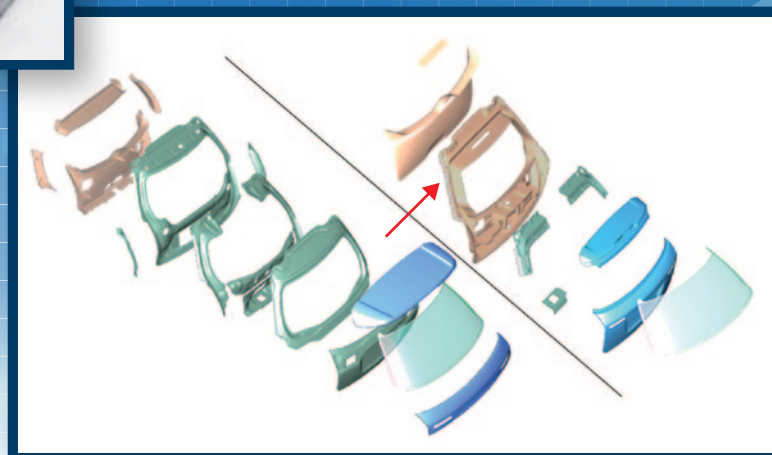
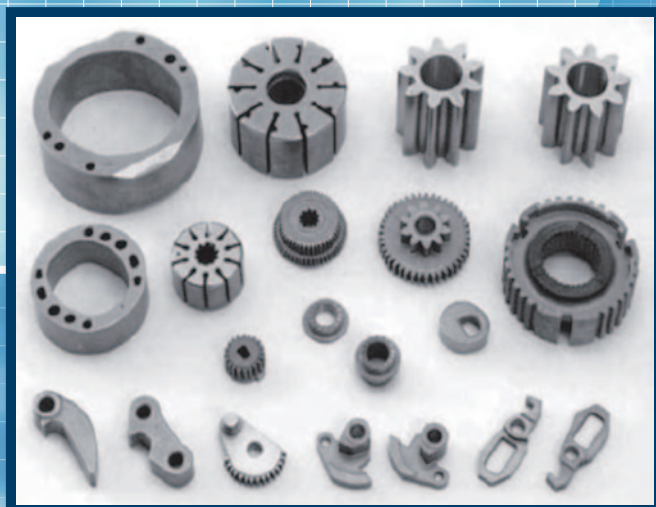


Hitachi Chemical Technical Report

No.58 / March 2016

Hitachi Chemical
Working On Wonders



HITACHI

CONTENTS

Commentary

- Automotive Components Business of Hitachi Chemical Contributing to Environmental Conservation and Energy Saving 3
Satoshi Takahashi

Review

- Automobile Parts for the Environment 5
Shigeru Kudo

Report

- Low Elastic Prepreg for Automotive Application “TD-002”, to Inhibit Solder Crack 13
Takayo Kitajima
- Advanced Analysis of Lead-Acid Batteries 15
Hiroki Hirano · Kazushige Kouno · Keiji Sumiya
- New Low Transmission Loss Material for Millimeter-wave Rader Module “AS-400HS” 17
Takao Tanigawa · Yuusuke Kondou · Yuuichi Shimayama · Tetsurou Irino
- Highly Thermal Conductive Mica Insulating Tape for Large-Capacity Generator 19
Yoshitaka Takezawa
- Advanced Thermal Insulator Using Inorganic-Organic Hybrid Porous Materials 21
Masato Miyatake · Tomohiko Kotake
- Halogen Free and Low Transmission Loss Multilayer Material for Next Generation High Speed Applications: “MCL-LW-900G/910G” 23
Masayuki Nakano · Keita Johno · Toshiyuki Iijima
- Reactive Hot Melt Adhesive for Fine Dispensing 25
Koji Suzumura · Kazuyuki Magome · Soichiro Komiya · Chika Kuramochi
- Advanced Analysis of Yellowing Transparent Film 27
Akihiro Unno · Hoko Suto · Kosuke Iwamoto
- Cu Paste for Low Temperature Metalization Process 29
Kosuke Urashima



Review : Automobile Parts for the Environment (p.5)



Executive Officer
Deputy General Manager
Energy Storage & Automotive Components
Business Headquarters


Satoshi Takahashi

Automotive Components Business of Hitachi Chemical Contributing to Environmental Conservation and Energy Saving

Hitachi Chemical, as a division of Hitachi Ltd., started its business manufacturing electrical insulating varnishes used for electric motors for the Japanese domestic market in 1912. It became an independent company after separation from Hitachi Ltd. in 1962 and remains so today. Electrical insulating varnish, our first original product, was the basis for all of our other products developed later. Our automotive components business started from manufacturing steering wheels by utilizing expertise accumulated from manufacturing electrical insulating varnishes in 1938 long before the separation from Hitachi Ltd., and has a history of nearly 80 years. Today we manufacture automotive related products including plastic molded products and sheets, brake friction materials, powder metallurgy products and starter batteries. Our automotive components business, one of the main businesses at Hitachi Chemical, earns approximately 30% of the total revenue of the Hitachi Chemical Group.

Of the four product categories above, our automotive components business headquarters, under my control, handles products three: plastic molded parts and sheets, brake friction materials and powder metallurgical products. We are promoting “Environment, Safety and Comfort” as our slogan throughout our business, from product manufacturing to supply. Especially in recent years, global environmental issues have become a big challenge for mankind and our activities to protect the environment are rightly focused on these global concerns. We are proud that Hitachi Chemical can contribute to the good of society.

Since the late 20th century, global warming has become a major concern worldwide. Especially, adverse impacts caused by human activities have become an important issue, and emission of greenhouse gas (with carbon dioxide as the main component) from human industrial activity has been considered as the main culprit. We, as members of industry, are must strive to eliminate such negative human impacts on the environment. Many countries have ratified the Kyoto Protocol and each country is working on reducing CO₂ emissions to achieve the reduction targets that were set and adjusted to suit the unique situation of each country. The automobile and automotive components industry sector, in which we work, has a very high impact, and contributes about 18% of total CO₂ emissions, prompting us to take particularly powerful and urgent countermeasures. Measures to reduce CO₂ emissions from automobiles include: ① improving fuel efficiency for energy saving, ② traffic flow



control and eco-drive, and ③ reducing vehicle miles of travel. Improving fuel efficiency, however, contributes the largest among them, and a significant effect can be expected from it. To further improve fuel efficiency, effective approaches include: ① reduction of vehicle body weight, ② automotive engine modification (lean burning, downsizing, dieselizing, ethanol for motor fuel application, idling stop, etc), and ③ automotive electrification (HEV, PHEV, EV) and fuel cell-powered automobiles. In following such industrial trends, we are manufacturing environmentally conscious strategic products, such as: ① plastic doors and gears for weight saving, ② turbo charger components produced from powder metallurgic materials for engine modification, and ③ inverter related plastic parts for automotive electrification.

Another environmental problem we face is air pollution. Caused by released and drifting environmentally hazardous substances in the air, this has been a serious problem with a wide range of impacts such as human health disorders, forest degradation, and other serious ecological impacts. Environmentally hazardous substances include sulfur dioxide, nitrogen oxide, suspended particulate matter, carbon monoxide, hydrocarbons and heavy metals. As one approach to controlling and reducing environmentally hazardous substances, after our successful achievement in leading developing asbestos-free brake friction materials, we are now working on copper-free brake friction materials because copper is considered as a heavy metal and is regulated. In the same way, we commercially produce extruded sheet with a plated surface like finish without using heavy metals or requiring plating solution. We work hard in this product category.

The examples introduced above are just a few; however, both plastics as a replacement for metals and powder metallurgic material as a replacement for casting and/or forging material are important products for weight saving, which closely linked to environmental protection. We are engaged daily with reducing or eliminating environmentally hazardous materials contained in friction materials and other products, and will further concentrate management resources on development of Earth-friendly products to accelerate our contribution to environmental protection.

Each product has its origin in development of the raw materials in which we specialize. We then manufacture each product, with stress on meeting customer demands and environmental protection throughout the process. In a wide range of applications, we seek opportunities to add value to each of the products we deliver to customers. Under this concept, we will continue to speed up the development process by taking full advantage of our collective expertise and focus on realizing the goal: “Contribution to the society through the development and deployment of pioneering technologies and products.”

Automobile Parts for the Environment

Shigeru Kudo

Energy Storage & Automotive Components Business Headquarters,
Marketing Center, Automotive Components Business Strategy Sector

Since global warming has become a serious problem, regulation of CO₂ emissions has been introduced globally as a main solution to the problem. CO₂ reduction programs of automotive manufacturers are becoming more active, since cars are one of the main CO₂ emission sources. As actual activities, weight reduction is an effective measure to improve fuel efficiency of cars, and automotive parts will take a great part in this solution. On the other hand, energy generation control to save automotive energy consumption, and the use of environmentally friendly materials to comply with regulations on hazardous substances are proceeding.

Our company has been manufacturing various kinds of automotive parts, and we are aggressively developing new products to achieve solutions to the environmental issues mentioned above. This report gives an overview of the R&D and manufacturing situation of automotive parts for weight reduction, thermal management and environmentally friendly materials.

1 Introduction

In recent years, amid heightened concerns about environmental degradation, auto companies are acting to improve fuel efficiency. We see this trend because of tighter fuel efficiency mandates worldwide, especially in Europe. Automobiles are a major source of CO₂ emissions, a major contributor of global warming. Each country has established a maximum allowable level of CO₂ emissions and it is especially stringent in Europe. The level of maximum allowable CO₂ emissions in Europe are scheduled to be tightened at the rate of 4% on average per year from 130 g/km in 2015 to 95 g/km around 2020. So, if Europe continues to tighten standards at the current pace, there is a possibility that it will be set to a very stringent level of 60 g/km around 2030.

Although environmentally friendly next generation vehicles such as hybrid electric vehicles (HEV) and electric vehicles (EV) are expected to increase soon, gasoline engine vehicles will still constitute 80% or more of new vehicles in 2020 and still high at 60-70% in 2030 according to the estimate by "The Next-Generation Automobile Strategy 2010" prepared by the Japanese government. Thus, our challenge should be: How much more can we reduce CO₂ emissions? If the prevalence rate of gasoline vehicles is assumed to be 70% and CO₂ emissions from HEV are assumed to be two-thirds (2/3) that of gasoline vehicles, then the level of maximum allowable CO₂ emissions will go down from 104 g/km in 2020, to 72 g/km in 2030, and if converted to fuel efficiency, it will be 18.0 km/L in 2015, 22.4 km/L in 2020, and 32.2 km/L in 2030. There are two approaches to overcome these challenges: one is to improve the power train and the other is to reduce vehicle body weight. If the contribution rate of weight reduction to fuel efficiency is assumed to be one fourth (1/4), and approx. 100 kg of weight reduction will be required to improve fuel efficiency by 1.0 km/L as shown in **Figure 1**. Thus, weight reductions of 110 kg and 356 kg are expected to be required in 2020 and 2030, respectively, according to the trial calculations¹⁾. If automotive weight increase for safety improvement and passenger comfort is additionally required in the future, the target of automotive weight reduction may be further raised.

Energy efficiency technologies that actively control energy produced in automobiles are being developed.

Meanwhile, regulations for hazardous substances used in automotive components are being phased in; ELV (The EU End-of-Life Directive [2000/53/EC]), RoHS (The Restriction of Hazardous Substances Directive 2011/65/EU), and REACH (Registration, Evaluation, Authorization and Restriction of Chemicals) have already been issued in advance in Europe. In the U.S., the states of Washington and California decided to restrict the use of copper of levels not less than 5 wt% by January 1, 2021 and not less than 0.5 wt% by January 1, 2025 in friction materials for sale or

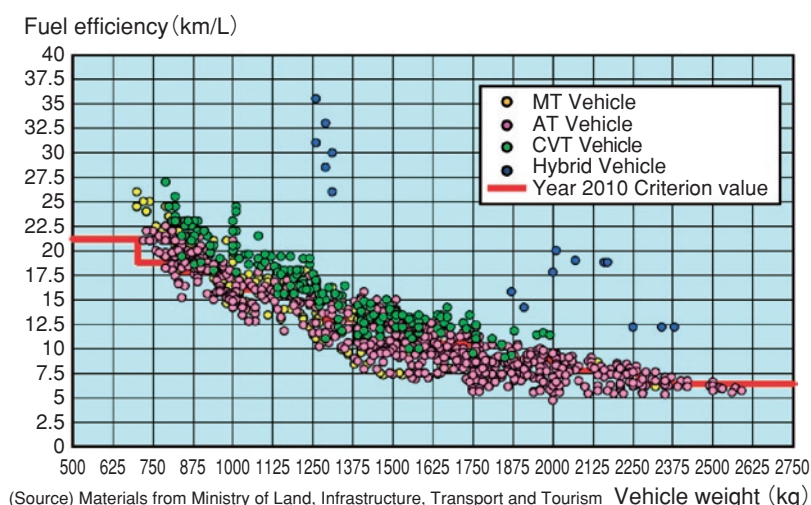


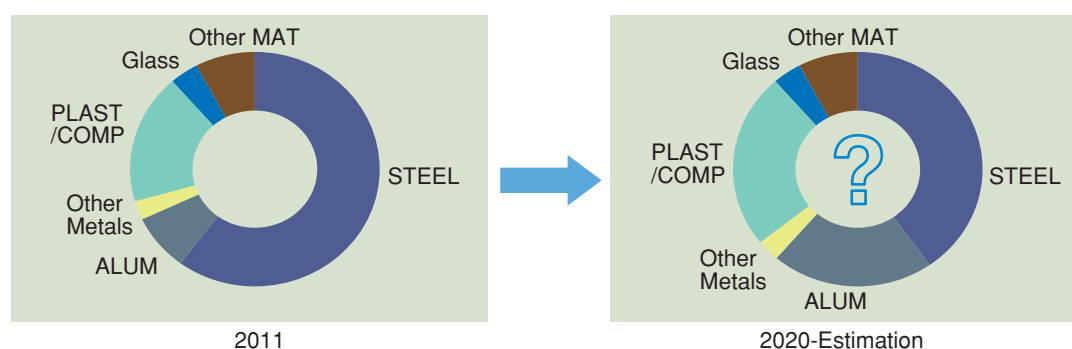
Figure 1 Relationship between 10 · 15 mode fuel consumption and automobile weight

installation in new motor vehicles. This regulatory movements has spread throughout the United States, leading to the agreement to the same restriction levels on January 1, 2015 by the Environmental Protection Agency (EPA), the Environmental Council of the States (ECOS) and the Motor & Equipment Manufacturers Association (MEMA).

Given the above background, actions by our company on automotive weight reduction such as resin molded automotive components and sintered material, thermal management products and our response to restricted hazardous substance in the case of friction material are introduced in this report.

2 Products developed for automotive weight reduction

Although iron based materials still make up a dominant share of materials for automotive applications according to a survey conducted by the Organisation Internationale des Constructeurs d'Automobiles (OICA), we predict the share of plastics and aluminum, etc. in automotive applications will increase through the replacement of iron based materials because of the weight saving (**Figure 2**).



(Source) Materials from OICA (Organisation Internationale des Constructeurs d'Automobiles): Steel Perspective for The Automotive Industry

Figure 2 Composition of materials of an average European automobile

What we call aluminum is actually an aluminum alloy including magnesium, copper and zinc, etc. for reinforcement. It has some unique properties such as low specific gravity: 2.7 (compared with 7.8 for iron), excellent corrosion resistance thanks to protection by oxidized surface film, good thermal conductivity and good casting performance. Aluminum alloy, however, has a drawback of poor formability due to its significantly smaller elongation after arriving at the maximum load compared to steel sheet^{2) 3)}, and its price per weight, almost 3 times that of steel sheet, is also a problem. Magnesium alloy is receiving attention, too, as it shows unique properties such as low specific gravity of 1.8, high thermal conductivity and high electromagnetic wave shielding effect. It also has a number of drawbacks including catching on fire when exposed to air, poor corrosion resistance, difficult magnesium alloy sheet forming and high cost. Therefore, we still have to overcome several hurdles before its commercial application⁴⁾.

Plastics, which are generally considered as representing non-metallic materials, are called “synthetic resin” or simply “resin”. In the automotive component field, fiber-reinforced plastic is also classified as “resin”. Thanks to its light weight (specific gravity: 0.9-2.5) and excellent formability, resin is used in various applications including interior/exterior components, functional components in an engine room, the electronics system, fuel system, safety system and even some of the components for the chassis and powertrain.

At our company, resin has been used as a material for interior components (instrument panel, console box, etc.), exterior components (resin rear door, bumper, etc.), functional components in an engine room (resin gear), and electronics system components (housing to construct an electronic power supply circuit in an inverter unit)⁵⁾.

On another front, there are number of ways other than replacing materials, including downsizing through the improvement of functional performance and/or wall thinning. At our company, powder metallurgy technology has contributed to downsizing of engine components in many ways, including turbocharger parts, axle bearing, bulb guide and bulb sheet.

In this report, we will explain the details of a resin rear door (interior component) and resin gear (functional component in an engine room) developed for automotive weight reduction, and downsizing by powder metallurgy technology in detail.

2.1 Interior/Exterior Component⁶⁾

Our company has a long history of metal to resin conversions for interior/exterior components, and our products made of resins have been used by many domestic and international car manufacturers. Among them, especially rear doors, made of resin and have been adopted as a commercial product since 2001 as an assembled module comprising the rear door itself, door glass and other parts, have been improving performance characteristics. As a result, we found substantial benefits in resin-made rear doors compared to conventional steel doors, such as light weight, more freedom in forming and consolidation of parts. **Figure 3** shows comparison of number of components between steel rear door and resin rear door.

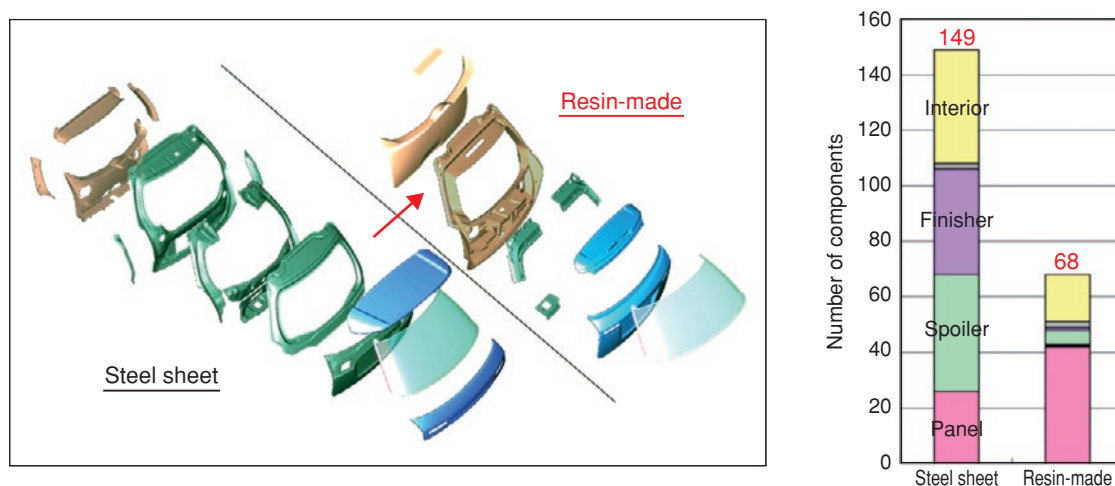


Figure 3 Effectiveness of back door resinification

Other than high strength and high stiffness, rear doors require multi-functional qualities such as vibration fatigue resistance, crash safety in the event of rear-end collision, dimensional stability after thermal (cooling/heating) cycling test, high creep resistance and high visual appearance quality. Conventional steel rear doors have met these quality requirements by hemming and welding inner and outer panels.

Required strength and stiffness for a resin-made rear door are basically provided by an inner panel. As shown in **Figure 4**⁷⁾, we use glass fiber reinforced injection molding grade polypropylene resin, which contains fiberglass with higher specific rigidity and higher specific strength than SMC (sheet molding compound) to make inner panels. (SMC is a compound for sheet molding method which requires a curing process under heat and pressure. The raw sheet consists of aligned short fiberglass bundles impregnated by resin paste which is a mixture of resin and fillers.) We use injection grade polypropylene resin, which offers superior heat resistance and visual appearance quality, to make outer panels.

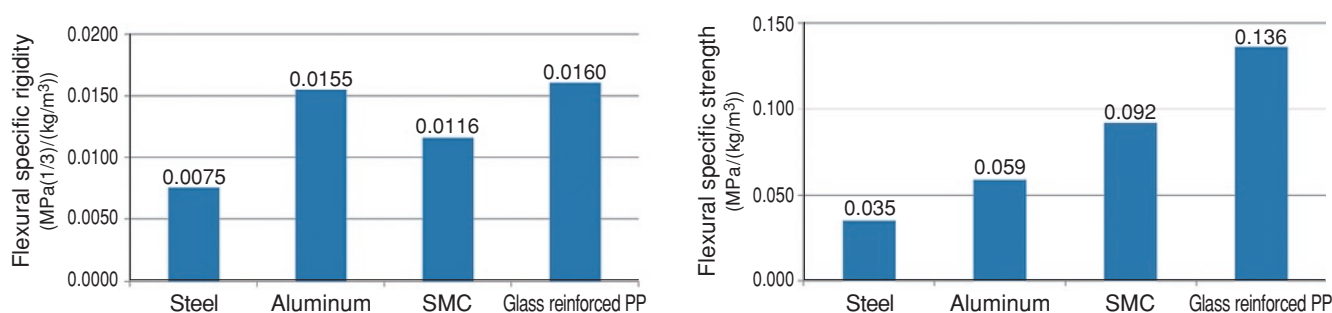


Figure 4 Selection of materials for inner panel

Designing plays a critical role to satisfy required functional performance for a resin-made rear door. At our company, we use CAE simulation technology for structural optimization. Case studies of warp phenomenon analysis of the inner panel are shown in **Figure 5**. Structural analysis results before and after implementation of warp countermeasures are coincident with actual measurement results of inner panels formed in the mold which was actually made for trial production. Adding ribs to the panel area proved effective as a countermeasure to prevent warping. Thanks to these technologies, our resin-made rear doors successfully achieved weight reduction by 30% compared to steel sheet rear doors.

For the future, we will further promote automotive weight reduction and improvements in product merchantability by panel thinning and re-examination of raw materials.

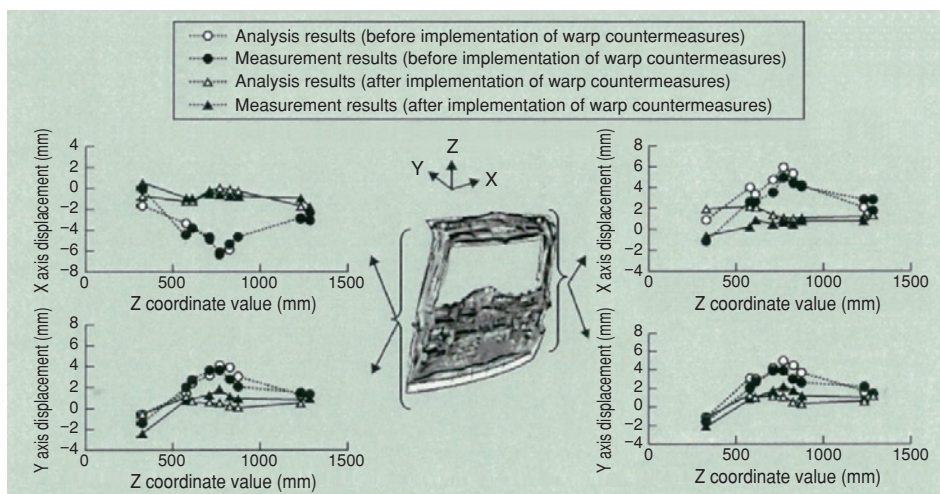


Figure 5 Warpage analysis of the inner panel made of glass fiber reinforced PP

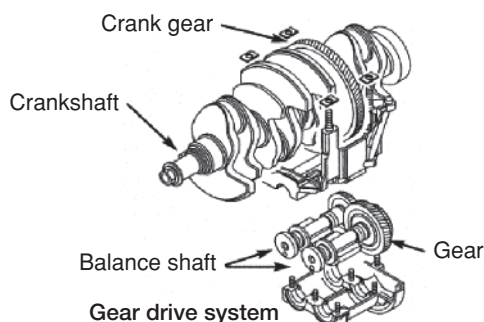
2.2 Resin gear⁸⁾⁹⁾

We started commercial production of resin gears for balance shaft to help save the weight of functional components inside an engine room in 2000. As shown in **Figure 6**, balance shaft drive system is designed and fitted to help negate the secondary harmonic typical of four-cylinder engines, with a mechanism that a shaft with unbalanced mass is rotated at a speed twice as fast as engine revolution speed. Our challenges were how to control stresses generated on meshing gear teeth, life of gears and noise caused by gear mesh friction.

A picture of a resin gear itself is shown in **Figure 7**. In our development process to convert metal gears to resin, we selected polyamide resin, considering its high strength and resistance against high operating temperature. We successfully achieved increased resin strength under higher temperatures by selecting an appropriate curing agent. Since resin by itself could not maintain its strength level for long, it was reinforced with fibers. Polyamide resin gears reinforced with selected fibers were made and their functional performances were measured. As shown in **Table 1**, measured strength and modulus of elasticity of PBO (poly p-phenylene-2,6-benzoxazole) fiber composite material were lower than those of aramid fiber composite material. Carbon fiber composite material showed high strength and high modulus of elasticity but we found this material attacked the mating steel gear tooth surfaces and wore them away. Thus, we decided on aramid fiber as the best option to reinforce resin. Short fibers, not long fibers, were selected to increase material strength.

To reduce the noise level created by gear mesh friction, we re-examined the gear cutting process to improve the dimensional accuracy of finished products. We experimented the cutting process with conventional dry hobbing without cutting fluid, but found improving the accuracy of a hobbed gear difficult because of the discontinuous process to cut multiple teeth. Then, we decided to select a shaving process and shaving cutter because of its better performance, such as less loading and better productivity. We improved its processing accuracy by examining the processing conditions.

We will continue to work on further reinforcement of resin gears by re-examining fibers for reinforcement and composition of composite materials, and promote their expanded applications in other locations.



(Source) Tamio Hirota, *Engine Parts Kodawari Daihyakka (Encyclopedia Focused on Engine Parts)*; Grand Prix Book Publishing, (2004), p.75, p.78

Figure 6 Mechanism of balance shaft system

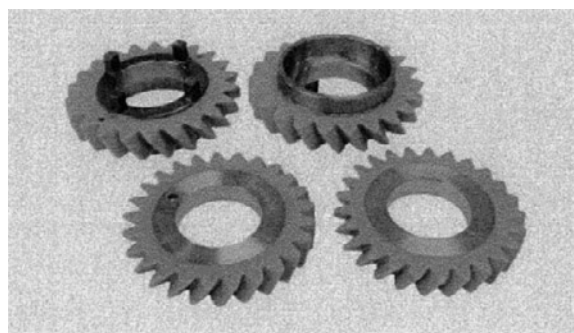


Figure 7 Resin balance shaft gears

Table 1 Mechanical properties of composite material

Test item	Unit	Carbon fiber composite material	BPO fiber composite material	Aramid fiber composite material
Flexural strength	MPa	580	190	220
Flexural modulus of elasticity	MPa	30,000	6,000	7,000
Compressive strength	MPa	400	150	270
Izod impact strength (without notch)	J/m	650	420	500

Resin: Polyaminoamide resin, Base material blending ratio: 50 vol%

2.3 Products of powder metallurgy¹⁰⁾⁻¹²⁾

Powder metallurgy is a material processing method to make raw material and/or parts by sintering metal powders and forming a metallurgical bond between them. The basic manufacturing process of powder metallurgy is shown in **Figure 8**. Powder metallurgy shows a number of unique characteristics including its ability to manufacture metals with a high melting point and alloyed metals, metal and non-metal composite materials, composite materials combining mutually insoluble metals, and to control porous materials, with good economic performance thanks to its simple process. Its products can also have unique properties that can't be obtained by regular steel because the finished product form or its approximate form can be obtained through the process of molding and sintering metals together with a degree of freedom in controlling alloy composition and metal structure.

High-strength sintered material has improved mechanical properties by adding alloying elements having a high harden ability and optimizing its method. On the other hand, there are many dispersed fine gas pockets called pores in powder metallurgy products as powder metallurgy uses metal powder as a raw material. Thus, a problem of impaired mechanical properties is caused by pores. We developed a densification technology to reduce pores and successfully developed a new material by combining this densification technology and material technology, and its mechanical strength was comparable to that of steel. As a result, thinning of component walls has become possible with this new material. An example of an automotive component made of high-strength sintered material is shown in **Figure 9**.

By taking advantage of the high degree of the freedom in material designing provided by powder metallurgy, we are developing various sintered materials with heat and wear resistance strong enough to meet specific operating conditions. We developed the technology to control the volume of the liquid phase formed during sintering process to have better material dispersion during the sintering process, and with it, we supply products having superior functional properties never before seen in conventional materials. As an example, high Cr material containing 20% chromium steel, in which about 30% carbide in the surface area is dispersed finely and uniformly, shows excellent wear resistance and oxidation resistance under 700°C or higher temperature conditions (**Figure 10**). This material is used in a downsized supercharged engine.

In the future, we will develop and release products that can contribute to automotive weight reduction and downsizing by applying the unique properties specific to powder metallurgy materials.

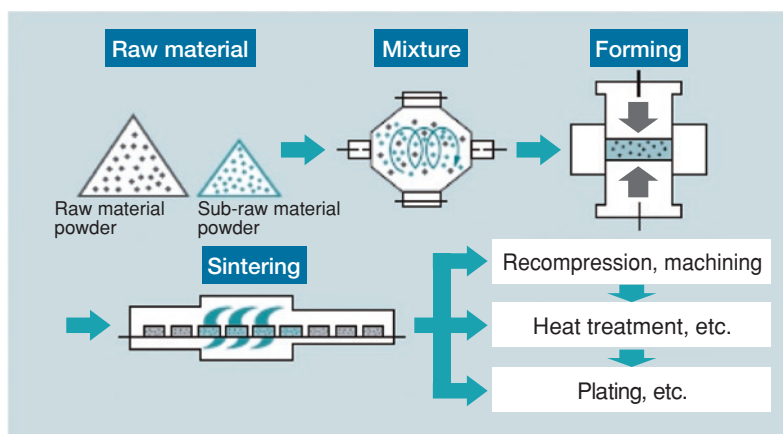


Figure 8 Manufacturing process of powder metallurgy



Figure 9 Products made from high strength sintered material

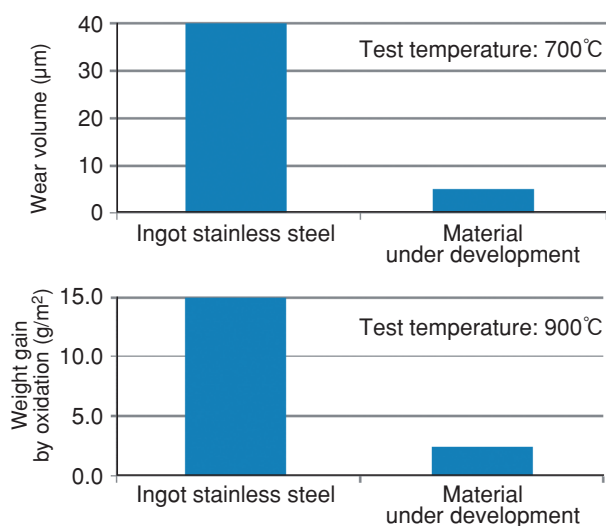


Figure 10 Anti-wear and anti-oxidation properties of developed material

3 Thermal management product

Technology to control heat received from the environment and generated inside an automobile is also important as an energy saving technology for automobiles. Our company is producing light-control films with the ability to control outdoor light transmission and room light transmission for light shielding, screening and heat insulation. We also developed thermoelectric materials that convert waste heat from automotive engines into electricity. We explain these subjects in detail below.

3.1 Light-control film^{12) 13)}

Our company started commercial production of light-control emulsions and films using our proprietary functional material, polymer synthetic technology and film coating technology on the basis of SPD (Suspended Particle Device) technology licensed from RFI (Research Frontier Inc.) in the USA. The principle of the light-control film is shown in **Figure 11**. This is an active light-control film which changes its color from dark blue to transparent when light-control particles are aligned parallel to the electric field after alternative voltage is applied to the transparent electrodes placed opposite each other. This light-control film shows unique characteristics including little haziness (an indicator of the transparency of film to indicate the degree of cloudiness), ability to steplessly adjust visible light transmission, and even with benefits of low power consumption. The structure of the light-control glass is shown in **Figure 12**, in which light-control film is placed between two sheets of glass via an adhesive layer. The thermal management effect is shown in **Figure 13** when light-control film is applied to the sun roof of an automobile.

In a simple simulation experiment under irradiation of light with a spectral distribution approximately that of sunlight, the surface temperature of a paper with black hair image color was lower by 10°C than transparent glass when voltage was “ON” and was lower still when voltage was “OFF”. So, both passenger comfort and energy saving can be provided when our light-control film is applied to an automobile sun roof.

We are developing achromatic black or gray color films which can easily coordinate with room designs for future use, as the color of the light-control material developed this time is dark blue when voltage is “OFF”.

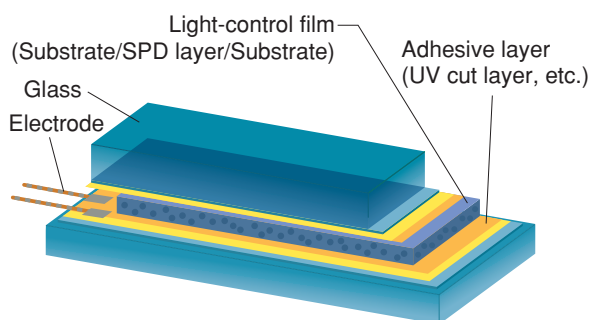


Figure 12 Structure of light control glazing

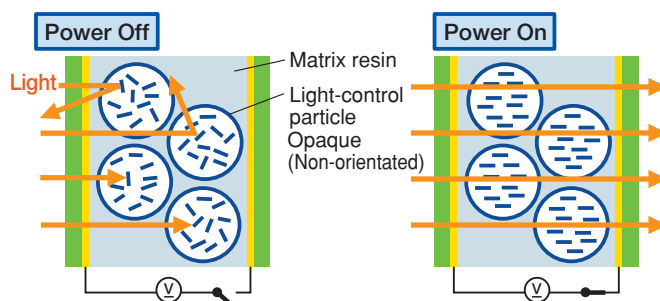


Figure 11 Fundamental driving mechanism of light control film

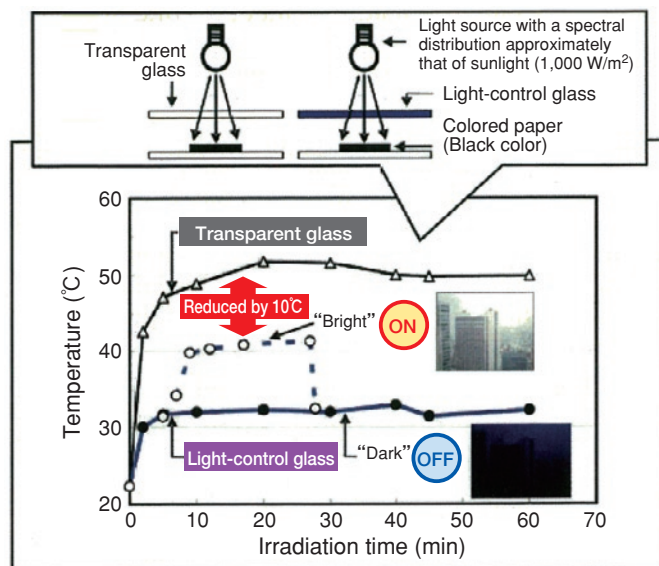


Figure 13 Surface temperature of black paper during the sunlight simulator test

3.2 Thermoelectric module¹⁴⁾

Thermoelectric conversion is an electricity generation method, in which heat (temperature difference) is converted directly into electrical energy through a phenomenon called the Seebeck effect. A thermoelectric module generally consists of two n- and p-type semiconductor elements connected via electrode in series. For practical applications at higher temperature, alleviating an effect of thermal stress distortion at the junction of a thermoelectric element and preventing performance deterioration due to diffusion of constituents of thermoelectric conversion members should be a key issue. So far, our company has developed a high-temperature module using an SiGe conversion element (**Figure 14**). This module was prepared by bonding an SiGe element produced by powder metallurgy technology with a molybdenum electrode using a special technique. We are continuing to develop new materials to achieve even higher performance and have obtained generation of a maximum output power of 1,000 mW/cm²

under the 620°C temperature difference using a module consisting of SiGe and Mg₂Si elements. This output value was 1.7 times higher than that of a conventional SiGe module (**Figure 15**).

This thermoelectric module is considered as a very promising technology to recover waste heat from automobiles by converting it to electrical energy, thereby improving fuel efficiency. We will continue to develop thermoelectric elements with even higher performance and manufacturing technology of larger size modules, and aim at commercialization of these products.

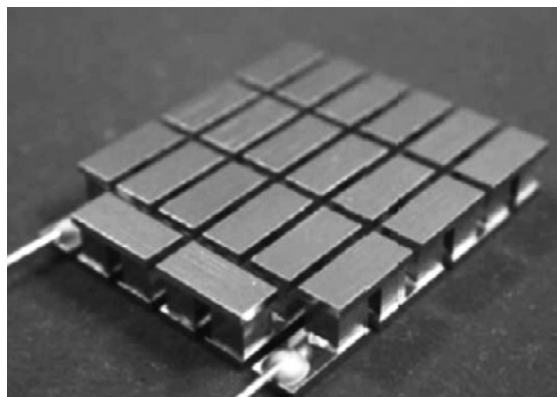


Figure 14 SiGe thermoelectric modules for high temperature

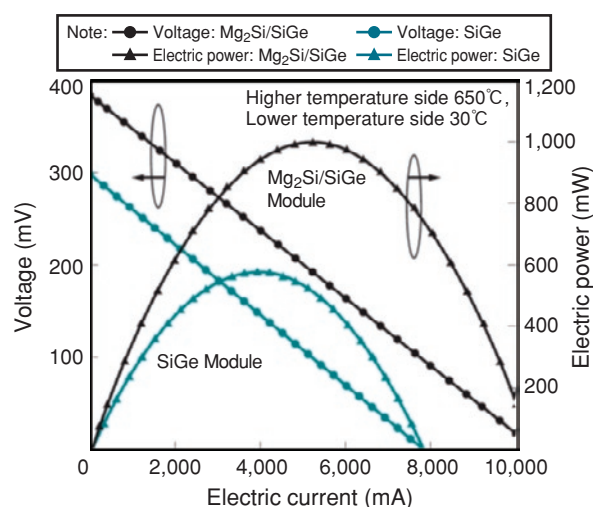


Figure 15 Electric current and voltage properties of two pairs of modules

4 Hazardous materials restraint product

4.1 Copper-free friction material

An automotive disc brake pad is an automotive component of a brake system. When the driver presses his foot against the brake pedal, two disc brake pads are clamped by pistons onto a cast iron rotor, which rotate together with an automotive wheel, and slow the automobile by the generated force of friction. A brake pad is prepared by attaching cured friction material cake, made from a resin compound reinforced with metal fibers, inorganic/organic fibers and more than 10 kinds of friction adjustment agents, to an iron plate¹⁵⁾. Brake pads using copper metal fibers have been the main type for 20 years, thanks to their low noise when braking and well-balanced performance, and even in recent years, the overseas market for brake pads using copper metal fibers are expanding, especially in North America. However, due to the legislative trends to restrict the use of copper in brake pads, development of copper-free friction material has become an urgent task.

Each manufacturer is actively involved in the research and development of copper-free friction materials¹⁶⁾⁻¹⁸⁾. **Figure 16** shows the functional performance of copper and its influence on brake performances. Copper has high thermal conductivity, a high melting point and excels in strength retention if used in fiber form. Therefore, simple copper replacement hurts brake performance at higher temperature and/or performance related to material strength. Our company researched the effects of copper quantitatively and performance shortcomings of copper-free material were overcome with multiple metal and inorganic raw materials, eventually resulting in our successful introduction of copper-free brake pads. No performance problem was encountered with our copper-free brake pad, and neither friction coefficient nor wear resistance were inferior to those of conventional products, as shown in **Figure 17**. Shear strength was also at the same level as that of conventional products.

Each auto manufacturer has finally started to equip certain models with copper-free brake pads. We consider that the trend to use copper-free brake pads in new models will accelerate. We expect the braking performance of copper-free brake pads to be improved to an even higher level by re-examining friction material composition and modifying the manufacturing process in response to weight differences between light and heavy vehicles, different performance requirements in different categories such as speed-prioritized sport cars or different approaches by auto manufacturers.

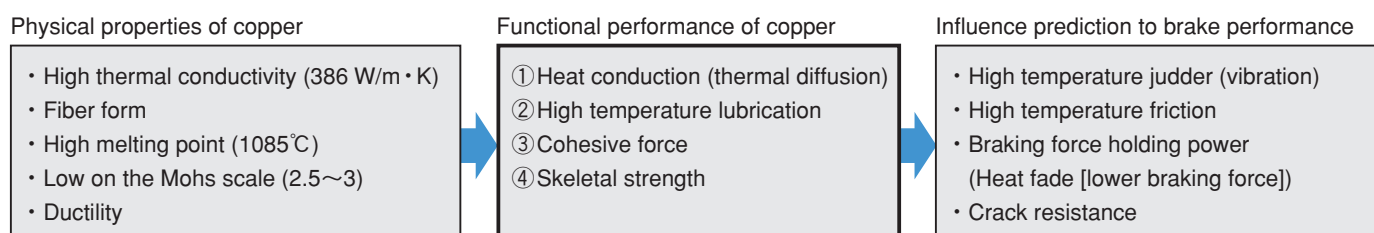


Figure 16 Estimate of influence of copper properties for brake performance

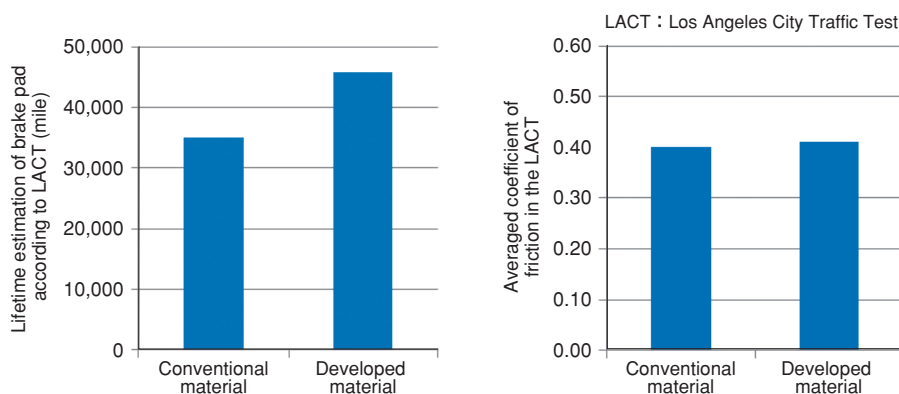


Figure 17 Friction properties of the new copper-free brake pad

5 Summary

We are living in an age in which we cannot talk about marketing without mentioning the environment. It is the same for the automobile industry, and we have to overcome difficult challenges in achieving both automotive performance improvements and environmental compliance simultaneously while rushing to comply with regulations imposed by each country. The current role of the automobile as a transportation system will not change in the future and automotive components making up an entire automobile will play a major role. Therefore, by means of superior automotive technologies and speeding up automotive R&D, we must contribute to better environmental compliance. We will do our best and contribute to society through the progress of the auto industry, in which environmental compliance can be realized through the aforementioned technologies and products incorporating future technical developments.

[References]

- 1) Daisuke Imanishi. (2015-9) *Developing lightweight vehicle bodies for 2030. (2030 Nen, Keiryoku no Shinario)*. Nikkei Automotive, pp.52-57
- 2) Yukio Kou. (March, 2006) *Vicissitude of Automotive Material. (Jidousha Sozai no Hensen)*. Japan Automobile Manufacturers Association, Inc. (JAMAGAZINE)
- 3) Takeo Sakurai. (2009) *Technical Trend of Aluminum Alloy Sheets for Automobiles. (Jidoushayou Arumi Goukinzai no Gijutsu Doukou)*. Kobe Steel Engineering Reports, 59, pp.121-127
- 4) Mitsui Global Strategic Studies Institute. (28 July, 2014) *Weight Reduction and Diversification of Automotive Structural Components. (Jidousha Kouzouzai no Keiryoku to Tayouka)*. Senryaku-Ken Report
- 5) Tetsuo Ito. (2013-1) *Automotive Parts for "Environment, Safety and Comfort Performance". (「Kankyo/Anzen/kaiteki Seinou」 o Jitsugensuru Jidousha Buzai)*. Hitachi Chemical Technical Report, 55, pp.47-50
- 6) Teruhiko Iwata et al. (2005-1) *Plastic Back Door Module for Automotive. (Jidoushayou Bakkudoa Mojuru)*. Hitachi Chemical Technical Report, 44, pp.21-26
- 7) Shigeo Suzuki. (17 July, 2015) *The Japan Society of Polymer Processing Lecture Material. (Purasuchikku Seikei Kakou Gakkai Kouen Shiryou)*.
- 8) Yasuyuki Hashimoto et al. (2006-2) *High Strength Resin Gear Materials. (Kou Kyoudo Jushi Giyayou Zairyou no Kaihatsu)*. Shin-Kobe Technical Report, 16, pp.10-15
- 9) Masao Sugiyama et al. (2009-2) *Improvement of Accuracy for Aramid Fiber Reinforced Resin Gear. (Aramido Seni Kyouka Jushi Giya no Seido Koujou)*. Shin-Kobe Technical Report, 19, pp.35-42
- 10) Tadayuki Tsutsui. (2011-9) *Recent Technology of Powder Metallurgy and Applications. (Saikin no Funmatsu Yakin Gijutsu to Sono Ouyou Seihin)*. Hitachi Chemical Technical Report, 54, pp.13-21
- 11) Kei Ishii. (2013-1) *Trends in Environmental and Energy-saving Technology for Automobiles and Corresponding Developments in Powder Metallurgy. (Jidousha ni okeru Kankyo/Sho-Ene Gijutsu Doukou to Funmatsu Yakin Gijutsu no Taiou)*. Hitachi Chemical Technical Report, 55, pp.51-54
- 12) Toshiaki Ishii et al. (2013-05) *Material Solutions for Clean Engines and Electric Vehicles. (Jidousha no Dendouka/Kurinka ni taisuru Koukinou Zairyou)*. Hitachi Review, 95, pp.49-55
- 13) Osamu Higashida et al. (2007-7) *Active Light Control Film for Glass. (Akutibugata Choukou Garasuyou Firumu)*. Hitachi Chemical Technical Report, 49, pp.7-10
- 14) Kudo Makoto et al. (2013-05) *Innovative Materials for Renewable Energy. (Saisei Kanou Enerugi no Katsuyou o Sasaeru Kakushin Zairyou)*. Hitachi Review, 95, pp.24-29
- 15) Yasuhiro Hara et al. (2003-7) *High Friction Coefficient Disc Pads for Automotive Brakes. (Burēkiyou Kou Masatsu Keisuu Disukupaddo)*. Hitachi Chemical Technical Report, 41, pp.45-48
- 16) Poh Wah Lee, et al. (2012) *Development of Cu-Free Brake Materials*, SAE technical paper 2012-01-1787
- 17) Yasuki Hattori et al., Nisshinbo Brake Inc., *Friction Material*, Japanese Unexamined Patent Application Publication No. 2013-245338, 2013)
- 18) Eri Itami et al., Akebono Brake Industry Co., Ltd. *Friction Material*, Japanese Unexamined Patent Application Publication No. 2013-076058, 2013

Low Elastic Prepreg for Automotive Application “TD-002”, to Inhibit Solder Crack

Takayo Kitajima

Laminate Materials R&D Dept., Advanced Performance Materials R&D Division,
Advanced Performance Materials Business Headquarters

1 Abstract

In recent years, hybrid vehicles and electric vehicles, which are applying advanced electronic controls, are increasing. As the ECU came to be mounted in the engine compartment, the solder crack issue comes from the stress due to the mismatching CTE between electronic components and PWB. Low elastic modulus material “TD-002” was developed as a material to solve this issue.

TD-002 has low elastic modulus and high elongation, and also has high reliability properties in CAF and heat resistance. TD-002 applied to the surface of PWBs of standard FR-4 material inhibits solder cracking, absorbing the soldering stress.

2 Functional characteristics of TD-002

- It has low elasticity and high extensibility.
- When applied to the surface of PWB, it absorbs stress applied on solder and inhibits cracking of the solder layer.
- It can inhibit solder cracking when used in combination with conventional materials, not necessarily requiring high functional materials (such as materials with low CTE)

3 Background of the Development

In recent years, the number of automobiles equipped with an electronic control unit (ECU), which are represented by fuel efficient hybrid cars and electric vehicles, has been increasing.

Accordingly, with expected rapid increase in quantity and high densification of mounted ECU, the trend of installing ECU in the limited space and high temperature environment such as engine room is getting stronger. In such a high-temperature environment, stress distribution is concentrated in solder joints created by the difference between the coefficients of thermal expansion (CTE) of mounted components and the substrate resulting in solder cracks and electrical connection problems (**Figure 1a**). One approach to this problem can be to use insulating layer materials with low modulus of elasticity and high extensibility to release the stress generated by the difference between the coefficients of thermal expansion (CTE) of mounted components and the substrate (**Figure 1b**).

Based on this concept, we developed low elastic modulus and highly extensible material for PCB, “TD-002” for automotive applications to inhibit solder cracks.

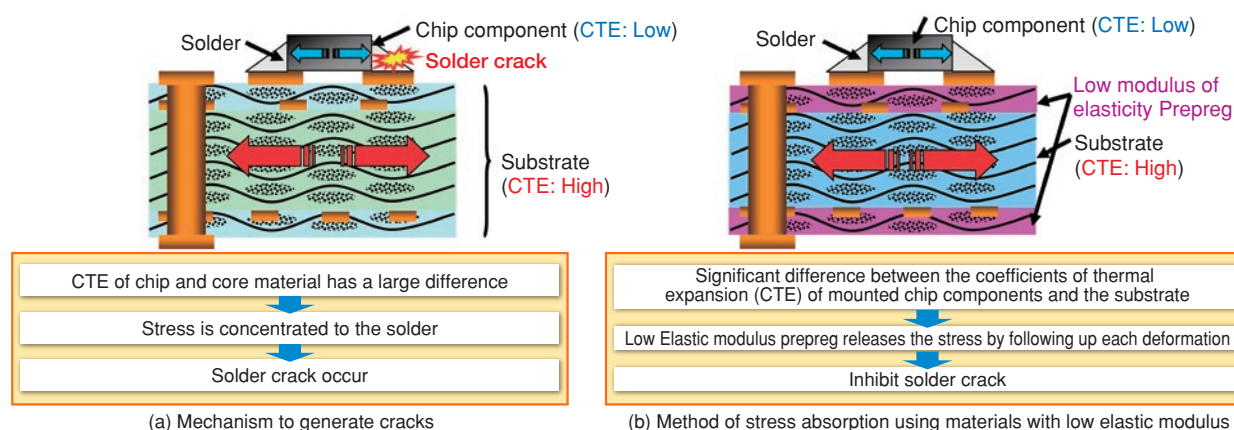


Figure 1 Mechanism of solder crack and stress absorption by low elastic modulus material

4 Technical details

1. Design concept of TD-002

TD-002 should have both low modulus elasticity and high extensibility to inhibit solder cracks, and high level of reliability required for PCB including insulation reliability and high temperature resistance. To achieve this, we designed a material that

can provide both functions using our own proprietary polymer technology for blending low elastic modulus and high extensible flexible resin with high temperature resistant thermosetting resin.

Product of TD-002 is in the form of prepreg, which can be multi-layered in combination with core materials, and does not require expensive low CTE substrate, resulting in total cost reduction to manufacture substrates.

2. Solder crack inhibition effect of TD-002

To confirm solder crack inhibition effect of TD-002, we prepared substrates for evaluation, which mounted components on either an FR-4 single component board or a multilayered substrate where TD-002 was laminated onto FR-4 core material and evaluated them by measuring solder crack growth rate after thermal shock test¹⁾. Evaluation results are shown in **Figure 2**. These evaluation results showed lower solder cracking rates for each surface mounted component using TD-002 than for that using FR-4 single component substrate; thus, it was confirmed that TD-002 was effective in inhibiting solder cracks.

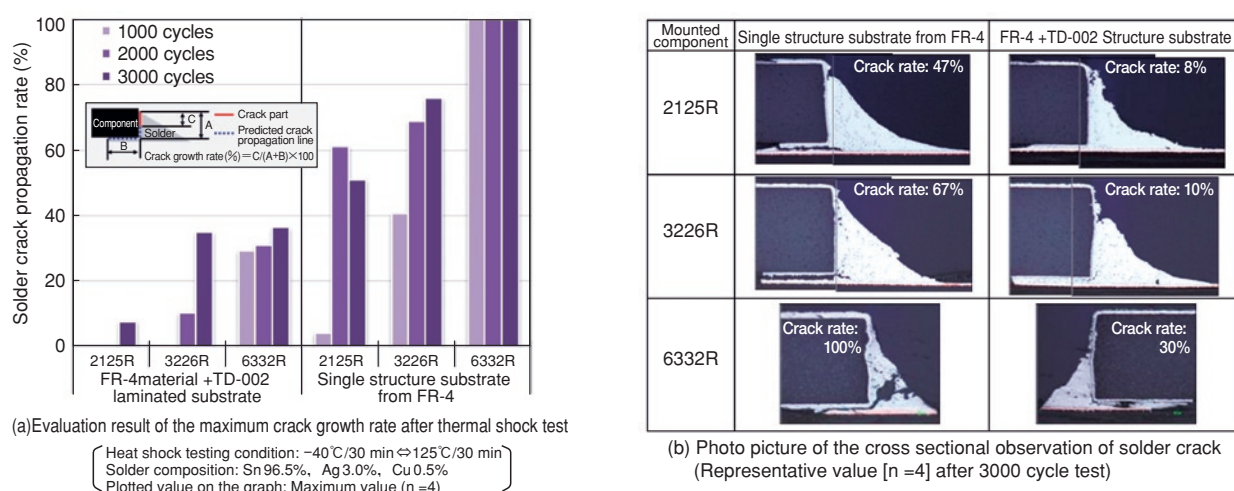


Figure 2 Reduction effect of solder crack by using TD-002

3. General properties of TD-002

General properties of TD-002 are shown in **Table 1**. TD-002 has one fourth (1/4) of FR-4 elastic modulus and about 4 times of FR-4 tensile elongation, and shows high deformation follow up property. Due to these properties, the stress caused by the difference between CTE of mounted components and the substrate during the heat shock test can be released (**Figure 1b**).

Also, other functional performance levels of TD-002 are on the same level as FR-4, indicating that TD-002 meets the high level reliability requirements for PCB.

Table 1 General properties of TD-002 (Thickness 0.4mm)

Item	Condition	Unit	TD-002	High Tg Halogen Free FR-4
Solder Heat Resistance	260°C Float	s	> 300	> 300
Tg ^{*1}	TMA	°C	155-170	155-170
CTE ^{*1}	X	TMA [<Tg]	6-9	12-15
	Y		6-9	14-17
	Z		80-130	30-40
Elongation ^{*2}	Resin only	Tensile 25°C	5.1	1.3
Elastic Modulus ^{*2}	Resin only	Tensile DVE 25°C	0.8-1.2	4.8-5.2
Flexural Modulus	Lengthwise	GPa	5-8	25-29
Dielectric Constant ^{*3}	1 GHz	—	3.6-3.8	4.4-4.6
Dissipation Factor ^{*3}	1 GHz	—	0.011-0.013	0.014-0.016
Volume Resistivity	C-96/20/65 + C-96/40/90	Ω · cm	1×10 ¹⁵ -1×10 ¹⁶	1×10 ¹⁵ -1×10 ¹⁶
Surface Resistance	C-96/20/65 + C-96/40/90	Ω	1×10 ¹⁴ -1×10 ¹⁵	1×10 ¹⁴ -1×10 ¹⁵
Insulation Resistance	C-96/20/65 + D-2/100	Ω	1×10 ¹⁴ -1×10 ¹⁵	1×10 ¹⁴ -1×10 ¹⁵
Water Absorption	E-24/50 + D-24/23	%	0.10-0.30	0.08-0.12
Copper Peel Strength	35 μm	kN/m	0.8-1.0	1.2-1.4
Flammability	UL-94	—	V-0	V-0
CAF properties ^{*4}	85°C/85%RH, DC100 V	h	> 2000	> 2000

*1 Heating Rate: 10°C/min

*2 Resin only, Thickness: t0.1 mm

*3 Measured by cavity resonator.

*4 Laminate thickness: t1.6 mm, Drill bit: Φ0.4 mm, T/H wall distance: 0.3 mm, Pre-condition: Reflow x 2 (Max 250°C)

5 Future Business Development

- Development of the next generation halogen-free substrate to inhibit solder cracks

[Reference]

- 1) Takayo Kitajima: JPCA Preliminary draft prepared for presentation at the Show 2015 NPI: Low Elastic Prepreg for Automotive Application "TD-002", to Inhibit Solder Cracks

Advanced Analysis of Lead-Acid Batteries

Hiroki Hirano Kazushige Kouno Keiji Sumiya

New Business Development Headquarters
Tsukuba Research Laboratory
Advanced Fundamental Technology Development Center

1 Abstract

Since their invention in 1859, lead-acid batteries have been used in automobiles, and in emergency and power-storage batteries. The market for these batteries has been expanding recently. On the other hand, Idling Stop System (ISS) vehicles are attracting attention as environmental friendly vehicles. The development of batteries for ISS has progressed to increase durability. However, the analysis of lead-acid batteries is very difficult because the conditions and structure of each component are changed by discharging and charging. Accordingly, we newly developed analytical methods to elucidate the two-and three-dimensional nanostructure, crystalline distribution and dispersion state of ingredients of lead-acid batteries.

2 Character of the analytical technology

- New analytical technologies suitable for various fields (**Figure 1**)
- Elucidation of deterioration mechanism in lead-acid batteries (lattice corrosion, dendrite shorting, muddy state of the positive electrode, etc.)

As individual cases of accomplishments,

- 1) In-situ observation of corrosive layer produced on the surface of a positive electrode grid according to 2D-mapping of chemical composition.
- 2) In-situ observation of the cross section of corrosive layer produced on the surface of a positive electrode grid through crystal structure distribution analysis using EBSD^{*1}.
- 3) 3D-structural analysis of crystalline salt deposition growth inside of a separator in a battery after short circuit using high-resolution X-ray CT technique.

^{*1} EBSD: Electron Backscatter Diffraction

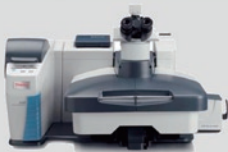

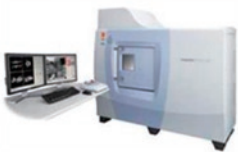
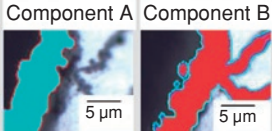
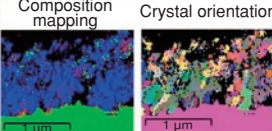
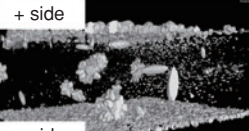
Field	2D Composition	2D Crystal Structure	3D Structure
Equipment	 Raman microscope	 SEM-EBSD	 High definition X-ray CT
Observation Object	Mapping of chemical state in sub-micro scale	Mapping of crystal structure in sub-micro scale	3D-observation of lead-acid batteries' separators in sub-micro scale
Output	 Distribution of composition on grid cross-section	 Distribution of crystal structure on grid cross-section	 3D-CT image of separator after hydration short

Figure 1 New analytical technologies suitable for various fields

3 Background of the development

Compared to lead-acid batteries for conventional vehicles, those for ISS vehicles have a tendency to become low due to continuing power supply while the engine is shut down or discharging power during restart. Therefore, batteries for ISS vehicles require excellent durability for charge and discharge cycles, high charge acceptance and high dendrite short circuit resistance. Although development at our company to improve charge acceptance and other attributes are under way²⁾, elucidating the deterioration mechanism for a lead-acid battery is important to further promote development. However, degraded state analysis through

conventional analytical methods remains difficult and there are many unsolved questions as temperature, specific gravity and the surface condition of active material greatly change due to the reactions between active material and electrolyte during charge/discharge cycles of lead acid batteries. So, we tried new multi-analytical approaches with high level capability to elucidate characteristic functions (visualization, quantification).

4 Technical details

In this research work, we newly developed the following multiple analytical methods enabling in situ observation and quantification of 2D- and 3D-nanostructure, crystal distribution and dispersion state of specific ingredients of lead-acid batteries. (1) Component distribution analysis: Visualization of component distribution in the corrosive layer produced on the surface of a positive electrode grid. (2) Distribution analysis of crystal structure: Crystal state visualization of the corrosive layer produced on the surface of a positive electrode grid. (3) 3D-structural analysis: In-situ observation of the microstructure inside a battery separator after short circuit. By applying these new analytical methods, the following facts about lattice corrosion, which is a degradation mode of lead acid battery, and dendrite-induced short circuit were revealed.

- 1) By visualizing 2D-component distribution, change in composition during the process of corrosion was clarified. In the past, elemental distribution analysis was performed using EPMA^{*2} but identification of chemical compounds was still difficult. So, by newly applying a mapping technique using Raman spectroscopy, it was elucidated that components of the corroded layer were composed of two different layers.
- 2) By visualizing 2D-crystal structure distribution, change in crystal structure during the process of corrosion was clarified. In the past, crystal structure in the surface layer was analyzed using X-ray diffraction technique, but evaluation of the crystal distribution was still difficult. So, we applied EBSD crystal structure distribution analysis. SEM^{*3} images of the cross section of the corroded layer and EBSD results are shown in **Figure 2**. It was revealed from observations including band contrast enhancing the outline of crystal particle images, crystal phase color to show crystal component distribution, and Euler color indicating the crystal orientation that corroded layer was polycrystalline and particle size became smaller toward the surface.
- 3) By visualizing the 3D-structure, deposition during short circuit was clarified. In the past, SEM was used to analyze the cross-section structure of a separator, but stereoscopic analysis of the deposition during short circuit was difficult. So, we newly applied a 3D-analytical method using X-ray CT technique. SEM images of the cross-section of a separator and 3D-images of the deposit using X ray CT technique are shown in **Figure 3**. By applying X-ray CT technique, it was revealed that SEM images of the deposit in Battery A were squamous and a minutely small deposit, which had not been confirmed by SEM imaging, was present in Battery B. This visualization technique to observe short circuited state by X-ray CT technique can contribute to the development of improved dendrite short circuit resistance.

^{*2} EPMA: Electron Probe Micro Analyzer ^{*3} SEM: Scanning Electron Microscope

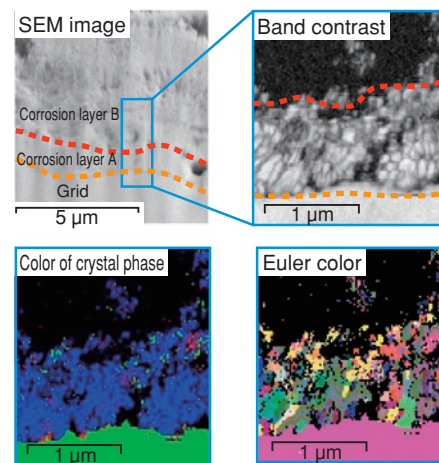


Figure 2 SEM image and dispersion state of crystal structure

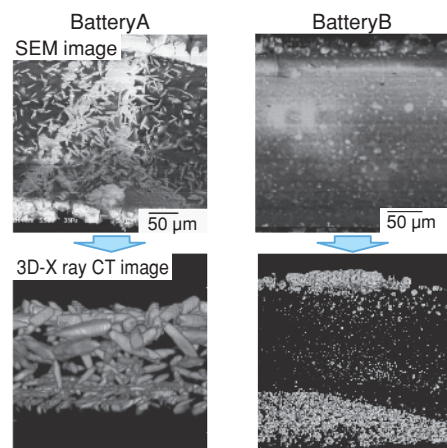


Figure 3 Cross-sectional SEM image and three dimensional structure analysis of separators after hydration short by X-ray CT

5 Future Business Development

- Technology deployments in the fields of electrical energy storage devices and related materials
- Detailed elucidation of the functional mechanism of inorganic/organic, solid/liquid composite materials for use in the fields of information/communication and life science

[References]

- 1) Fuji Keizai Management Co., Ltd. (2015) *A Perspective of Future Materials for Energy and Large Capacity Rechargeable Applications* [Enerugi-, Oogata Denchi- Zairyou no Shourai Tenbou]. Volume of "Field of Next Generation Environment-Friendly Vehicles" [Jisedai Kankyou Jido-sha Bunya Hen]
- 2) Shingo Araki, Toshio Shibahara. (2014) "Flooded Type ISS Battery with Improved High Durability and High Charge Acceptance" [ISS-Sha You Taikyuu Kou Juuden Ukeire -Sei Namari Denchi]. Hitachi Chemical Technical Report, 57, p.18

New Low Transmission Loss Material for Millimeter-wave Radar Module “AS-400HS”

Takao Tanigawa Yuusuke Kondou Yuuichi Shimayama Tetsurou Irino

Telecommunication Materials Development Center,
Tsukuba Research Laboratory,
New Business Development Headquarters

1 Abstract

Recently, the safety driving support system utilizing millimeter-wave radar has been spreading. Since the study of automatic driving is also active, then the market of the millimeter-wave radar for automobile is expected to increase rapidly in the future^{1)~2)}.

The newly developed low dielectric material, AS-400HS, has more excellent electric property and workability compared to conventional thermoplastic composite materials utilizing PTFE and LCP. Furthermore, it can propose the new design such as multilayer antenna for ultra-wide band by buildup.

2 Characteristics of the product

- It has excellent dielectric properties.
- It has a good workability such as applicability of laser via hole drilling and good in plating uniformity.
- It can be used for a multilayer antenna as it can be fabricated into a build-up multilayer printed board.

3 Background of the development

Significant manufacturing cost reduction of radar is needed for full-fledged applications for collision prevention radar for vehicle; therefore, switching from traditional metal antenna or ceramic material substrate based antenna to fluorine resin (PTFE) or liquid crystal polymer (LCP) substrate based antenna is now being studied. These thermoplastic resins, however, have certain workability issues including material processing by drilling/laser and plating uniformity, resulting in higher processing cost as a bottleneck in wide applications for collision prevention radar for vehicle.

Then, using new thermosetting resin deriving from our proprietary resin technology, we started development of new low transmission loss materials having dielectric property equal to and workability better than other PTFE or LCP based materials for substrate.

4 Details of the technology

1. Development concept of AS-400HS

We used thermosetting resin which we developed using our proprietary resin design technology and has superior dielectric properties. To satisfy both superior dielectric properties and better adhesive strength, a low profile copper foil can be selectable and still be able to provide excellent transmission performance. AS-400HS can be fabricated into buildup multilayered substrate for antenna because it is a film made from thermosetting resin, which is different story for PTFE or LCP based materials.

2. General properties of AS-400HS

General properties of AS-400HS are shown in **Table 1**. Its electrical properties include Dielectric Constant (Dk) of 3.0 and dielectric dissipation factor(Df) of 0.0023 at 10 GHz, and shows better values than those of traditional PTFE or LCP based substrates. As heat resistance parameter T-300 (per IPC TM-650) was 60 minutes or longer, and its thermal decomposition temperature was 460°C (5% weight loss), heat resistance of AS-400HS should be excellent. Its excellent workability including via formation by laser drilling, laser processing and easy electroplating was confirmed as shown in **Figure 1**. Furthermore, L1-L2 Laser IVH (via diameter: 0.10 mm, via pitch: 0.50 mm, insulation layer 100 μm, thermal cycle: at 65°C (15 min) ⇔ 125°C (15 min)) showed no drops in connection resistance value after 3,000 cycles, and had good reliability without no insulation deterioration after 2000 testing hours using a comb structure test pattern (line/space 65 μm/65 μm, 85°C/85%RH, 100 V).

3. Transmission characteristics of AS-400HS

Evaluation results of transmission characteristics (transmission loss) of microstrip line of AS-400HS are shown in **Figure 2**. It has a transmission line characteristics better than those of PTFE or LCP based materials even in millimeter wave band (transmission loss reduced by 34% at 76 GHz compared to PTFE based material substrate).

Table 1 Properties of AS-400HS

Item	Condition	Unit	AS-400HS	Material A*2	Material B*2
Resin system		—	Thermosetting	Thermoplastic LCP type	Thermoplastic PTFE type
Dk (10 GHz)*1	A	—	3.0	3.0*3	3.0*3
Df (10 GHz)*1	A	—	0.0023	0.0020*3	0.0013*3
CTE (XY-axis)	TMA (30-120°C)	ppm/°C	80	—	17
CTE (Z-axis)	TMA (30-120°C)		36	—	30
	TMA (250-300°C)		53	—	—
Tg	TMA	°C	—	—	30
	DMA		190	—	—
Elastic Modulus	DMA	GPa	3.0	3.4	1.2
Heat resistance	288°C/20 s dip	—	PCT-5 h Pass	—	—
	T-300	min	> 60	—	—
Td	TGA 5% loss	°C	460	—	—
	Low profile	kN/m	0.77 (VLP)	0.70	—
Peel strength (RT)	Profile free		0.60	—	—
Water absorption	D-23/24	%	0.1	0.05	—
Insulation reliabilities*4	85°C/85%RH, DC100 V	hr	> 2000 (< 1%)	—	—
IVH connection reliabilities*5	-65°C (15 min) ⇄ 125°C (15 min)	cycle	> 3000 (> 1.0×10 ¹¹ Ω)	—	—

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

*4 Line/Space: 65 μm/65 μm, Precondition: Reflow x 6 (Max 265°C)

*5 L1-L2 Via: Φ0.10 mm, Pitch: 0.50 mm, Thickness: 0.10 mm, Precondition: C-168/85/85 + Reflow x 6 (Max 265°C)

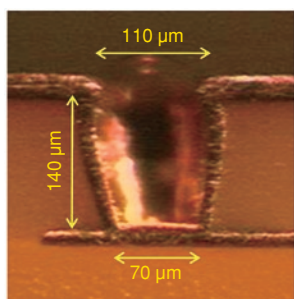


Figure 1 Cross section of laser via

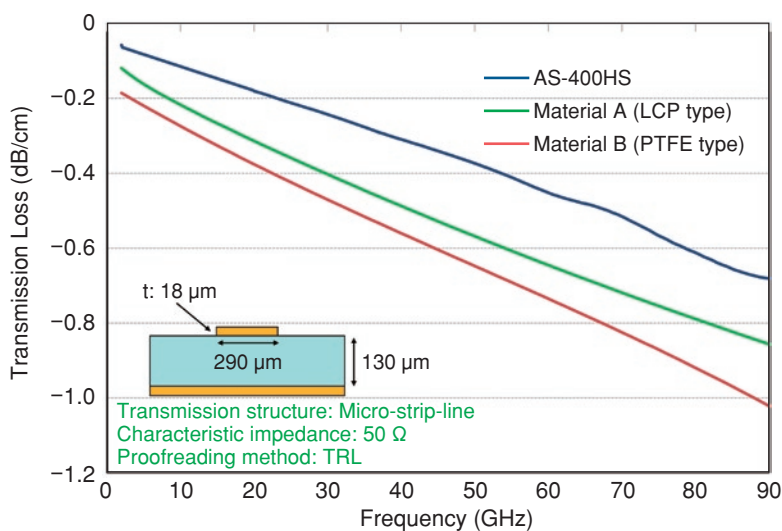


Figure 2 Transmission loss of AS-400HS

5 Future Business Development

- Development of new low transmission loss material for millimeter-wave radar

【References】

- 1) *Milimeter Wave Solution 2007* [MiriHa Soryu-shon 2007]. Yano Research Institute Ltd. (2007)
- 2) *Market trend of Milimeter Wave Radar (2015)* [MiriHa Re-da-Shijou Doukou (2015)]. Japan Marketing Survey Co., Ltd

Highly Thermal Conductive Mica Insulating Tape for Large-Capacity Generator

Yoshitaka Takezawa

Social Infrastructure-related Materials Development Center,
Tsukuba Research Laboratory,
New Business Development Headquarters

1 Abstract

Electricity demand is tending to increase worldwide and thermal power generation is a mainstream means of generating power. Generally, a water direct cooling system is used for a large-capacity turbine generator, but the cooling structure including the waterway is complicated, so an indirect hydrogen cooling system without a waterway is expected for a large-capacity turbine generator. When the highly thermal conductive mica insulating system would be applied to hydrogen cooling generators, it is possible to expand power capacities of generators. In this paper, I report the development of a mica insulating tape indicating the thermal conductivity 2 times higher than the conventional products.

2 Characteristics of the product

- Thermal conductivity twice as high as conventional tape.
- Development of 2 types of highly thermally conductive insulating tape including dry type for vacuum pressure impregnation other than prepreg.

3 Background of the development

Our company has been engaged in development works in both fields of resin and filler for insulation material with highly thermal conductivity by focusing on the development of insulating adhesive sheet and other products for use in power device²⁾. During the development process, we established a technology for self-aligning epoxy resin during curing process with high thermal conductivity, and filler dispersion technology to optimize balance between thermal conductivity and insulation property with a trade-off relationship with thermal conductivity. Then, with the intention to break into the field related to social infrastructure, we promoted studies on thermal conductivity improvement for mica insulating tape to be used in a generator, which was selected as a target and our highly thermally conductive material technology can be helpful. Especially since high level insulation of mica insulating tape is required for applications in a generator; filler shape was optimized and homogeneous dispersion technology was developed and applied to prevent electric field concentration.

4 Details of the technology

(1) Material design concept

Mica insulating tape has a two-layer structure constituted of a mica layer and a glass cloth impregnated with resin as shown in **Figure 1**.

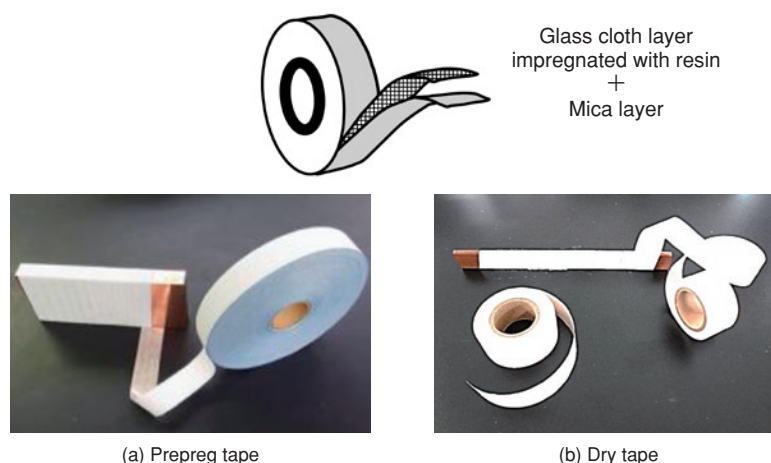


Figure 1 Developed highly thermal conductive mica insulating tapes

Prepreg tape as shown in **Figure 1(a)**, wherein mica layer is fully impregnated with resin, shall be wound around a coil multiple times, then directly used for fabrication by press molding and curing. On the other hand as shown in **Figure 1(b)**, dry tape, which is not impregnated with resin, shall be wound around a coil multiple times, immersed in low viscosity resin solution, impregnated with resin under vacuum-pressure, then used for fabrication by press molding and curing. Our company developed two types (prepreg and dry type) of mica insulating tapes with high thermal conductivity to meet needs of both processes.

(2) Characteristics of the material

Sixteen layered cured prepreg and dry tape insulating laminates were prepared and thermal conductivity of both cured insulating laminates were measured by steady state thermal conductivity measurement method with results shown in **Figure 2**. We confirmed levels of thermal conductivity of both cured insulating laminates were twice as high as that of comparative insulating laminate having the same structure using conventional tape, to which, however, our highly thermally conductive resin technology was not applied. Both prepreg and dry tape cured insulating laminates had the same level of insulating performance as that of the comparative laminate.

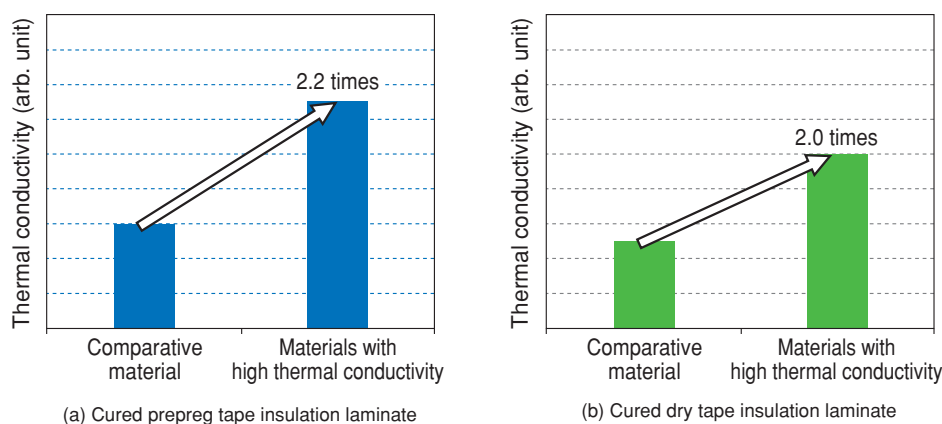


Figure 2 Thermal conductivities of cured mica insulating laminates

5 Future Business Development

- Development of tapes having 5 times higher thermal conductivity using high thermal conductive self-aligning epoxy resin

【References】

- 1) Hiroaki Tomiki et al., Toshiba Review 65 (2), pp.48-51 (2010)
- 2) Yoshitaka Takezawa, Hitachi Chemical Technical Report, 53, pp.5-10 (2009)

Advanced Thermal Insulator Using Inorganic-Organic Hybrid Porous Materials

Masato Miyatake Tomohiko Kotake

Frontier Technology Development Center,
Tsukuba Research Laboratory,
New Business Development Headquarters

1 Abstract

With the growth of superconducting technology and the spread of liquefied natural gas and hydrogen in recent years, the use of cryogenic liquid is increasing rapidly. Generally, vacuum multi-layer insulation materials called “Super-Insulation” are applied for keeping ultra-low temperatures in these fields and further insulation performance is urgently required. We focused on nano-porous materials which are suitable for insulation layers of Super-Insulation and developed inorganic-organic hybrid porous materials which realize ultra-low thermal conductivity and flexibility. The developed Super-Insulation using these hybrid porous materials for insulation layers shows the superior heat-insulating property under a vacuum condition on a liquid nitrogen tank.

2 Characteristics of the development product

- Excellent heat insulating properties compatible with flexibility.
- Heat insulating material can be thinned down.
- Excellent workability by integration of reflective layer and heat insulating layer.

3 Background of the development

Evacuated multi-layer insulation called “Super-Insulation” is used to keep cryogenic liquid such as liquid nitrogen, helium and hydrogen cold. Super-Insulation usually consists of reflective layer (such as aluminum foil and deposited aluminum film) and heat insulating layer constituted of resin mesh or non-woven fabric; these layers are laminated alternately and used under a vacuum condition. In response to current trends toward reduction of energy losses and narrowing available space, we are required to further improve heat insulating properties of Super-Insulation and make it thinner.

We focused its attention on nanoporous material that has lower thermal conductivity than resin mesh or non-woven fabric as a heat insulating layer for Super-Insulation. Heat insulating properties of inorganic nanoporous material can be significantly improved by controlling porosity and nanostructure; however, its brittleness made film formation and handling difficult. Given such a situation, we tried and developed inorganic-organic hybrid porous materials having both high insulation capabilities and flexibilities; we eventually incorporated them into Super-Insulation.

4 Technical details

Characteristics of inorganic-organic hybrid porous material are shown in **Table 1**. Internal structure of inorganic-organic hybrid porous material observed by scanning electron microscopy is shown in **Figure 1**.

Developed inorganic-organic hybrid porous material has an average fine pore diameter of 20 nm and forms 3D-nanonetwork structure. Also, by incorporating flexible skeleton into this hybrid porous material, its thermal insulating properties become compatible with flexibilities that were impossible for conventional inorganic nanoporous materials or composite materials.

Table 1 Characteristics of hybrid porous materials

Item	Unit	Characteristic value
Porosity	%	80-90
Average pore diameter	nm	20
Thermal conductivity	W/(m · K)	0.020
Compressive modulus of elasticity	MPa	0.1-0.4

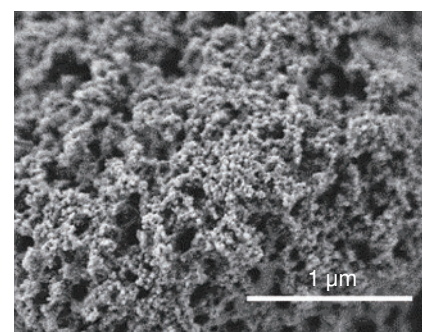


Figure 1 SEM image of hybrid porous materials

Structure of Super-Insulation using inorganic-organic hybrid porous material as a heat insulation layer is shown in **Figure 2**. Our developed Super-Insulation has a structure integrating both reflective and heat insulating layers wherein inorganic-organic hybrid porous material was coated on deposited aluminum film and shows good workability. It also has an excellent flexibility and will not cause cracks in the heat insulating layer during fabrication. Measured results of heat insulating properties using vertical liquid nitrogen tank (-196°C) under the vacuum condition are shown in **Figure 3**. By using our developed Super-Insulation, the thickness of heat insulation layer and the heat flux can be reduced by 50% or more compared to conventional materials using resin mesh for heat insulation layer while maintaining the same number of layers.

Our developed inorganic-organic hybrid porous material can be formed into a coating film on any substrate other than aluminum and processed into powder form (**Figure 4**). Thus, this material can be used in applications including not only cryogenic equipment but also a wide variety of applications requiring high heat insulating capability.

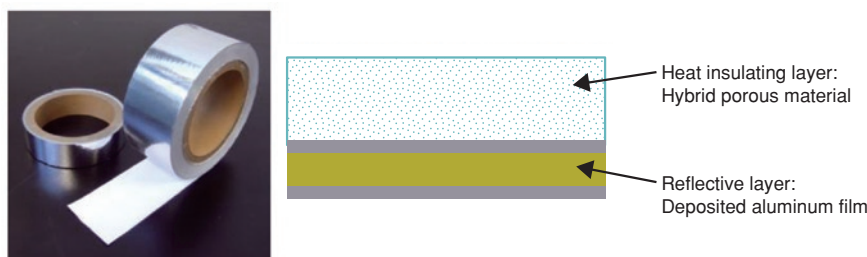


Figure 2 Components of our Super-Insulation

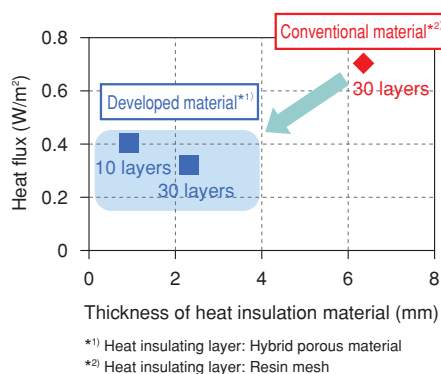


Figure 3 Heat insulating properties under a vacuum condition on a liquid nitrogen tank

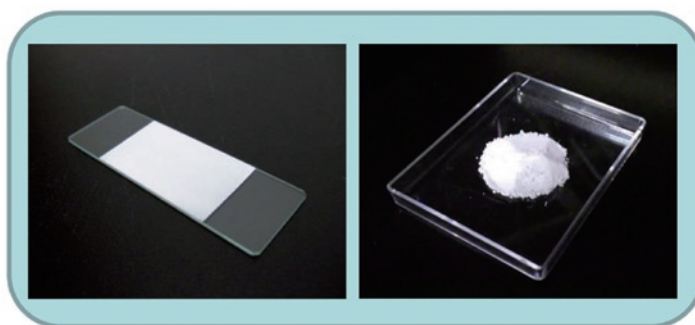


Figure 4 Appearance of coating and powder

5 Future Business Development

- Sales promotion of newly developed products
- Find new applications for inorganic-organic hybrid porous material

[References]

1) NEDO Commentary (2010) *Superconducting Technology*

2) NEDO (2014) *White Paper on Hydrogen Energy*

Halogen Free and Low Transmission Loss Multilayer Material for Next Generation High Speed Applications: “MCL-LW-900G/910G”

Masayuki Nakano Keita Johno Toshiyuki Iijima

Laminate Materials R&D Dept.,
Advanced Performance Materials R&D Division,
Advanced Performance Materials Business Headquarters

1 Abstract

The information communication terminal devices using communication networks are advancing transmission capacity and speed. As a result, the transmission speed of the network devices also is becoming faster. So, high-speed and high-frequency response of the PWB is also indispensable. Especially in the high-speed digital field, the demand for PWB material with excellent high frequency characteristics than the PWB materials of current low-transmission-loss is increasing¹⁾. In this situation, we have developed a new halogen-free low transmission loss material “MCL-LW-900G” for next generation high-speed networks.

2 Characteristics of MCL-LW-900G/910G

- Unique characteristics that can contribute to the reduction of transmission loss.
- High heat resistance and high glass transition temperature (Tg).
- Environmentally compliant material incorporating halogen-free flame retardant.

3 Background of the development

In recent years as shown in **Figure 1**, transmission capacity, transmission speed and frequency of digital signals handled by information and communication electronics equipment such as computers, servers and routers have become larger, faster and higher, respectively. In response to such technical trends, it is crucial to change the functional performance of printed circuit boards used in such equipment to meet the requirements of high-speed high-frequency communications. So far, our company has introduced MCL-FX-2 and several other multilayer materials used for high-frequency applications.

Under such circumstances, the transmission rate of digital signals handled by network communication equipment for next-generation high-speed applications may come down to 25 Gbps. To satisfy this transmission rate, we estimated a parameter of high-frequency property to be Df of 0.0035 (at 10 GHz) or less from market requirements, but functional performance of conventional base materials are not good enough to satisfy such Df. Against such a background, we developed base materials that can

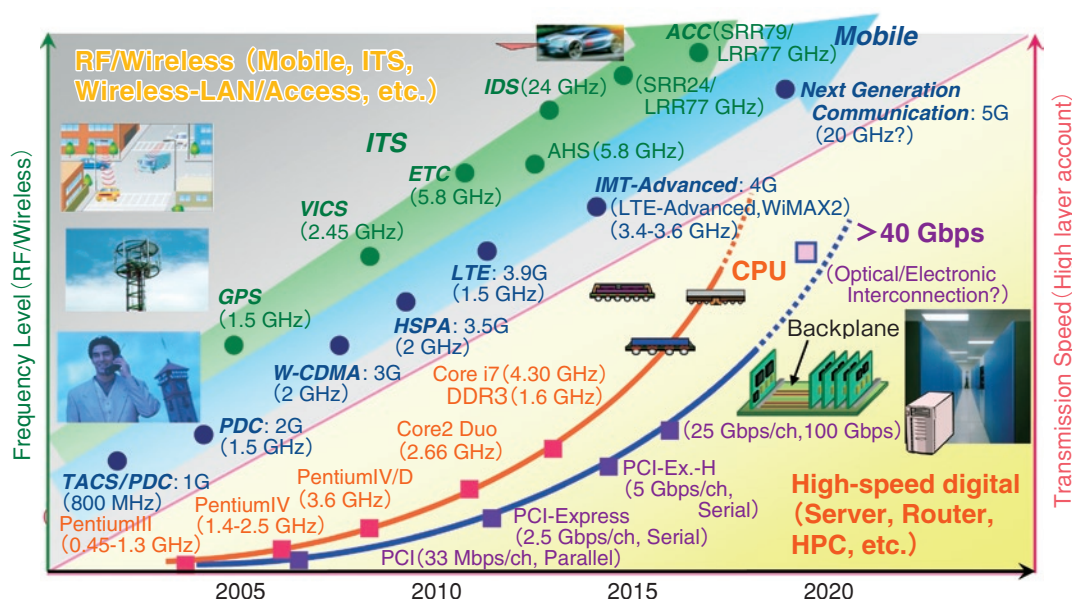


Figure 1 Changes in the transmission rate of the electronic device

accommodate a wide range of requirements for next-generation high-speed and high-frequency applications with the help of our own proprietary resin property modification technology.

4 Technical details

1. MCL-LW-900G design concept

We developed a resin with a low dielectric constant and high heat resistance with the help of our own proprietary resin property modification technology, and we used it for MCL-LW-900G. Then, we selected halogen-free flame retardant with high thermal decomposition temperature, together with small drop in glass transition temperature (T_g) and dielectric constant. We also used copper foil having a finely roughened surface to reduce conductor losses.

2. General characteristics of MCL-LW-900G

General characteristics of MCL-LW-900G are shown in **Table 1**. MCL-LW-900G (E-glass cloth, copper foil: RT foil) has Dk = 3.57 and Df = 0.0044 Dk at 10 GHz. MCL-LW-910G (low-dielectric glass cloth, copper foil: HVLP foil) shows Dk = 3.32 and Df = 0.0028.

Further, MCL-LW-900G shows excellent heat resistance such as TMA T_g: approx. 200°C and T-300 min. ≥ 60.

Table 1 General properties of MCL-LW-900G/910G

Item		Unit	LW-900G	LW-910G	FX-2	Teflon material
Resin system		—	Thermosetting		Thermosetting	Thermoplastic
Glass type		—	E-glass	Low Dk glass	E-glass	E-glass
Flame retardant chemicals		—	Halogen free		Halogen	—
Dk (JPCA-TM001)	10 GHz	—	3.57	3.32	3.45	2.62
Df (JPCA-TM001)	10 GHz	—	0.0044 ^{*1}	0.0035 ^{*1} 0.0028 ^{*2}	0.0058	0.0038
Copper foil peeling strength (18 μm)	RTF	kN/m	0.75	0.75	0.60	1.2 (general purpose copper foil)
	HVLP		0.63	0.63	—	
T _g	TMA	°C	198	198	185	30
CTE	XY	ppm/°C	13	13	15	18
	Z (α1)		40	40	47	105
	Z (α2)		250	250	110	310
Resistance to soldering heat testing	288°C	s	> 300	> 300	> 300	> 300
T-300	TMA	min	> 60	> 60	> 60	—
Flame resistance	UL-94	—	V-0	V-0	V-0	V-0
Reliability (CAF, IST, etc.)	—	—	Good	Good	Good	—

^{*1, *2} Values calculated from the results of measured energy loss-rate (RT foil: Rz ≒ 3 μm, HVLP foil: Rz ≒ 1.2 μm).

3. Transmission characteristics of MCL-LW-900G

Results of measured transmission loss of MCL-LW-900G below 20 GHz are shown in **Figure 2**. MCL-LW-900G has excellent transmission characteristics as shown by MCL-LW-910G (HVLP foil) with transmission loss of 32.4 dB/m at 20 GHz which is lower by 15 dB/m than that of MCL-FX-2, suggesting that it can contribute to the reduction of transmission loss.

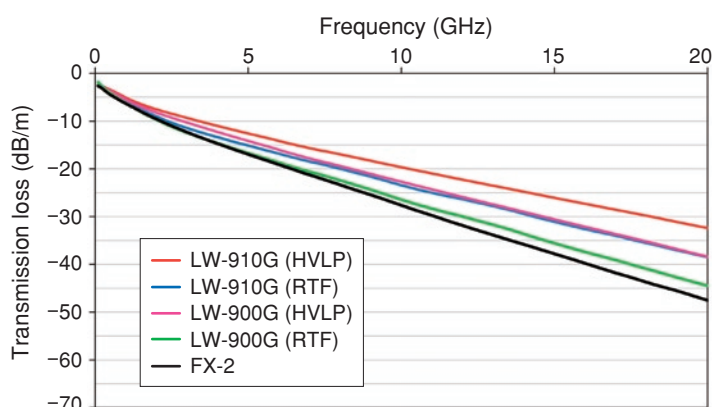


Figure 2 Transmission loss measurement results

5 Future Business Development

- Development of BU film for vehicle mounted millimeter wave radar

[Reference]

- 1) Kazutoshi Danjobara, *Preliminary Draft Collection of JPCA Show2014NPI Presentation*, pp.21-23

Reactive Hot Melt Adhesive for Fine Dispensing

Koji Suzumura Kazuyuki Magome Soichiro Komiya Chika Kuramochi

Polymer Materials R&D Dept.,
Advanced Performance Materials R&D Division,
Advanced Performance Materials Business Headquarters

1 Abstract

In recent years, narrow-bezel display is applied for various smart phones. But it is difficult to apply double-side stick tape because adhesion strength and punching accuracy are insufficient at this application. Therefore new process which use liquid-type adhesive has been investigating at device manufactures. HC has newly developed reactive-hot-melt adhesive Hi-PURSHOT 8958 and 4777 available for narrow-bezel structure. These materials shows shorter cure time, fine dispense ability and good adhesion properties to various substrates such as metals, glass, and plastics. Hi-PURSHOT 4777 also has a light-shading ability and it is effective to avoid the leakage of light wave.

2 Characteristics of the product

- Non-solvent, one-component moisture curable hot melt adhesive
- Fine-line gluing by dispenser is possible (< 0.4mm)
- Able to provide waterproofing ability (comparable to IPX-7rating)

3 Background of the development

Hitachi Chemical group developed reactive hot melt adhesive products, the Hi-Bon series, using its own polyester resin synthesis and urethane modification technologies, and sells them for use in various applications such as construction material, bookbinding, fiber and automobiles¹⁾. Subsequently, we made multiple improvements in the adhesive properties to expand the use of our products into the electronics equipment market, and introduced Hi-PURSHOT, a reactive hot melt adhesive for fine-line dispensing, to the market in 2010. This product has already been selected by many companies for waterproof digital cameras and waterproof smart phones because of its fine-line dispensing and waterproofing capabilities. Application to a narrow-bezel structure, however, required us to provide better adhesion to various frame body materials, falling impact resistance and light-shading effect. So, we re-examined the material design to use a polyol component as a main raw material and successfully developed Hi-PURSHOT 8958 and 4777, applicable to a narrow bezel structure.



Figure 1 Appearance of Hi-PURSHOT



Figure 2 Appearance of dispensed sample

4 Details of the technology

1) Characteristics of Hi-PURSHOT 8958, 4777

Product characteristics and characteristics of the cured layer are shown in **Table 1**. Hi-PURSHOT 8958 and 4777 have higher shear strength of cured layer adhered on various substrate materials. These products are also designed so as to provide higher elongation and strength of cured layer to enhance falling impact resistance. Again, Hi-PURSHOT 4777 has a high visible light shading capability with light transmittance equal to or less than 0.01% measured at 100 µm thickness.

Table 1 General properties of Hi-PURSHOT

Product name		Unit	8944	9753	8958	4777
Applied substrate		—	For plastic substrate	For metal/glass substrate	For metal/glass/plastic substrate	For metal/glass/plastic substrate
External appearance		—	White/Half-transparent	White/Half-transparent	White/Half-transparent	Black/Light-shading
Viscosity (110°C)		Pa · s	5	7	6	8
Open time min.		min	2	4	2	2
Characteristics of cured layer	Tensile strength	MPa	30	5	12	11
	Elongation at break	%	690	1300	1300	1200
	Young's modulus	MPa	60	25	40	20
	Visible light transmittance* ¹⁾	%	—	—	—	< 0.01
	Waterproof ability	—	Comparable to IPX7	Comparable to IPX7	Comparable to IPX7	Comparable to IPX7
Shear bond strength* ²⁾	Polycarbonate resin	MPa	4.4	3.8	4.4	4.0
	Acrylic resin		3.1	1.9	3.4	2.6
	Stainless steel		1.2	2.8	2.6	2.6
	Aluminum		1.0	3.5	3.6	3.7
	Glass		1.7	3.2	3.2	2.7

*¹⁾ Averaged visible light transmittance measured at 100 μm thickness *²⁾ Adhesive layer thickness: 50-70 μm, Pulling speed: 10 mm/min

2) Ability to moisture cure

The relationship between time to moisture cure and shear bond strength is shown in **Figure 3**.

Development products show faster curing than conventional ones, for example, 2 hours for Hi-PURSHOT 8958 and 4 hours for Hi-PURSHOT 4777 are adequate to generate enough shear bonding strength.

As a result, lead time at clients can be reduced substantially.

3) Waterproof ability

Results of waterproofing test are shown in **Table 2**, and external appearances after testing are shown in **Figure 4**.

No water penetration was observed after hot-melt-dispensed and pressure-bonded test pieces with dispensed line width of 0.5 mm and bonded layer thickness of 0.1 mm were placed 1 m under water for 30 min.; it showed excellent water proofing ability.

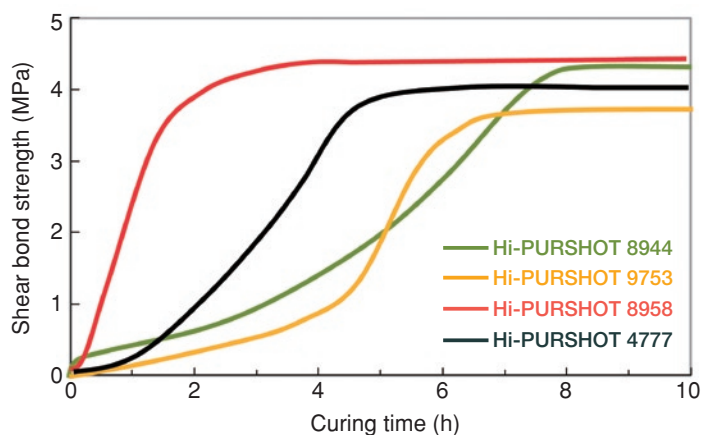


Figure 3 Behavior of shear bond strength

Table 2 Water-proof ability

Product name	8958	4777
Waterproof ability (comparable to IPX-7)	No water penetration	No water penetration

Shape of test piece

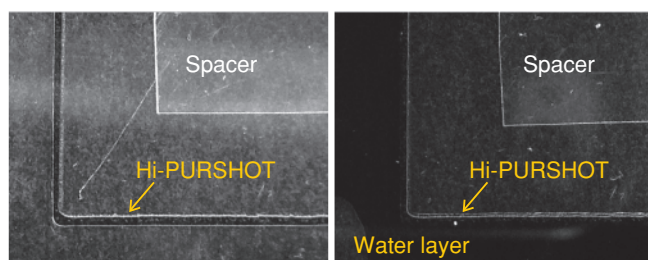
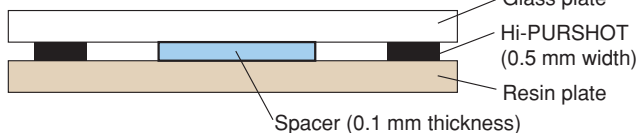


Figure 4 Appearance after water-proof test (Hi-PURSHOT 4777)

5 Future Business Development

- Development of material with increased bond strength and higher falling impact resistance while pursuing our goal toward even more fine line dispensing

[Reference]

- 1) Tatsuya Amano, Journal of The Adhesion Society of Japan, 40(6), p.265-26 (2004)

Advanced Analysis of Yellowing Transparent Film

Akihiro Unno Hoko Suto Kosuke Iwamoto

New Business Development Headquarters, Tsukuba Research Laboratory

1 Abstract

The market for transparent films for electronic devices and touch panels is expanding every year. To maintain transparency of the film over a long period, inhibition of yellowing is one of the most important problems^{1), 2)}. In order to develop an advanced transparent film, the yellowing mechanism has to be elucidated. However, the analysis of yellowing compounds in the film is difficult owing to the small amount. So, we developed a new analytical method to clarify the structure of yellow compounds in this study. Our method uses one of two different techniques based on whether the yellow compounds can be extracted by a solvent or not. In both cases we succeeded to clarify the structure of yellow compounds using the established methods.

2 Feature of analysis technique

- Analysis technique for yellowing compounds that is adapted to analysis sample
- Analysis technique that can distinguish yellowing compounds from other constituents with high probability
- Method of structural analysis capable of evaluating minute amounts (100 ppm) of yellowing compounds

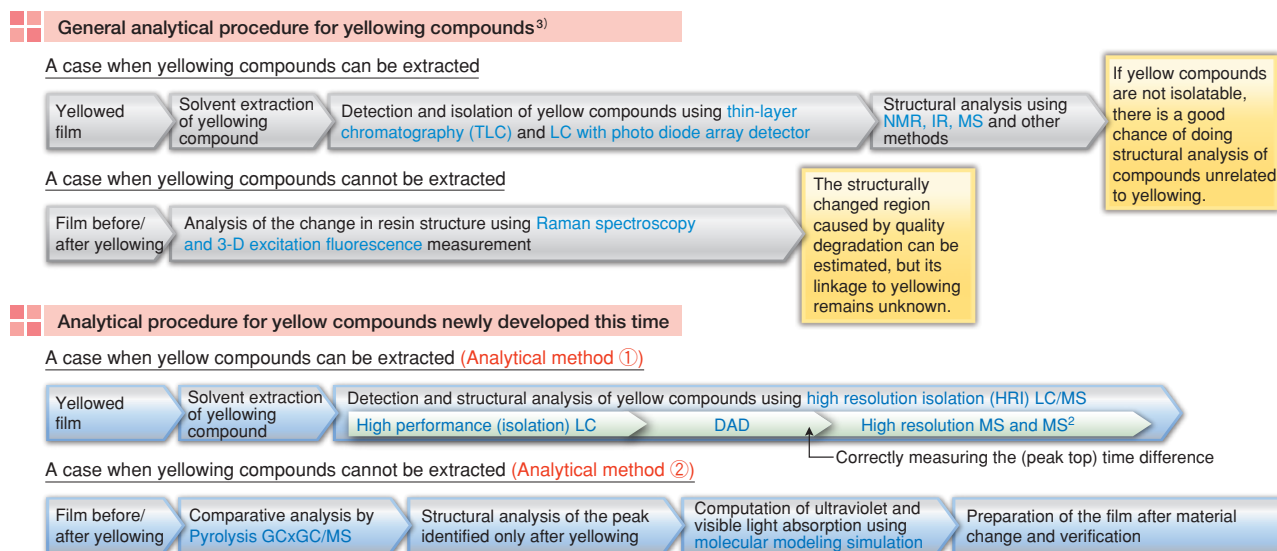


Figure 1 Comparison of a general analytical method of yellow compounds in yellowed film and the developed method

3 Background of the developments

Yellowed film that was the analytical target of this study was transparent film for use in touch panel and vehicle mounted display modules. Enough additives could not be used because transparent films for touch panel turned yellow after exposure. We received requests to elucidate the yellowing mechanism to help promote the development of films that can contain sufficient amounts of additive. In the case of transparent film for use in a vehicle-mounted display module, the mechanism of yellowing must be clarified in advance to make a policy decision on composition modification. So, we started development of analytical techniques applicable to each film to clarify the structure of yellowing compounds.

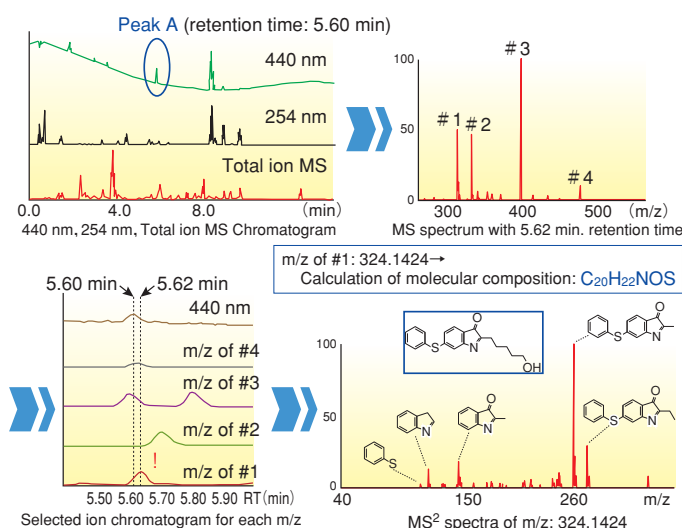
4 Technical details

In this study, we developed new multiple-track analytical procedures to meet situations when yellowing compounds can be extracted or not extracted as shown in **Figure 1**. Examples, where our developed analytical methods are applied, are shown below.

- 1) As an example for the case when yellow compounds can be extracted, we introduce an example of analytical procedures for yellowing compounds in transparent film for use in touch panels. When extracted solution of yellowing compounds was analyzed using an analytical method (1), an absorption peak at 440 nm was identified by photo-diode array detector (**Figure 2**). This

peak was considered as yellowing compounds and the MS spectrum to analyze was that located at a position with the same retention time shift between photo-diode array detector and mass spectroscopy (0.02 min. in this case). However, as shown from appearance of the mass spectral peaks, there were many compounds that eluted at the same retention time while each compound was separated by LC, so it was difficult to identify yellowing compounds from a particular m/z value. To distinguish between these m/z values, we wrote selected ion chromatograms for each m/z and determined the m/z with time shift of 0.02 min. between the selected ion chromatogram and the peak top at 440 nm as yellowing compounds. Once the m/z value to analyze was identified, we analyzed the MS² spectrum of that peak and determined the structure of a yellowing compound from fragmentation peaks. By correctly identifying the structure of yellowing compounds as exemplified in this case, we could figure out the structure of additives and blending ratios that would not produce yellowing compounds.

- 2) As an example of the case when yellowing compounds cannot be extracted, we introduce an example of analytical procedures used to identify yellow compounds in transparent film for use in a vehicle mounted display module. Only peaks specific to yellowing compounds in yellowed film were extracted after films before/after yellowing was analyzed by pyrolysis GC/MS (**Figure 3**). Then, we identified the structure of pyrolyzed material with help of the structural analysis of peaks appearing only in yellowed film, employing structural information from mass spectrometry. The determined structure of yellowing compounds can be considered as the one evolved during the weathering test. To deduce the intramolecular structure causing yellowing, we computed the absorption wavelength and oscillator strength of each compound by molecular modeling simulation (**Figure 3**). As a result, we found pyrolyzed material having the structure shown in **Figure 3** could possibly be seen as yellow and deduced the structure of pre-weathering exposure chemical compound. To verify such a finding and estimation, we prepared a film not containing materials deduced to be the source of yellowing, and confirmed the lower yellowing level after weathering test, and no yellow compounds were detected by pyrolysis GCxGC-MS. Thus, even when yellowing compounds could not be extracted, we were able to estimate the source material of yellowing once a particular molecular structure of pyrolyzed material was determined as a source of yellowing and were therefore able to deduce the structure and blending ratio of additives that would not produce such yellowing compounds.



Cu Paste for Low Temperature Metalization Process

Kosuke Urashima

New Business Development Headquarters,
Tsukuba Research Laboratory

1 Abstract

Printed electronics are expected to be used as environmentally compatible material, because the manufacturing cost is lower and the amount of the metal waste amount is less than the conventional photolithography method. Recently, silver is mainly used as the conductive paste. However, the application of silver paste has been limited to the part of the device, because of the high price and the ion migration in fine wiring. Therefore, the replacement of silver to the cheaper and more reliable copper is expected. We developed a copper paste for low temperature metalization process to be capable of wiring on the resin film.

2 Characteristics of the new product

- Possible to sinter at 150 °C or lower temperature
- Volume resistivity of 17 $\mu\Omega \cdot \text{cm}$
- Possible to form 5 μm thick membranes by screen printing

3 Background of the development

Since 2003, we have been developing the copper oxide that can form a compact copper layer by sintering in a reducing gas atmosphere¹⁾. However, users have been requesting a material that would be much easier to treat and thus some handling issues regarding this copper oxide were pointed out by them. For example, it was the requirement of the atmospheric condition of reducing gas and difficulty to make thicker film. Therefore, we started the development of copper particles in 2013 by focusing on low melting point copper particles which was obtained by reducing mixture of copper carboxylate and amine compound. In 2014, we established the synthesis process of relatively low temperature metalized copper particles by optimizing the mixture composition.

4 Technical details

The appearance of sintered copper membrane samples after screen printing of the developed product on resin film is shown in **Figure 1**. Properties of a metalized layer are shown in **Table 1**. With the application of the copper paste, it is possible to form electric circuits on heat-sensitive materials such as PET film and is expected to be able to apply flexible devices.

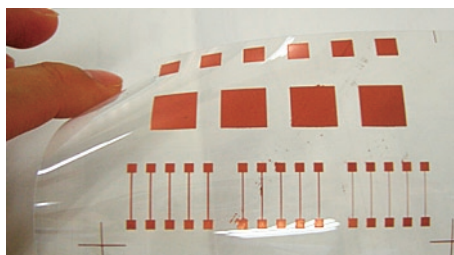


Figure 1 Appearance of Copper Paste after Sintered on Resin Film

Table 1 Cu Paste Properties

Item	Unit	Development product
Thickness of screen printed film after sintering	μm	1~5
Volume resistivity (sintering condition: 140 °C and 1 h, N ₂ gas atmosphere, reduced pressure)	$\mu\Omega \cdot \text{cm}$	17

Our copper particle size is controlled in the sub-micron range (100-200 nm). Generally, the smaller the particle sizes of gold or silver, the lower the melting point. Therefore, nano gold or silver particles can be metalized at lower temperature than the melting point of bulk. In the case of copper particles, however, most of copper particles do not fuse and thus volume resistivity is worse than the sub-micron size as shown in **Figure 2**. We estimate that small copper particles are likely to be oxidized due to increasing surface area and thus less conductive although the melting point might be lower. Since developed copper particles has not only low melting point also oxidation resistance by optimizing particle sizes, it is capable of metalization at low temperature. The conductive membrane made of our copper paste indicates lower volume resistivity after low temperature metalization because the copper particles have appropriate particle size for both features. In the future, we will continue to develop this material and release it on the market of printed electronics.

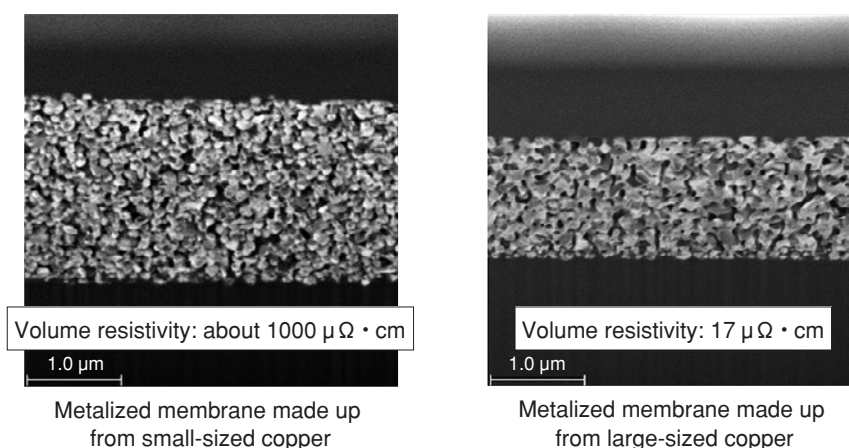


Figure 2 Cross-sectional Images of Cu Paste after Sintered

5 Future Business Development

- Deployment into the market of printed electronics
- Investigation of new applications

[Reference]

- 1) Y. Kumashiro, H. Nakako, K. Kuroda, K. Yamamoto, "Printing Materials for Flexible Electronics Device", Proceedings of International Conference on Electronics Packaging 2010, TB3-1 (2010)

Editor's Note

Responding to the outcomes of the UN climate conference (COP21) and the Paris Agreement, a guideline for global warming countermeasures, we foresee environment and energy saving measures will progress globally. Additionally, since separate countermeasures for each region are required, we will do our best to expand R&D activities into materials in various fields.

In the first half of the current issue, we picked special topics of technology for reducing fuel consumption of cars, among technologies related to environmental and energy savings. Since fuel efficiency becomes a key factor even under the new auto-related tax measures effective from April, 2014, we will continue development of new technologies to further improve automotive fuel efficiency, capitalizing on the unique characteristics of our materials. In the second half of the current issue, we introduce technologies that can contribute to energy savings in various fields in the future.

In closing, we hope the results of activities fulfilling our company's philosophy "Contribution to the society through superior product development to explore new era." will be of help for global warming countermeasure.

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.58

March 2016

Hitachi Chemical Co., Ltd.

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

New Business Development 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

© 2016 Hitachi Chemical Co., Ltd. All rights reserved.
