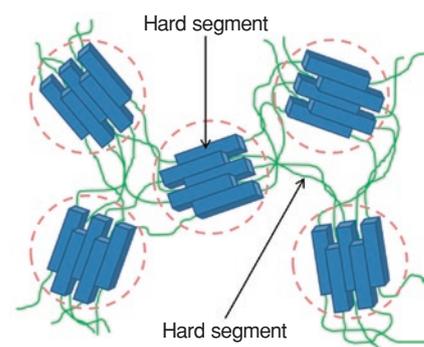


Figure 1 Resin design model of MCL-HS100

we also developed MCL-HS100 (E), for which low dielectric glass is used as the glass cloth.

2. General Characteristics of MCL-HS100

General properties of the MCL-HS100 and MCL-HS100 (E) when using E-glass and low dielectric glass are shown in **Table 1**. The coefficient of thermal expansion of the MCL-HS100 is 7 ppm/°C, which is lower than that of the low transmission loss material MCL-LW-900G. In addition, the MCL-HS100 has dielectric characteristics of Dk = 4.0 and Df = 0.0055 at 10 GHz. These characteristics are lower than those of the low thermal expansion material MCL-E-705G. Thus, it was verified that MCL-HS100 has a lower thermal expansion property than MCL-LW-900G and has a lower dielectric property than MCL-E-705G. Furthermore, since Tg was found to be 230°C using the TMA method and T-288 indicates 60 minutes or more, MCL-HS100 was recognized to have excellent heat resistance.

3. Warpage Characteristics of MCL-HS100

Samples of MCL-HS100 (E) using low dielectric glass were created for the purpose of measuring warpage using the shadow moiré method. **Figure 2** shows the results of warpage measurement. We found that the warpage of the package substrate of MCL-HS100 (E) was less than that of the low transmission loss material MCL-LW-910G. It was also lower than that of the low thermal expansion materials MCL-E-700G and MCL-E-705G.

4. Transmission Loss of MCL-HS100

A three-layer printed circuit board was created to perform the measurement of transmission loss in a strip line structure, the results of which are shown in **Figure 3**. It was found that MCL-HS100 (E) shows less transmission loss than the low thermal expansion materials MCL-E-705G and MCL-E-770G.

Table 1 General properties of MCL-HS100 (thickness 0.8mm)

Item	Unit	MCL-HS100	MCL-HS100(E)	MCL-E-705G	MCL-LW-900G	MCL-LW-910G
Glass type	—	E-glass	Low Dk-glass	E-glass	E-glass	Low Dk-glass
Tg	TMA	°C	230	230	260	198
CTE	X < Tg	ppm/°C	7	7	6	13
	Z < Tg	ppm/°C	25	25	13	40
Flexural Modulus	GPa	25	25	33	19	19
Dk (10 GHz)	—	4.0	3.5	4.4	3.5	3.3
Df (10 GHz)	—	0.0055	0.0035	0.0080	0.0045	0.0030
T-288 (Without copper)	TMA	min.	> 60	> 60	> 60	> 60



- Substrate : Coreless-5Layer
- Package size : 14 x 14 mm
- Chip size : 7.3 x 7.3 mm
- Chip thickness : 150 μm
- Underfill thickness : 50 μm (CEL-C-3730-4)
- L1,5: 12 μm Cu 100%, L2, 3, 4: No copper, SR-
- PPG construction
 - HS100 (E) : (1078, R.C.: 63%) x 4ply
 - E-700G (R) : (1078, R.C.: 66%) x 4ply
 - E-705G : (1078, R.C.: 65%) x 4ply
 - LW-910G : (1078, R.C.: 61%) x 4ply

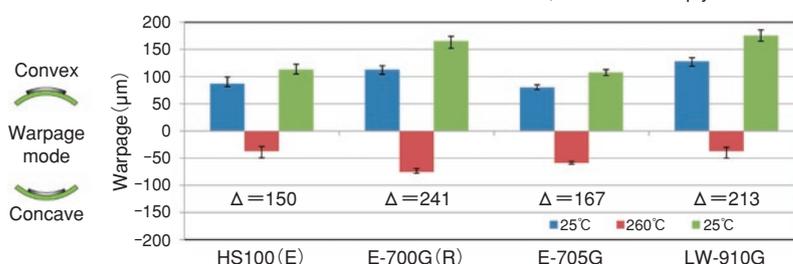


Figure 2 Warpage evaluation result of MCL-HS100

(Measurement conditions)
 Evaluation PWB: Strip-line
 Temperature & Humidity: 25°C/60%RH
 Characteristic impedance: Approx. 50 Ω
 Proofreading method: TRL



- Trace width (w): 0.12-0.14 mm
- Dielectric thickness (b): 0.23-0.26 mm
- Trace thickness (t): 18 μm

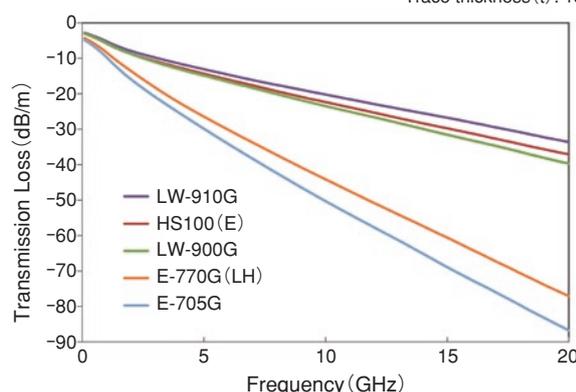


Figure 3 Transmission Loss of MCL-HS100

5 Future Business Development

- Development of next-generation materials that qualify as both low transmission loss materials and low thermal expansion materials, and that are suitable for high frequency

[Reference]

- 1) Tomokazu Shimada: JPCA Show 2016 NPI Presentation Proceedings pp. 47-49

Reliability Improvement Technologies for Epoxy Molding Compounds on Lead Frame Package

Shinya Nakamura

Advanced Performance Materials R&D Division,
Electronics-related Materials Development Center,
Encapsulation Materials R&D Department

1 Abstract

Recently, there are strong requirements to improve the reliability of semiconductor packaging for automotive devices, which are increasing, and to reduce cost by eliminating moisture-proof packaging. Correspondingly, reducing delamination of epoxy molding compounds (EMCs) at the surface on a lead frame at reflow has been strongly required. In this study, the reduction of water absorption and modulus, and the improvement of adhesion strength on a lead frame were investigated. As a result, we found epoxy resins that can reduce water absorption and modulus, and new adhesion promoters. By combining these technologies, we developed new EMCs that can reduce delamination after reflow.

2 Background of the Development

In recent years, the number of built-in semiconductors has increased as electronics have become increasingly used for automobiles.¹⁾ Standards for reliability tests of built-in semiconductors, such as AEC-Q100, were established with stricter conditions relative to the conditions for consumer use.²⁾ To pass a strict reliability test, such as the b-HAST (the biased highly accelerated stress test), it is necessary to reduce the delamination of epoxy molding compounds on the surface of the lead frame in the reflow process.

In addition, to reduce costs, we need to eliminate moisture-proof packaging not only for built-in semiconductors but for semiconductors for consumer use. Thus, we need to improve the moisture sensitivity level (MSL) against water absorption at reflow.

At the same time, the conventional gold wire has been replaced with copper wire to reduce costs, even though the latter corrodes more easily than the former. Regarding the use of copper wires, we already know that additives containing sulfur atoms used to improve adhesion with lead frames adversely affect the corrosion of the wire bonding zone.³⁾ For this reason, additives that do not contain sulfur atoms are required.

Taking these points into consideration, in this study, we created technology that enables us to reduce delamination at reflow regardless of whether additives containing sulfur atoms are used, and developed new products as reported below.

3 Characteristics of Developed Product

- Development of epoxy resin enabling a reduction in the modulus almost at reflow temperature resulted in a reduction in the stress at reflow and an improvement in delamination resistance at reflow.
- The improvement of adhesion promoters improved both the adhesion strength at reflow temperature and the delamination resistance at reflow.
- Adhesion promoters containing no sulfur atoms improved the delamination resistance of sulfur-free epoxy molding compounds, which are strongly requested by customers, at reflow.

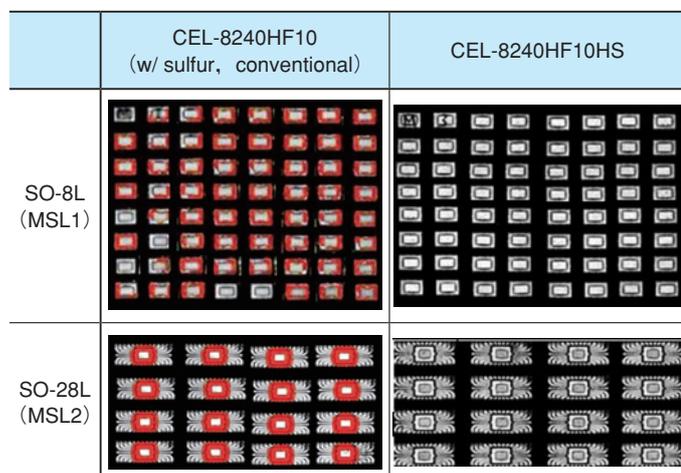
4 Technical Details

It is assumed that the delamination at reflow is mainly caused when the sum of the volatile expansion stress (volatilization stress) at reflow temperature (260°C) of water accumulated in the interface between the lead frame and the epoxy molding compounds due to water absorption and the stress (thermal expansion stress) generated by the difference in the linear expansion between the lead frame and the epoxy molding compounds exceeds the adhesion strength of the epoxy molding compounds and the lead frame. That is to say, the reduction in the volatility stress and thermal expansion stress and the improvement in the adhesion strength are required for the measure preventing delamination at reflow. Since a reduction in the water absorption ratio is required to decrease volatility stress, we examined epoxy resin capable of reducing the water absorption ratio in this study. Concerning the reduction in the thermal expansion stress, we examined stress reduction due to modulus reduction almost in the vicinity of the reflow temperature in this study. Concerning the improvement in adhesion strength, we examined new adhesion

promoters in this study.

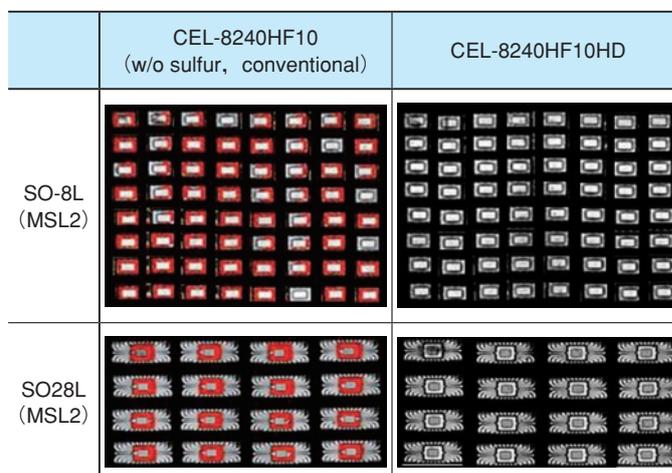
As a result, the improvement in the epoxy resin achieved a reduction in the water absorption ratio and modulus at around 260°C, and the improvement in the adhesion promoters achieved an increase in adhesion strength.

In addition, although the new standard adhesion promoters are assumed to be those containing sulfur atoms for the purpose of improving adhesion strength in the silver plated zone, sulfur-free material that is highly required from the viewpoint of the improvement of long-term reliability at high temperature in case of using copper wire has also been developed. Comparisons between the developed materials (CEL-8240HF10HS and CEL-8240HF10HD) and the conventional materials are shown in **Figure 1** and **2**, and the properties of developed materials are shown in **Table 1**.



MSL1 Condition: 85°C/85%RH/168 h, MSL2 Condition: 85°C/60%RH/168 h
Reflow Condition: 260°C x 10 s x 3 times
Pre-bake Condition: 125°C x 24 h
SO-28L (Cu alloy) Die pad; Ag plated, 4.1 x 5.2 mm, Die size; 2.2 x 3.2 mm
SO-8L (Cu alloy) Die pad; Ag plated, 2.8 x 4.3 mm, Die size; 1.5 x 2.6 mm

Figure 1 CSAM images after reflow (w/ sulfur)



MSL2 Condition: 85°C/60%RH/168 h
Reflow Condition: 260°C x 10 s x 3 times
Pre-bake Condition: 125°C x 24 h
SO-28L (Cu alloy) Die pad; Ag plated, 4.1 x 5.2 mm, Die size; 2.2 x 3.2 mm
SO-8L (Cu alloy) Die pad; Ag plated, 2.8 x 4.3 mm, Die size; 1.5 x 2.6 mm

Figure 2 CSAM images after reflow (w/o sulfur)

Table 1 Property of developed items

Item	Unit	CEL-8240HF10 (w/ sulfur, conventional)	CEL-8240HF10HS	CEL-8240HF10 (w/o sulfur, conventional)	CEL-8240HF10HD	
Epoxy resin	—	Current	Modified	Current	Modified	
Hardener	—	Current	Current	Current	Current	
Flame retardant	—	No	No	No	No	
Additives	—	Current w/ sulfur	Modified w/ sulfur	Current w/o sulfur	Modified w/o sulfur	
Filler content	wt%	89	89	89	89	
Spiral flow	cm	115	120	115	125	
Gel time (175°C)	s	32	33	32	35	
Flexural modulus at 260°C	MPa	700	600	700	500	
Water absorption (85°C/85%RH/168 h)	%	0.20	0.17	0.20	0.18	
Adhesion (260°C)	Cu	MPa	1.3	1.4	1.3	1.3
	Ag	MPa	0.6	0.8	0.5	0.6
Cl ⁻ (121°C, 2 atm, 20 h)	ppm	10	10	10	10	
Reliability (Cu Wire)	b-HAST (130°C/85%RH)	—	336 h Pass	336 h Pass	336 h Pass	336 h Pass
	HTSL (200°C)	—	1500 h NG	1500 h NG	1500 h Pass	1500 h Pass

Values listed above are typical and should not be used for specification purpose

5 Future Business Development

- Level up of sulfur-free material by exploring the technology for adhesion promoters containing no sulfur atom
- Development of technology for improving reflow resistance suitable for high voltage

【References】

- 1) Latest Trend Study of Semiconductors Related Players 2015, Fuji Chimera Research Institute, Inc. May 2015
- 2) AEC-Q100-Rev-H, September 11, 2014

- 3) Hidetoshi Kuraya, Fumiaki Aga, Hideki Ishii and Kousuke Azuma: Influence of mold resin properties on high temperature storage life of Cu wire package, 24th Microelectronics Symposium Proceedings, pp. 339-342 (2014)

Insulating Varnish of Motor for Hybrid Vehicle and Electric Vehicle

Tatsuhito Fukuhara

Electrical Performance Materials R&D Dept.,
Social Infrastructure-related Materials Development Center,
R&D Headquarters

1 Abstract

In recent years, the demand for fuel-efficient hybrid vehicle (HEV) and electric vehicles (EV) is increasing. Automotive motor is mounted adjacent to engine where is always in high temperature environment compared with temperature in which usual general motors are used. The temperature could be higher when the motor is running in high output.

Therefore, it is necessary to cool the motor down with immersing directly in Automatic Transmission Fluid (ATF). Since it causes direct contact between ATF and the cured varnish which adheres several motor parts together, both heat resistance and ATF resistance are required for insulating varnish.

Furthermore, the conventional insulating varnish contains volatile organic solvents that should be reduced to meet increasing requirement for reduction of gas ignition risk and environmental impact with low volatile organic compounds (VOC). To fill this demand, we has developed a new HEV/ EV motor insulating varnish, "WP-2008", which has outstanding resistance to both heat and ATF, and possesses low VOC that cannot be achieved with conventional products.

2 Characteristics

- Heat resistance of 200°C/1000 h.
- ATF resistance of 150°C/1000 h.
- Low VOC (volatilization volume at curing ≤ 1 wt%) containing no solvent.

3 Background of the Development

Insulating varnishes are sold in the market since 1912 as an establishment product of our company and have been used in various fields.

This product is typically applied to automotive motors and required properties are high heat resistance and ATF resistance evaluated based on adhesion strength.

Therefore, an improvement in heat resistance and ATF resistance was performed by examining the compositions of base resin. Since a reduction in the environmental load is essential as the market trend in recent years, a reduction in the VOC is also required.

However, it was difficult to realize a reduction in VOC in conventional varnish because the diluent uses volatile organic solvent. Therefore, we established technology for manufacturing insulating varnishes with a small amount of VOC and heat and ATF resistance by optimizing resin compositions and substituting low volatile materials having reactivity for solvents.



Figure 1 Insulating Varnishes provided by Hitachi Chemical

4 Technical Details

1. Development Concept of WP-2008

Increasing the molecular weight of the base resin is generally an effective method for improving heat- and ATF-resistance to maintain adhesion. However, because the method causes the solvent compatibility to deteriorate, it is not effective in reducing VOCs.

In order to realize coexistence of these trade-off characteristics, optimization of the base resin structure using our unique resin denaturation technology improved compatibility, enabling the adoption of special acryl base monomers with low volatility as the diluent.

2. Heat and ATF resistances

Heat and ATF resistance was evaluated based on the adhesion shear force ($\phi = 0.82$ KMK-22A) using the Stracker method.

Figure 2 and **3** show the results of evaluation of the adhesion shear force after the heat and ATF resistance tests.

The adhesion shear force of the general conventional varnish WP-2763 (LF) was 20 (N) after the heat resistance test (200°C/1000 h) and was significantly lower at 13 (N) after the ATF resistance test (150°C/1000 h in ATF). On the other hand, the adhesion shear force of WP-2008 was 113 (N) after the heat resistance test (200°C/1000 h) and 110 (N) after the ATF resistance test (150°C/1000 h in ATF). That is to say, the high adhesion force required for electric automobiles is held.

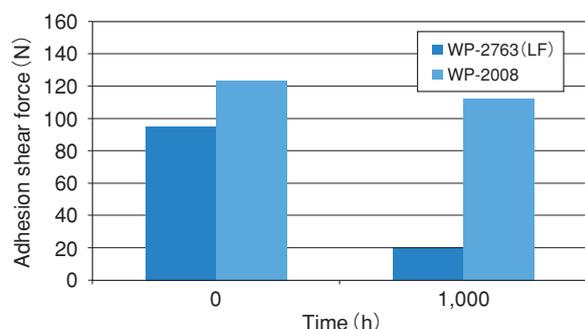


Figure 2 Adhesive after Heat resistance

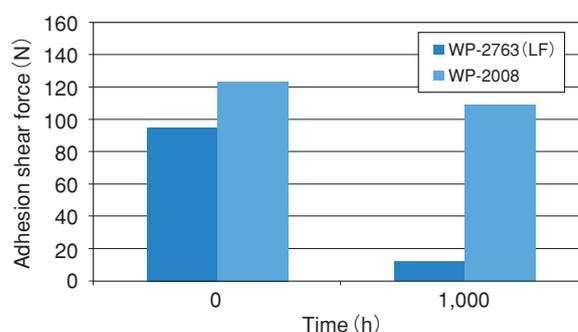


Figure 3 Adhesive after ATF resistance

3. General Characteristics of WP-2008

Table 1 shows general properties of WP-2008.

The VOC content of WP-2008 is about 1/25 of the general conventional varnish WP-2763 (LF), which was a far lower value. This property enabled to reduce the environmental load.

In addition, the flash point as high as 176°C allowed a reduction in the risk of ignition.

Table 1 General properties of WP-2008

Item	Unit	Developed product WP-2008	Conventional product WP-2763 (LF)
Advantage	—	Low VOC and high heat resistance	—
Viscosity (25°C)	Pa · s	1.7	0.1
VOC content*1	%	1	25
Flash point	°C	176	31
Gelation time (120°C)	Minutes	6.5	12
Pot life (40°C)	Days	30	30
Adhesion shear force (23°C)	N	123	95
Curing condition	°C/h	130/1	130/1

*1 Sample varnish of 5.0 g was put into a metal petri dish ($\phi = 60$) to measure the rate at which the weight decreased after curing.

5 Future Business Development

- Development of materials for the next generation electric vehicles
- Exploration of application to other fields

Porous Aluminum for Heat Exchanger

Takehiro Shimoyama

Energy storage and tribology materials R&D Dept.,
Social Infrastructure-related Materials Development Center, R&D Headquarters

Keita Sone

Core Technology Research & Innovation Center,
Research & Innovation Promotion Headquarters

1 Abstract

To reduce global power demand, high performance of heat exchangers for inverters, IT devices and automotive devices (condensers, radiators) has been demanded. Hitachi Chemical has developed a new sintering method for aluminum powder, which was previously thought to be difficult to sinter. We have designed porous aluminum for a heat exchanger that takes advantage of its high specific surface area. In this paper, we describe features of the developed product, development history and technical contents.

2 Characteristics of Developed Products

- A high specific surface area (heat transfer area) can be achieved by a porous structure.
- Since aluminum is used as a base metal, the product is lightweight and has high thermal conductivity.
- The maximum porosity can be controlled up to 98%.

3 Development History

Porous metals have been expected as one of the most promising candidates for next-generation industrial material. Because of high porosity and high specific surface area, porous metals provide excellent functions such as shock absorption, damping, sound absorption, thermal insulation, and heat dissipation.

Particularly, a porous metal with open-cell structure is being considered for application to heat exchangers and electrode materials, because it allows fluid to flow easily and have large contact area with fluid. Focusing on its lightweight and high thermal conductivity, our company has developed a method for manufacturing porous aluminum with open-cell structure.

4 Technical Content

In general, aluminum powder has a stable oxide layer on the surface, making it difficult to sinter, even if performed in a reducing atmosphere. Therefore, we have developed new technology for sintering aluminum powder in a depressurized atmosphere. In this process (template method), we coated a resin form with aluminum powder and then the foam was thermally removed through the debinding process. Finally the debinded foam structure consisted of aluminum powder was sintered. By changing the specifications of the resin form and the conditions of the aluminum powder coating, we were able to control the porous structure such as the porosity and pore size. The appearance and the SEM image of the developed porous aluminum are shown in **Figure 1**, and the specifications of the porous aluminum are provided in **Table 1**. The developed porous aluminum has a complete open-cell structure with a pore size of 0.5 mm to 20 mm and a porosity of 93% to 98%.

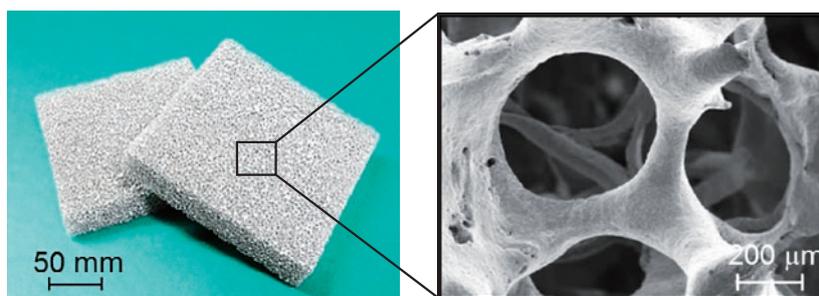


Figure 1 Appearance of porous aluminum and its micro-pore structure

Table 1 Characteristics of porous aluminum

Item	Unit	Characteristics
Porosity	%	93-98
Pore size	mm	0.5-2.0
Structure	—	Open Cell
Specific surface area	m ² /m ³	550~2,000
Compressive strength	MPa	0.15 (porosity 97%)

Currently, to take advantage of the developed porous aluminum, we are working on applying this material to heat exchangers. **Figure 2** shows a comparison of the conventional fin (corrugated fin) and the porous fin. The porous aluminum has the following advantages: fluid easily flows through the open cells, and the contact area between the fluid and the porous aluminum is large. The application of the developed porous aluminum to a heat exchanger could increase the heat transfer area. This makes it possible to achieve higher performance and reduce the size of heat exchangers. Thus, the industrial value of the developed porous aluminum is high.

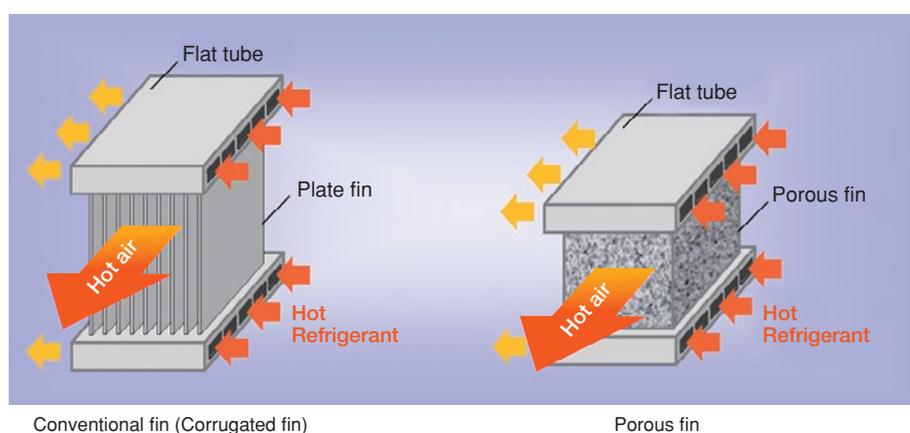


Figure 2 Structural comparison of conventional fin and porous fin heat exchangers

5 Future Business Development

- Promote sales and extend the application of developed porous aluminum

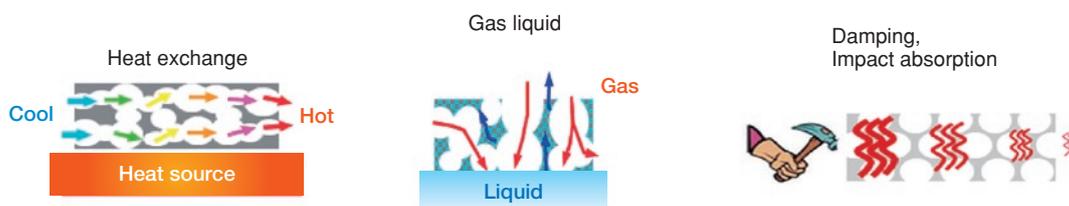


Figure 3 Applications

[Reference]

- 1) H. Koshita, "Development of highly porous aluminum with an open-cell structure", PM2014 World Congress manuscript preprint, 2014, pp.496-504.

Hot-melt Adhesive for Automotive Interior

Yuzuru Takahashi

Polymer Materials R&D Dept.,
Social Infrastructure-related Materials Development Center,
R&D Headquarters

1 Abstract

Various solvent-based adhesives (SBAs) are used for automotive interiors. High-performance reactive SBAs (RSBAs) are used particularly for doors because customers demand severe shape characteristics and heat-resistance. However, SBAs affect the environment and RSBAs complicate the process control. We have developed solventless and non-reactive hot-melt adhesives “ZH601-1” and “ZH551-4” to resolve these problems. These new products are applicable to doors. They contribute to eliminating solvents by replacing SBAs, and can be used in the precoat method because these products are non-reactive. Moreover, they can shorten lead time, since solventless and non-reactive hot-melt adhesives can reduce the solvent drying process and the reactive process compared with RSBAs.

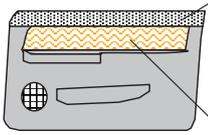
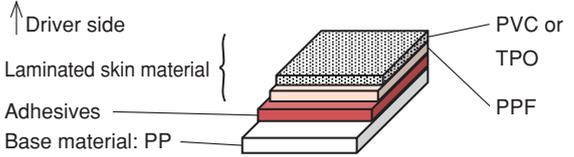
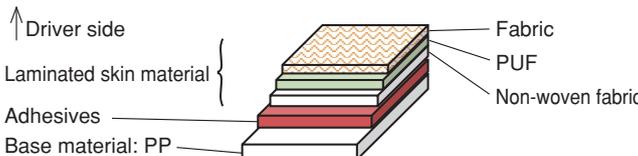
2 Characteristics of the New Product

- Hot-melt adhesives for automotive interiors (solvent-free and non-reactive) can be applied to doors.
- Lamination of pre-coated skin material can be stored due to PVC plasticizer resistance (ZH601-1 for vacuum forming).
- The new product can be applied to the press-contact adhesion method, because of its long open time (ZH551-4 for press-contact adhesion).

3 Background of the Development

Adhesives for automotive interiors, especially for doors, were improved in response to the market demand for a non-primer, one-liquid, and VOC13-removed substance with strong adhesive qualities. Currently, one-liquid, solvent-type reactive adhesives are mainly used.¹⁾ On the other hand, there is a demand for adhesives capable of removing VOC and reducing process costs. The vacuum-forming method uses one-liquid, solvent-type potential-curing adhesives corresponding to the pre-coating method (coating before storing). This method is capable of integrating the coating process by using a roll coater for continuous coating and is reported to be a way to reduce process costs.²⁾ For this method, we developed a solvent-free, non-reactive hot-melt adhesive (YH171-1P).³⁾ However, YH171-1P was easily affected by plasticizer migration during lamination after the PVC surface layer was pre-coated. In addition, the press-contact adhesion method could not be applied to conventional hot-melt adhesives that require adhesion via high-temperature melting, because the high temperature press deteriorated the quality of the fabric. For these reasons, we designed and developed Hi-Bon ZH601-1 and ZH551-4, which can be applied to each method.

Table 1 Configuration of adhesives for door

Schematic diagram of a door	Location	Adhesion method	Configuration	Solvent-type adhesives*
	Upper	Vacuum forming		<ul style="list-style-type: none"> • YA211-1 • 1212
	Ornament	Press-contact adhesion		<ul style="list-style-type: none"> • 1755 • 1255

PP: polypropylene, PVC: polyvinyl chloride, TPO: thermoplastic olefin resin, PPF: polypropylene foam, PUF: polyurethane foam.

*: Our grade of one-liquid type reactive adhesives

4 Technical Details

The general properties of Hi-Bon ZH601-1 and ZH551-4 are shown in **Table 2**. ZH601-1 for vacuum forming has adhesion qualities equivalent to that of YH171-1P, and improved PVC plasticizer resistance. Test results are shown in **Table 3**. In addition, ZH551-4 for press-contact adhesion achieves adhesion even for 60 seconds of open time (time from removal of the heat source until contact adhesion, hereinafter referred to as OT). For press-contact adhesion, to prevent deterioration of the fabric quality, a long OT is essential as the work time for the customer and heat radiation time. Our polymer alloy technology resolved the issue where a long OT generally caused a significant decrease in the heat resistance of hot-melt adhesives.⁴⁾ **Figure 1** shows the cooling solidification behavior of ZH551-4. A long OT and heat resistance were simultaneously achieved by maintaining storage modulus G' and by decreasing the rising speed.

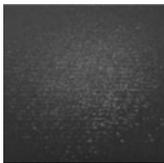
Table 2 General properties of new products

Item		Unit	YH171-1P		ZH601-1	ZH551-4
Method of applying adhesives		—	Vacuum forming		Vacuum forming	Press-contact adhesion
Properties	Appearance	—	Light yellow		Light yellowish white	Light yellowish white
	Viscosity (180°C)	mPa · s	10,000		20,000	33,000
	Softening point (ring and ball method)	°C	145		145	140
Adhesion conditions	Substrates (base material)	—	PP		PP	PP
	Substrates (skin material)	—	PPF/PVC	Non-woven fabric/ PUF/fabric	PPF/PVC	Non-woven fabric/ PUF/fabric
	Open time	s	5	60	5	60
	Surface temperature of hot-melt at contact adhesion	°C	120	30	120	30
Adhesive properties	Peel strength (23°C, 200 mm/min, 25 mm wide)	N	33.0 B	No adhesion	32.0 B	22.0 B
	Peel strength (80°C, 200 mm/min, 25 mm wide)		22.5 B	No adhesion	23.0 B	18.5 B
	creep (80°C, 100 g load, 24 h, 25 mm wide)	mm	0	No adhesion	0	3 A

Coating method: roll coater, coating amount: 100 g/m², adhesion strength: 0.05 MPa

Failure condition symbol: A (adhesive failure from base material side), B (material failure of skin material)

Table 3 Result of plasticizer resistance test

Item	YH171-1P		ZH601-1	
Appearance of PVC side				
	Before test	After test: Not acceptable because of contamination	Before test	After test: Acceptable (no contamination)

Pre-coated skin material (PVC, PPF, hot-melt adhesives) lamination, 9.8×10^{-4} MPa, 50°C, 168 h

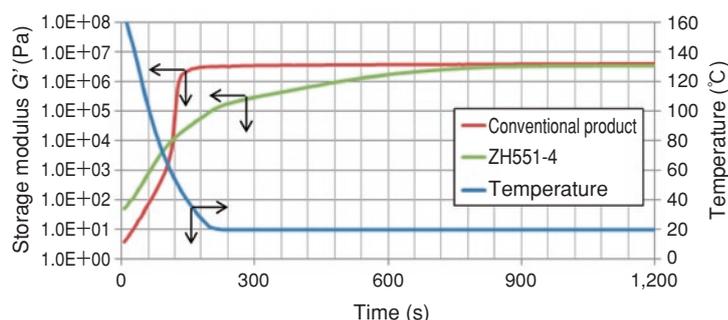


Figure 1 Cooling solidification behavior of “ZH551-4”

5 Future Business Development

- Promote adoption by automotive interior manufacturers

[References]

- Shunichi Saeki: “Adhesives for Automotive Interior Materials: Present Situation and Prospects—Solvent-Type Adhesives for Door Ornaments”, Polyfile, Vol. 48, pp. 21-25 (2011)
- Tetsuya Oda, Atsushi Kawada: Development of Procoat Adhesive for All Olefin Instrument Panel, Honda R&D Technical Review, 14, 143-150(2002)
- Hideyuki Kakinuma et al.: “Precoated Surface Material for Vehicular Interior Material and Manufacturing Method of Vehicular Interior Material”, Patent Publication 2004-284575, 2004
- Ikuo Komamine: “Hot-Melt Viscous Adhesives: Real Technology for Hot-Melt Adhesives”, CMC Co., Ltd., 2000, pp. 119-120

Copper Free Brake Pads with Stable Friction Coefficient

Masamichi Mitsumoto

Advanced Functional Materials R&D Dept.,
Social Infrastructure-related Materials Development Center,
R&D Headquarters

1 Abstract

Highly controlled brake systems such as “regenerative brakes” and “automatic brakes” have become common for automobiles over the past few years. It is essential for the new brake systems to maintain stable brake force, so the stability of friction coefficient generated by brake pads is becoming increasingly important. On the other hand, requirements for eco-friendliness of materials contained in brake pads are getting tighter, and regulations to eliminate copper will start in North America from 2021^{1, 2)}.

To cope with this situation, we have developed “copper free brake pads with stable friction coefficient” by substitution of alternative materials to perform copper functions, such as thermal conductivity and lubricating property, and improvement to reduce the component change of the friction surface before and after braking. As an additional result, we have achieved brake noise reduction.

2 Characteristics of the Product

- The product contains no copper (conforms to the copper regulation to be enacted in North America from 2025).
- The friction coefficient remains stable after high-temperature braking and when left in high-humidity environments.
- The brake rarely squeaks or emits other low frequency noises.

3 Background of the Development

Copper has a melting point higher than 1000°C and high ductility. As a result, it forms a film on the friction interface (**Figure 1**), causing an increase in the thermal conductivity and heat resistance of the brake pads (**Figure 2**). This is why copper is an essential material for brake pads. However, the copper contained in the friction powder discharged by braking has the risk of contaminating water.^{3, 4)} For this reason, a regulation was established in North America, limiting the copper content in brake pads to 5 wt% or less by 2021 and to 0.5 wt% or less by 2025.

Furthermore, as a result of the spread of high-performance brake systems, the friction coefficient of brake pads is now required to be even more stable than before. In addition, in EVs and HEVs where the silence of the drive system has dramatically improved, there are now higher standards regarding the reduction of squeaking or low frequency noises emitted by brakes. Because the breaks squeak or emit low frequency noises when the friction coefficient increases or changes during one-time braking, a stable friction coefficient is important.

In light of this history, we developed copper-free brake pads with the added value of a stable friction coefficient.

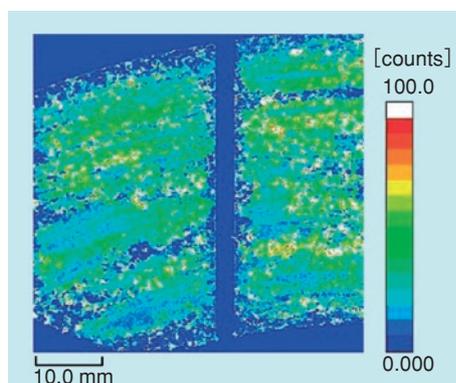


Figure 1 Copper layer on the brake pad formed after 500°C braking (EDX)

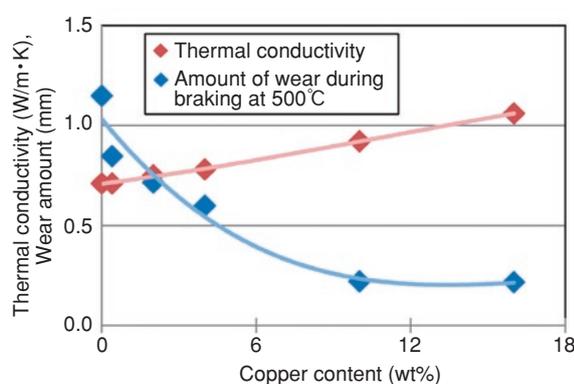


Figure 2 Lowering of thermal conductivity and wear resistance of brake pad by copper reduction

4 Technical Details

Product properties

As shown in **Table 1**, the developed product has a level of thermal conductivity and wear resistance similar to the current product containing copper. In addition, the change in the friction coefficient before and after a high-temperature braking history is less than that of the conventional product, and the rise in the friction coefficient after leaving a highly humid environment is low. As a result, the generation of squeaking or low frequency noises from the brake is low, meaning the pads are better than the current product.

Achievement technique

For the purpose of improving thermal conductivity, we selected graphite with a high degree of graphitization and small grain size⁵⁾, and optimized the content to maintain the friction coefficient (**Figure 3**).

Furthermore, we selected the most suitable types of titanate in order to improve high temperature lubricity. The melting point and frictional property of the titanate vary depending on the components and crystal structure.⁶⁾ In this development, titanate with a melting point near that of copper and with a lamellar crystal structure was selected to increase high temperature lubricity.

Because copper has a high intermetallic cohesive force against a disc rotor with cast iron as the partner material, the current product formed excessive metallic film after 500°C braking as shown in **Figure 1** and **Figure 4-A**. Generally, since intermetallic friction presents large fluctuations in the friction coefficient due to the disturbance from the change in the interface temperature,⁷⁾ excessive formation of copper and iron film impairs the stability of the friction coefficient. Graphite, selected as an alternative material for copper in this development, and titanate, with a lamellar crystal structure that has low cohesiveness with iron, can restrict the excessive formation of metallic film (**Figure 4-B**). As a result, the friction coefficient of this developed product showed a stable friction coefficient against the disturbance from the braking conditions and history, thus achieving a reduction in squeaking or low frequency noises from the brake.

Table 1 General properties of the new product

Item		Unit	Current product	Development target	Developed product		
Copper content		wt%	15 <	0	0		
Thermal conductivity		W/m·K	1.0	1.0	1.0		
Stability of friction coefficient	Before high temperature braking	30 km/h 2.9 m/s ²	—	0.40	0.40±0.04	0.38	
		50 km/h 2.9 m/s ²	—	0.42		0.38	
		100 km/h 2.9 m/s ²	—	0.46		0.40	
		200 km/h 5.8 m/s ²	—	0.31		0.38	
	After high temperature braking	30 km/h 2.9 m/s ²	—	0.45		0.40	
		50 km/h 2.9 m/s ²	—	0.48		0.42	
		100 km/h 2.9 m/s ²	—	0.46		0.44	
		200 km/h 5.8 m/s ²	—	0.30		0.36	
	After leaving in high humidity*	5 km/h 1 MPa	—	0.58		≤ 0.50	0.49
	Friction life**		—	○		○	○
Squeaking or low frequency noises of brake**		—	○	◎	◎		

*At 30°C for 6 h under an environment of 75% relative humidity **Outsourced evaluation of real automobiles

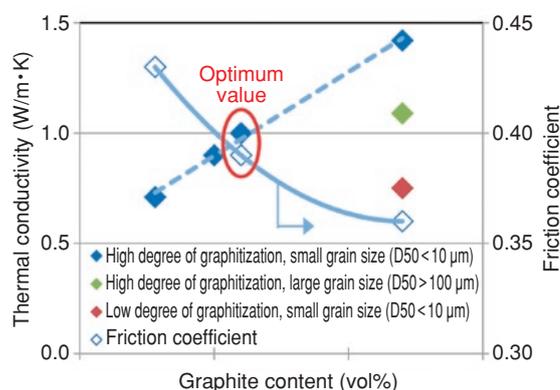


Figure 3 Optimization of degree of graphitization, size and contents of graphite

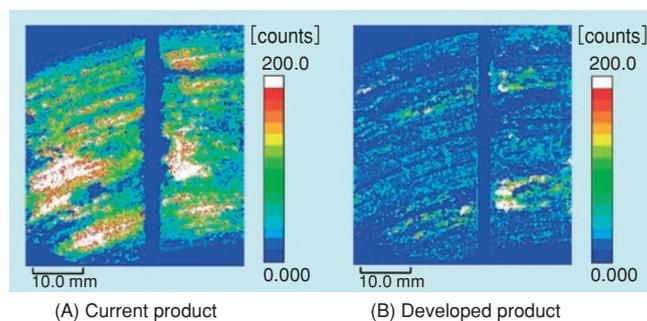


Figure 4 Iron distribution on the brake pad from disc rotor after 500 °C braking (EDX)

5 Future Business Development

- Start of mass production of developed product
- Expansion of application of copper-free brake pads to high load vehicles

[References]

- 1) Washington State Senate Bill SB6557, An act relating to limiting the use of certain substance in brake friction materials
- 2) California State Senate Bill SB346, Hazardous materials: motor vehicle brake friction materials
- 3) Copper Action Plan Report, City of Palo Alto Regional Water Quality Control Plant (2007)
- 4) Engberg, C. C., The Regulation and Manufacture of Brake Pads: The Feasibility of Reformation to Reduce the Copper Load to the

- San Francisco Bay, Stanford University (1995)
- 5) Mikio Miyake et al.: "New introduction to carbon material." *REALIZE Science & Engineering* pp. 47-49 (1996) (in Japanese)
- 6) Kosuke Inada, Minoru Aki and Yoshinori Yamamoto: Relationship between powder properties of titanate compounds and brake performance, SAE technical paper 2005- 01-3925 (2005)
- 7) F. P. Bowden, D. Tabor: *The Friction and Lubrication of Solids*, Clarendon Press, Oxford, pp.33-121 (1986)

Demonstration Project of Power System Stabilization with the Hybrid Battery Energy Storage System

Yoshikazu Hirose Shinichi Sano Hisaki Takeuchi Shigeo Aone

Industrial Battery R&D Department,
Advanced Battery & System Development Center,
R&D Headquarters

1 Abstract

The introduction of renewable energy is being promoted as a global warming countermeasure. The increase of naturally fluctuating power supplies, such as wind and photovoltaic power generation may influence the stability of the power supply. The introduction of a battery energy storage system is an effective method considered as a solution to this problem.

Hitachi group developed a hybrid battery energy storage system and started a demonstration project in 2015. The hybrid battery energy storage system was installed to solve problems occurring during an increase of the naturally fluctuating power supply on Izu-Oshima Island, Tokyo, where the effect of introducing the battery energy storage system could be tested relatively easily.

2 Purpose and Effect of Demonstration Test

- Verify the effectiveness on power supply stabilization of a hybrid battery energy storage system.
- Examine optimization of battery energy storage systems with capacity and output necessary for use in actual fields.
- Contribute to effective utilization and introduction of renewable energy.

3 Background of the Development

In a power system, hourly load fluctuations (power demand) caused by various factors and power generation (power supply) are controlled to keep them balanced. Loss of balance between the power demand and the power supply (demand and supply) causes fluctuations in the frequency and voltage and affects the stability of the power supply. Although adjustments to demand and supply are conventionally performed by controlling the output of the power generation (power supply) side, the larger scale introduction of naturally fluctuating power supplies might make the adjustment of output difficult within the current range. As a measure, attention is being paid to securing the ability to make adjustments using a power storage system; typical examples of focus are a variable-speed pumped-storage power generation system and a battery energy storage system. Although variable-speed pumped-storage power generation systems are a very effective means of making adjustments because the system can adjust power for large capacity and at high speed with a wide frequency control range, such systems have problems such as site conditions being restricted and the need for a long construction period.

This development concluded that a battery energy storage system can be applied to a wide frequency control range equivalent to that of a variable-speed pumped-storage power generation system (**Figure 1**). Hitachi Chemical has expanded the range of application of lead-acid batteries by achieving a longer service life and higher input/output based on safe, low cost lead-acid batteries with long sales records for industrial applications. In addition, in order to enable frequency control corresponding to pumped-storage power generation, we verified the effectiveness of the hybrid battery energy storage system by connecting this system to a real system for demonstration tests, in which frequency control function was enhanced by using lithium ion capacitors (hereinafter, LiC) that offer excellent short-time input/output. This research was implemented by Hitachi, Ltd., and Hitachi Chemical Co., Ltd., from 2011 to February 2016 in the NEDO Grant Program titled “Technology Development for Safe and Low Cost Large Scale Battery Energy Storage System.” In addition, demonstration tests are being conducted on Izu-Oshima Island, Tokyo, by connecting a 1.5 MW hybrid battery energy storage system to the real system from 2015 in cooperation with TEPCO Power Grid, Inc.

*NEDO: National Research and Development Agency New Energy and Industrial Technology Development Organization

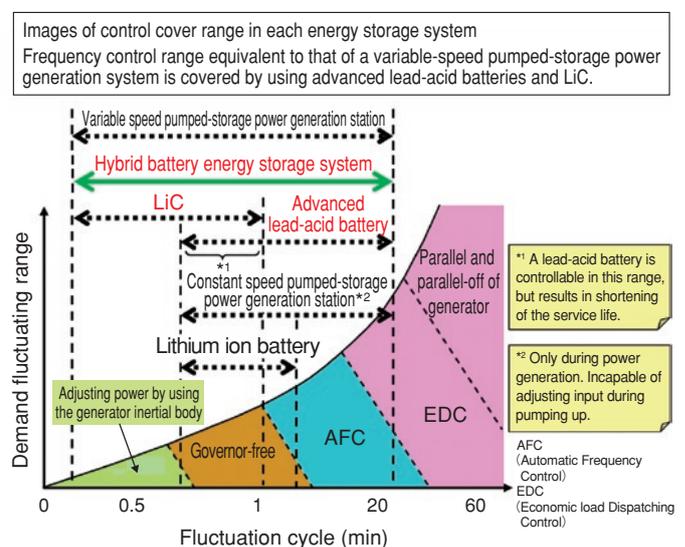


Figure 1 Conceptual diagram of each control range in the BESS

4 Technical Details

Introducing battery energy storage systems encounters the problems of cost and battery service life. Because a lead-acid battery has input/output characteristics lower than that of a lithium ion battery, the system requires larger battery capacity (Wh) in order to secure system output (W), which leads to the problem of a high initial cost. We considered that improving the short-time output characteristics of a battery could decrease the battery capacity and reduce the initial cost and foot print of the battery in comparison with conventional batteries.

Table 1 shows the design concept of this development. In the new design, the coexistence of higher performance and a longer service life are the key points. At this time, an essential condition is that the adopted design avoids great increases in the manufacturing cost by utilizing existing manufacturing facilities and materials common to those for the current product group.

Table 2 shows the results of evaluating the designed battery. The newly designed product achieved all target values for higher performance. A trial calculation was performed to determine the effect brought about by achieving higher performance. As a result, we concluded that in the case of a system that discharges 1 MW of electricity for 0.25 h, the required battery capacity could be reduced by roughly 50% and the foot print by roughly 47% compared with the current product, leading to a reduced initial cost.

Figure 2 shows the advanced lead-acid battery actually installed on Izu-Oshima Island, and **Figure 3** shows the appearance of the LiC facility. In this battery where higher performance was achieved, the remaining problem is battery life in actual use. To evaluate the service life, we will retrieve the battery actually used on Izu-Oshima Island for investigation and continuously conduct in-house bench tests to clarify the difference from the designed value and pursue the feasibility of practical applications.

Table 1 Design concept of the advanced lead-acid battery

Item	Higher performance	Life elongation
Target	[Improvement in output characteristics] Achieve a maximum discharge current of 1.0 CA (Compared with current product*: 2.5 times) [Higher capacity at high rate discharge] Improve one-hour rate capacity (Compared with current product: 1.4 times)	Design life: 20 years
Problem	Structure of current product makes it difficult to achieve higher input/output. →New design of battery structure required.	The result of a field product investigation revealed deterioration mainly due to corrosion of the positive electrode lattice.
Means for achieving	◇Increase the number of terminal poles. Examine the structure of the terminal part by simulations to reduce resistance of the part and to improve output characteristics.	Positive electrode lattice to be newly designed to achieve 20-year durability.
	◇Design of pole plate structure (Larger number of films) Reduce the current density to achieve higher capacity.	
Technical problem	Reduction in lattice thickness and increase in the number of pole plate structures improve the high rate discharge characteristics.	Reducing the lattice thickness lowers lattice durability and life durability.

*1 Compared with LL1500-W (manufactured by Hitachi Chemical Co., Ltd.) as the current product

Table 2 Test results of the advanced lead-acid battery

Check item	Current product*1	Target value	Result
Improvement in output characteristics	Discharge impossible due to voltage drop at discharge (F.V. = 1.8 V/cell)	Achieve max. discharge current of 1.0 CA	1.0 CA discharge achieved for 900 sec or more (F.V. = 1.8 V/cell)
Higher capacity at high rate discharge	Assume capacity at 0.60 CA discharge as 1 (F.V. = 1.8 V/cell)	1.4 times compared to the current product	3.1 times compared to the current product was achieved (actual value) (F.V. = 1.8 V/cell)
Life elongation	Investigation of field product performed Deterioration mode identified	Design life: 20 years	New design finished using past knowledge, etc. In-house bench tests and demonstration tests are continuously conducted for practical use evaluation.



Figure 2 Advanced lead-acid battery systems which were installed on Izu-Oshima



Figure 3 Lithium-ion capacitor systems which were installed on Izu-Oshima

5 Future Business Development

- Continuously evaluate life performance under practical use
- Productize an advanced lead-acid battery

[Reference] Website of the National Research and Development Agency New Energy and Industrial Technology Development Organization: News Release, June 4, 2015

New Development of High Heat Resistance and Low Dielectric Thermosetting Resin, “S. F. Resin”

Masaki Takeuchi Eri Yamada

New Material Business Development Center,
R&D Headquarters

1 Abstract

In recent years, thinning of devices and components has led to a problem of warping, which may reduce connection reliability. Low elastic resin material has attracted attention as a possible solution. However, its application range, typified by acrylic resins, is limited, due to low thermal decomposition temperature. New “S. F. Resin” has low elasticity, high heat decomposition temperature, low dielectric constant, low moisture absorption rate, and many other excellent characteristics. These properties contribute to the development of a “no warp” heat-resistant temporary fixing material, laminating adhesive, high frequency corresponding material, moisture-proof coating agent, and buffer coating agent.

2 Characteristics of the Product

- Has low elasticity, high thermal decomposition temperature, low dielectric characteristics, and a low moisture absorption rate.
- Has self-polymerizable characteristics by peroxide and UV, and reactivity with epoxy resin.
- By addition to film materials, etc., the product achieves low elasticity, low dielectric characteristics, and low moisture absorption rate without lowering heat resistance.

3 Background of the Development

In recent years, the thinning of devices and components has led to the problem of warping in various fields: such as warping of heat resistant fixing materials, laminating adhesives, high frequency corresponding materials, moisture-proof coating agents, and buffer coating agents. Although one solution for the warping problem is to reduce the elasticity of laminated materials, low elasticity resin so far represented by acryl resin had the problems of moisture absorption and thermal decomposition. Therefore, we developed an “S.F. resin” to achieve low elasticity, a high thermal decomposition temperature, a low dielectric constant, and a low moisture absorption rate by combining maleimide resin, which provides excellent heat resistance, and a skeleton of low elasticity and low moisture absorption, and started examining its application to various fields.

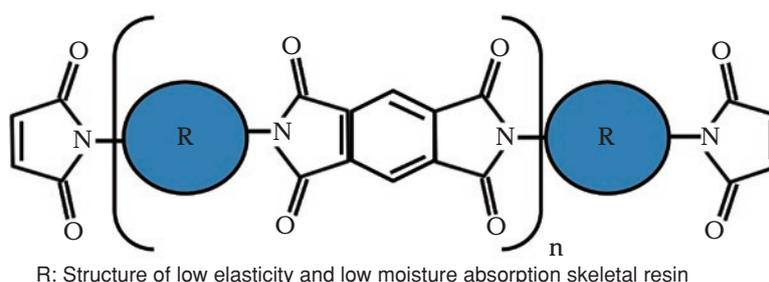


Figure 1 Structure of “S. F. Resin”

4 Technical Details

“S.F. resin” is composed of a base of the maleimide imide group, which provides excellent heat resistance, and the skeleton of low elasticity and low moisture absorption. “S.F. resin” thereby achieves low elasticity, a high thermal decomposition temperature, a low dielectric constant, and a low moisture absorption rate. The general properties of a resin film thermoset after adding peroxide to the “S.F. resin” are shown below (**Table 1**). Although thermoset “S.F. resin” has an elastic modulus as low as 0.08 GPa at normal temperature, it has excellent heat resistance with a 5% thermal decomposition temperature of 435°C (**Figure 2**). In addition, the

thermoset “S.F. resin” shows the dielectric characteristics of a specific dielectric constant of 2.4 and a dielectric loss tangent of 0.0018 at 10 GHz, which are almost equivalent to those of the LCP substrate material (**Figure 3**). We are developing temporary fixing materials with high heat resistance for glass processing (using high heat resistance and low elasticity). We are also developing low transmission loss materials for millimeter-wave radar, utilizing low dielectric characteristics.

Table 1 Properties of “S. F. Resin”

Item	Condition	Unit	S.F. Resin	Material A	Material B	Material C ^{*2}
Resin System		—	Bismaleimide	Acryl	Soluble Polyimide	LCP
Dk(10GHz) ^{*1}	A	—	2.4	2.9	3.3	3.0 ^{*3}
Df(10GHz) ^{*1}	A	—	0.0018	0.0240	0.0200	0.0020 ^{*3}
CTE (X-Y)	< Tg	ppm/°C	120	110	100	—
	> Tg	ppm/°C	180	—	—	—
Tg	TMA	°C	84	160	185	—
Elastic Modulus	DMA	GPa	0.08	0.40	0.70	3.40
Td	TGA-1%loss	°C	375	250	300	—
	TGA-5%loss	°C	435	320	350	—
Peel Strength	Low Profile	kN/m	1.6	1.8	1.8	0.7
Water absorption	D-23/24	%	0.05	0.3	0.8	0.05
Dielectric breakdown voltage	1mm, 25°C	kV/mm	30	22	30	—
	1mm, 150°C	kV/mm	30	—	—	—

*1 Cavity resonator perturbation method *2 Catalog value *3 Strip-line method

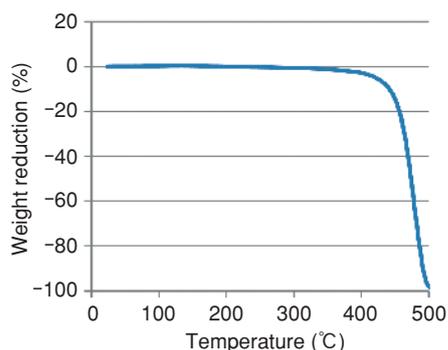


Figure 2 Measurement of TGA

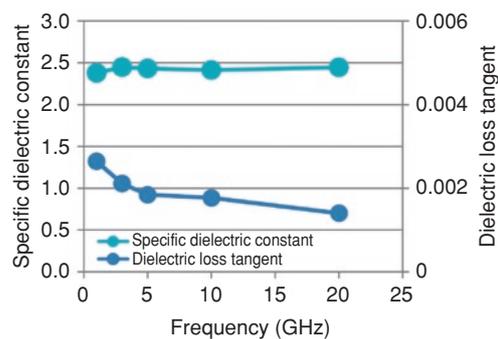


Figure 3 Dielectric property

5 Future Business Development

- Develop highly heat resistant temporary fixing material for glass processing
- Develop low transmission loss material for millimeter-wave radar
- Develop additives for composite materials
- Develop buffer coating film

[Reference]

- 1) Yoshihiro Nakamura: “Technology Trends and Future History of Semiconductor Packaging Substrate Material.” Hitachi Chemical Technical Report No. 55 (2013)

Shock Absorbing Material

Akihiro Yoshida Naoki Takahara Takanori Miya

Core Technology & Innovation Center,
Research & Innovation Promotion Headquarters

1 Abstract

We have found out that material with weak three-dimensional cross-linking in the structure shows response to shear stress. Furthermore, we developed a shock absorbing material utilizing the network structure. The newly developed material absorbs shock better than the conventional material with a network structure of covalent bonds.

2 Characteristics of the New Product

- Has a three-dimensional cross-linking network structure with weak bonds.
- Shows stimulation response to shear stress.
- Shows shock absorption.

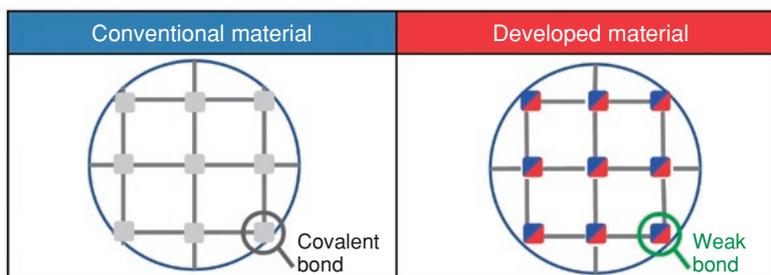
3 Background of the Development

As part of the development of biomimetic materials, we proceeded with the research and development of novel industrial materials focusing on the fact that biological materials, such as DNA and proteins, express responses to stimulation that utilizes weak hydrogen bonds.¹⁾ During this process, we developed materials that introduced a three-dimensional cross-linking network structure with weak bonding energy between the molecules of polymer chains to discover the expression of the response to shear stress. We found that stimulation response technology is useful for alleviating shock force in addition to shear stress, so we developed the shock absorbing materials reported below.

4 Technical Details

Materials such as acryl base resins and silicon base resins with low elasticity are conventionally used as shock absorbing materials. These resin materials have a three-dimensional cross-linking network structure with covalent bonds. In contrast, products developed by reference to biological materials have the feature of having a three-dimensional cross-linking network structure that uses low energy bonds (**Table 1**).

Table 1 Network structure of conventional and developed material



The relationship between the storage elastic modulus and shear stress was evaluated to investigate the response of developed materials to shear stress (**Figure 1**).

As a result, it was found that the storage elastic modulus of the developed material was lowered by a shear force at around 10,000 Pa or more. On the other hand, the storage elastic modulus of conventional materials showed almost constant values without relating to shear stress. These results indicate that only the developed material shows stimulation responses where the elastic modulus varies depending on the shear stress. In addition, it was estimated that the developed material expresses stimulation response,

because a three-dimensional cross-linking network with weak bonds collapsed under high shear stress.

Based on the above results, we hypothesized that a stimulation response technology can be established by considering not only shear stress, but also shock force, and applied this developed material to shock absorbing sheets to conduct drop weight tests. In these tests, balls were obliquely dropped on a film made of the developed material, the colored area on pressure sensitive paper was assumed to relatively correspond to the intensity of shock absorbing energy, and it was evaluated that the smaller the relative value, the better the shock absorption (**Figure 2** and **Table 2**).

The developed material showed results where the value at point A was lower than that of the conventional material and the coloring of pressure sensitive paper was not found at point B, meaning that the shock absorption of the developed material exceeded that of the conventional material. It was considered that the conventional material absorbed the shock by deformation of the material caused by the dropping ball, while the developed material showed shock absorbability owing to the breakage of weak bonds at the same time of material deformation (**Figure 3**).

Hereafter, we will further proceed with the development of materials focusing on the deployment to various shock absorbing and stimulation response-related fields by taking advantage of the moderate network structure.

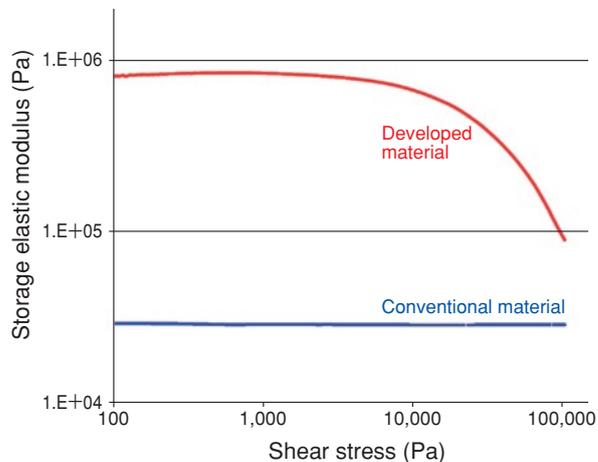


Figure 1 Relationship between modulus of elasticity and shear stress

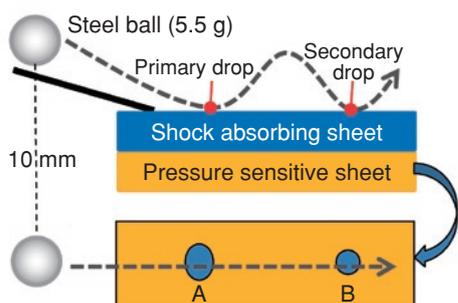


Figure 2 Method of the drop weight test

Table 2 Result of the drop weight test

Measuring point	Conventional material	Developed material
A	100	89
B	32	0

• The smaller the value, the higher the shock absorption.

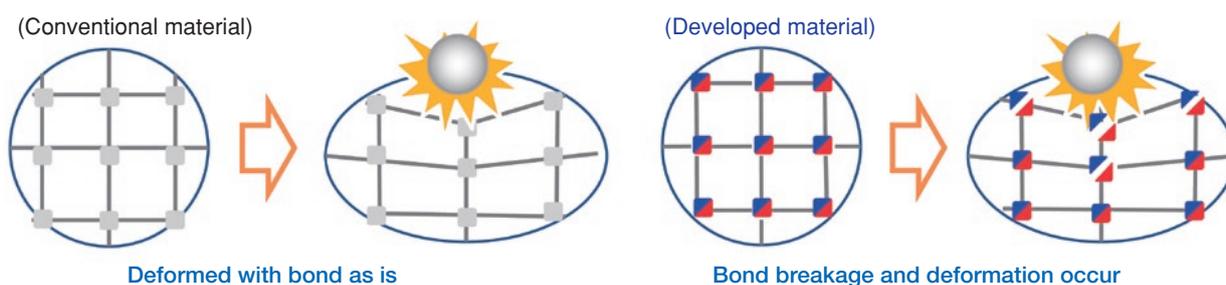


Figure 3 Speculated mechanism when shocked

5 Future Business Development

- Deploy into shock-absorbing fields
- Explore new applications

[Reference]

1) A. Yoshida, N. Takahara, "A new optical clear adhesive material for next generation display", Material Research Society 2016, EP-14 (2016).

Exosomal mRNA Analysis kit from plasma and urine, “ExoComplete”

Mieko Ogura

Hitachi Chemical Co. America Ltd.
R&D center

1 Abstract

The ExoComplete kit is a seamless system capable of isolating exosomes and microvesicles (Extracellular Microvesicles: EMVs) from biological samples such as plasma and urine but also quantifying EMV mRNA. EMVs are membrane vesicles released from various cell types. They include exosomes (30 nm–150 nm in diameter) and microvesicles (100 nm–1000 nm in diameter). There is growing evidence that EMVs play a role in intercellular communication and their contents of proteins, lipids, miRNA, mRNA and DNA have clinical interest as potential biomarkers in diagnosis, prognosis and monitoring of various health conditions including cancer detection. Compared to conventional ultracentrifuge methods, our method can capture the equivalent or better yield of EMVs far more rapidly and high throughput. Accordingly, we launched the ExoComplete kit for research use in September 2015.

2 Characteristics of the New Product

- EVs can be captured easily in a short time
- Excellent reproducibility
- High-throughput

3 Background of the Development

Conventional methods such as ultracentrifugation, density gradient centrifugation and gel permeation chromatography are versatile and powerful methods for isolating EVs, these methods, however, have many issues such as reproducibility, complicated methodology, and lengthy protocols (procedures can take from 8 hrs to 30 hrs). In recent years, technical advances have been made in the field of EV isolation. Improving knowledge and emerging novel technologies include magnetic beads and column methods using antibodies or lectin for quick and easy detection. These methods, however, still demonstrate low reproducibility and difficulty in processing many samples. Here, we have developed a seamless and high-throughput method to capture EVs from clinical samples (urine, plasma, etc.) and to purify mRNA in a few steps. We have used a previously developed mRNA purification platform and combined it with an exosome isolation technology. **Figure 1** shows the procedural flow. This kit can accommodate a range of sample volumes and has two types of flow. The tube format (up to 12.5 mL) can be used for large volume specimens such as urine, cell culture media, etc. and the 96-well plate format (up to 0.4 mL) can be used for small volume specimens such as plasma and serum, etc.

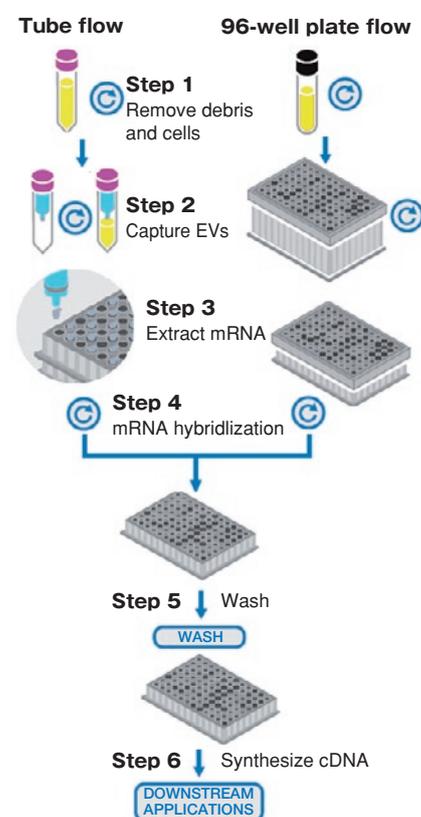


Figure 1 Procedural flow

4 Technical Details

In order to isolate exosomes, and micro vesicles (30 nm–150 nm), we examined a filter material base with a combination of electrostatic and size-exclusion properties. Furthermore, using two-layer membranes with different pore sizes reduced clogging and improved EVs capture.

1) Verification of captured EVs

Scanning electron microscope (SEM) analysis of urinary particles captured on the filter fiber. The exosomes were labeled with anti-CD63 antibody (exosome surface marker) and colloidal gold with silver enhancement. The filter was analyzed by the backscattering mode (**Figure 2**).

2) Comparison with conventional methods (ultracentrifugation)

EVs were captured from the same urine sample (10 mL) by the ExoComplete kit or conventional ultracentrifugation method followed by gene expression analysis of the housekeeping genes, β -actin (ACTB) and glyceraldehyde 3-phosphate dehydrogenase (GAPDH) by qPCR. The data confirmed that ExoComplete provides comparable or even superior results to the ultracentrifugation method in terms of mRNA assay sensitivity and reproducibility (**Figure 3**).

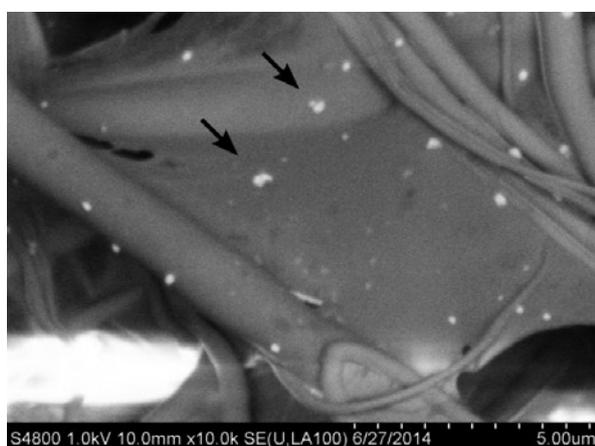


Figure 2 SEM image of EVs captured in the filter membrane ¹⁾

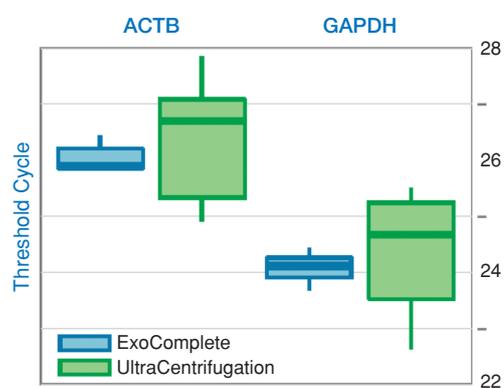


Figure 3 Comparing the conventional method (ultracentrifugation) to our method

5 Future Business Development

- Deploy to clinical inspections in inspection centers

【Relevant patents】

US Patent Nos. 5976797, 6638428, 6844158, 7258976, 7214781/ 7374881/7741023/7745180/7939300, 7981608, 7968288, 8076105, 8101344, 7816081, 7838239/ 8268982, 8268566; JP4772055, EP1802776, ZL200580035896.6, JP4945554, KR10-0983450, JP5706913

【Reference】

- 1) Murakami T, et al. Development of Glomerulus-, Tubule-, and collecting Duct-Specific mRNA Assay in Human Urinary Exosomes and Microvesicles. PLOS/One 2014: Vol 9 Issue 10 e109074

High-density Sintered Sprocket for Silent Chain Made by Die Wall Lubrication Compacting with Liquid Coating

Satoshi Onodera

Core Technology Center, Production Integration Division,
Production Innovation Headquarters

1 Abstract

Sintered sprockets for silent chains of automobile engines require high contact fatigue strength on tooth surfaces. So, the sprockets are densified ($7.5\text{Mg}/\text{m}^3$) by removing the residual pores of the tooth surface layer using the tooth flank form rolling method. However, due to the rise of other processes, we started developing an inexpensive densification process to replace the tooth flank form rolling method. Die wall lubrication compacting with liquid coating, which allows high-density compaction of raw powders with the amount of added lubricant minimized using a die uniformly coated with lubricant film, was developed. As a result of this development, industrial production of a low-cost sprocket for silent chains omitting the tooth flank form rolling process was successfully realized.

2 Features of This Technology

- The developed lubricant has two or more times the release capability compared to the general compacting method.
- Lubricant film coating technology utilizing die action is advantageous from the viewpoint of compacting speed (productivity).
- The usage with sprockets for silent chains of timing trains for automobile engines contributes to expanding the application of powder metallurgical products.

3 Background of the Development

Increasing the output and rotation speed of automobile engines tends to increase the stress generated in the sprockets of the engine valve mechanism, due to friction with the chain. Sprockets are required to have high contact fatigue strength for specifications of silent chains that enable a significant reduction in engine noise. One technique for obtaining high contact fatigue strength in sintered parts is densification. The manufacturing methods of sintering forging, compacting twice and sintering twice, warm compaction, and tooth flank form rolling have been industrialized so far.

On the other hand, it is increasingly important for powder-metallurgy processing to enhance cost competitiveness because the acceleration of globalization in recent years has caused parts suppliers for automobile manufacturers to rapidly advance into developing countries. In addition, cost reductions are also required due to the emergence of other methods, such as forging and cutting.

For the above reasons, we started developing die wall lubrication compaction to provide the features of high density and high strength to provide high productivity and excellent cost competitiveness.

4 Technical Details

(1) Mold release characteristic of developed lubricant

We decided to start from the development of a lubricant capable of providing excellent mold release capability in the powder compacting process and, after various investigations, we developed a new lubricant containing mineral oil added to a solid lubricant and extreme-pressure agent. **Figure 1** shows the mold release force in comparison with that of general compacting when Fe-Cu-C base powder was subjected to die wall lubrication compaction to obtain a cylindrical shape (20 mm in diameter × 30 mm in height) at a compaction pressure ranging from 400–1500 MPa using this lubricant. We discovered the following: the mold release force of die wall lubrication compaction using the developed lubricant was at a level lower than that of general compacting, this tendency was significant in higher

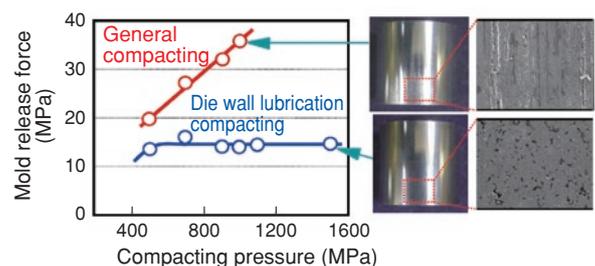


Figure 1 Mold releasability of developed lubricant

compacting pressure, and compaction pressure at 1000 MPa or more reduced the force by 50% or more in comparison with general compacting.

(2) Method for applying lubricants

Following the above, we developed a lubricant film formation technique having the feature that the procedure is completed within a general die action cycle, from release of the mold in the compacting process to the return to the powder filling process. **Figure 2** shows a schematic diagram. Lubricant supplied through the interior of the die is applied to the internal wall and sides of each die during the die action from the mold release position to the powder filling position. This enables high density products to be manufactured without impacting the compacting speed (productivity).

(3) Applicable products

The proprietary development of die wall lubrication compacting with a liquid coating resulted in the successful industrialization of low cost, high density sprockets while omitting tooth flank form rolling, which is the current manufacturing method. **Figure 3** shows a typical product. This product has many holes for weight reduction and is subjected to multi-stage punch forming. We developed a technology capable of forming a uniform lubricant film all over the die wall surface to satisfy compacting requirements, and minimized the constraint conditions for products to which this method is applied.

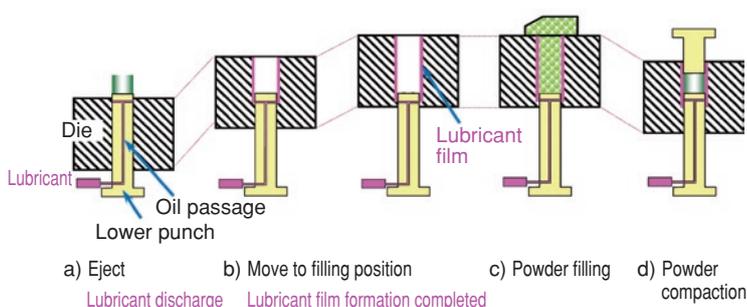


Figure 2 Diagram of steps in the lubricant application method



Figure 3 High-density sintered sprocket for silent chain made by die wall lubrication compacting with liquid coating

5 Future Business Development

- Expand the market for high density products differentiated from the products of competitor companies
- Create next-generation high densification technology to prepare the way for new product development

[References]

- 1) S. Onodera, A Hamano, K. Oofuji :“The Development of Advance Die Wall Lubricating Compaction”, Proceedings of the 2012 Powder Metallurgy World Congress & Exhibition(2012)
- 2) Katsuhiko Ueda, Terufumi Machida, Makoto Iwagiri and Koichi Fukagawa: “Optimization of Die-wall Lubrication Compacting Method of Iron Powder and Static/Kinetic Friction Analysis of Ejection Behavior,” The Journal of the Japan Society of Powder and Powder Metallurgy 48 (2001) 907-914 (in Japanese)
- 3) W.G. Ball, F.W. Hinger, R.A. Mckotch and H.D. Pflingstler. “Replacing internal with External Lubricants”, Advances in Powder Metallurgy & Particulate Materials, 3(1994)pp.x71-82.

Editor's Note

We have started several open innovation initiatives to respond to increasingly diverse and complex customer needs. We are now collaborating with customers in the “Open laboratory” to evaluate customer’s devices and to propose total solutions in the form of semiconductor packages. The “Commentary” and “Review” portions of this report introduce these initiatives, while the technical reports describe some of the new products created in the Medium-term Management Plan.

In January, we established the “Innovation center” to identify how our various materials-related technologies can be connected to future markets. The center will serve as a space for exchanging opinions and working with our customers, as well as a place for visitors to get hands-on experience working with our materials. We hope you will stop by.

To realize our corporate mission of contributing to society through the development of superior technologies and products, we will strive to create innovative value as a frontrunner in our research and development activities, the results of which we will disclose in future reports. We look forward to hearing your open and honest opinions.

MY

Contact Information for Inquiry

- Please access our Internet homepage address as follows and fill in the query form, or contact us at our office.

Homepage Address for Contact:

https://www8.hitachi.co.jp/inquiry/hitachi-chem/en/general/form.jsp?UM_QNo=1

Hitachi Chemical Technical Report No.59

March 2017

Hitachi Chemical Co., Ltd.

Marunouchi 1-9-2, Chiyoda-ku, Tokyo 100-6606, Japan

Research & Innovation Promotion Headquarters TEL. (03) 5533-7408

Masato Yoshida

Production cooperation Hitachi Document Solutions Co., Ltd.

East21 Tower, 6-3-2 Toyo,

Koto-ku, Tokyo 135-0016, Japan

TEL. (03) 3615-9000

© 2017 Hitachi Chemical Co., Ltd. All rights reserved.
