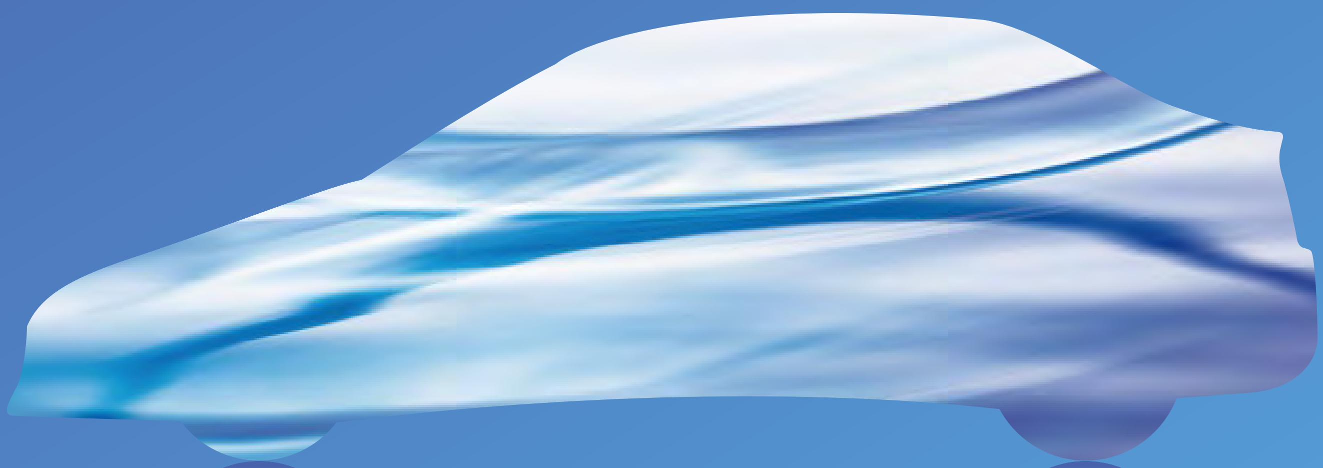
Silicone Materials for Automobiles



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Shin-Etsu Silicone

Silicone Fluids and Secondary Products for Automotive Applications

The auto industry has been unremitting in its pursuit of development of automotive technologies to improve safety, comfort, and fuel efficiency. Silicones have frequently been used as automotive materials, and Shin-Etsu has been using the latest technologies to develop products to meet evolving needs. In these pages we will present examples of some typical applications, mainly featuring silicone fluids and their secondary products.

Introduction

In recent years, automakers have taken efforts to make safer vehicles that are more comfortable and eco-friendly by adding car navigation systems, sensors and other features, while making vehicles lighter and more fuel-efficient. In this article, we will discuss some of the places where silicone fluids and their secondary products (emulsions, oil blends) are used. We will also discuss auto chemicals and subsidiary materials used in the manufacture of auto parts.

1. In-vehicle materials

1-1. Sensor fill materials, damper materials KF-96

For years, dimethyl silicone fluid (KF-96) has been used as a gloss enhancer for automotive waxes, as a fill material in rubber dampers, and a damping medium in instrument meters. Today, it is used in more wide-ranging applications, as a fill material in sensors and a damping medium for auto seats.

1-2. Power transmission components (fan couplings, etc.) KF-967, KF-9006

These heat-resistant silicone fluids have enhanced oxidation stability, achieved by adding heat-resistance improvers to dimethyl silicone fluid. They are used as fan coupling fluids and in other torque transmission applications, and as a heating medium in automobiles **(Table 1)**.

1-3. Modifier for synthetic leather seat materials Double end-capped carbinol-modified fluids Single end-capped diol-modified fluids

Carbinol-modified siloxanes can be used to improve the slickness and texture of urethane-based synthetic leather seats. The double end-capped carbinol types (KF-6001, KF-6002, KF-6003) improve cold resistance and texture, while the single end-capped diol-modified types (X-22-176 series) improve slickness.

1-4. Weather strip coating agent X-32-1291

X-32-1291 is a solvent-based coating agent for sponge type rubber weather strips. It helps prevent wear and reduces squeaks when windows are opened and closed.

1-5. Modifier for tires and rubbers KBE-846

Tires compounded with silica are known to help boost fuel economy and provide better grip on wet roads. Unfortunately, silica-compounded tires wore out quickly and were therefore not practical. Later, KBE-846 was developed by researchers who realized that sulfide silane could be used to improve the wear life of silica-compounded tires.

1-6. Plastic & rubber modifiers Master pellets and acrylic silicone powders

Silicone master pellets are plastics compounded with highly polymerized siloxanes (30-50% by mass). Blended into plastics at roughly 0.1-2% concentration, they improve mold release properties, which helps boost molding speed. In addition, the silicone gradually bleeds out to provide a sustained lubrication effect. Acrylic silicone powders have good miscibility with PVC resin, EPDM and other synthetic resins. Also, the silicone component on the powder surface acts to improve tribological properties and provide anti-blocking properties, anti-wear properties and reduce noise created when parts rub together (Photos 1 & 2).

2. Automotive chemicals, other applications

2-1. Glass water repellents X-24-9418

The fluorosilicone water repellent X-24-9418 is fluorosilicone in an isopropyl alcohol solution. Used to treat various substrates, at

Table 1: Silicone fluids for fan couplings

Parameter \ Product name	KF-967	KF-9006
Appearance	Tan transparent liquid	Tan liquid
Viscosity at 25°C mm²/s	1,000-15,000	6,000-20,000
Features	For closed systems Good viscosity-temperature characteristics	For closed systems Good heat resistance
Base fluid type	Dimethyl silicone	Methylphenyl silicone
Heat-resistance improver	Aromatic amine	Aromatic amine

(Not specified values)

Table 2: Glass water repellents

Parameter \ Product name	X-24-9418
Appearance	Colorless transparent liquid
Viscosity at 25°C mm²/s	2.8
Specific gravity at 25°C	0.794
Active ingredient %	3
Diluent	Isopropyl alcohol
Water contact angle*	105°
Hexadecane contact angle*	55°
Water fall angle*	15°

* On glass substrate, after drying for 1 day at room temperature. (Not specified values)

Photo 1: Electron micrograph of acrylic silicone powder

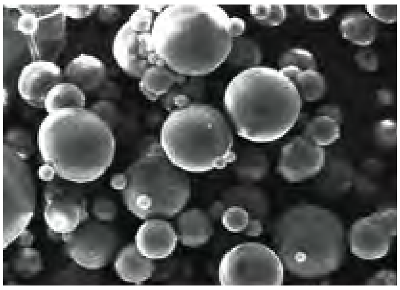


Photo 2: Silicone master pellets

Table 3: Rubber & plastic molding release agents

Parameter \ Product name	KM-862T	KM-740T	KM-742T	KM-722T	KM-244F
Appearance	Creamy white liquid	Creamy white liquid	Creamy white liquid	Creamy white liquid	Pale yellow liquid
Active ingredient %	60	38	28	30	100
pH	4.0	6.0	6.0	7.0	—
Ionicity	Nonionic	Nonionic	Nonionic	Nonionic	—
Features	High viscosity dimethyl silicone emulsion	Low viscosity dimethyl silicone emulsion	Low viscosity dimethyl silicone emulsion	Medium viscosity dimethyl silicone emulsion (contains xylene)	Polyether silicone

(Not specified values)

room temperature it forms a uniform film with exceptional water repellency, oil repellency, release properties, and antifouling properties **(Table 2)**.

2-2. Car waxes and car wash detergents

Dimethyl silicone fluid (KF-96) has long been used as a gloss enhancer for car body waxes, and more recently as a tire gloss enhancer. For certain applications, it is mixed with fluids containing high-molecular-weight silicone resin (KF-9021, KM-9717) or acrylic silicone (X-22-8000, -8100 series) to improve film durability.
In car wash machines, the wax component is often an amino silicone emulsion or other silicone with amino groups, which improve adsorption onto car body panels. (Polon MF-14EC, X-52-800 series)

2-3. Tire & hose mold release agents, aluminum die-casting release agents

Silicone emulsions are used as release agents when molding tires, radiator hoses, fuel hoses, and other rubber parts **(Table 3)**. Alkyl- or alkyl-aralkyl-modified silicone fluids (or their emulsions) are used as release agents for aluminum die-casting **(Table 4)**.

Table 4: Aluminum die-casting release agents

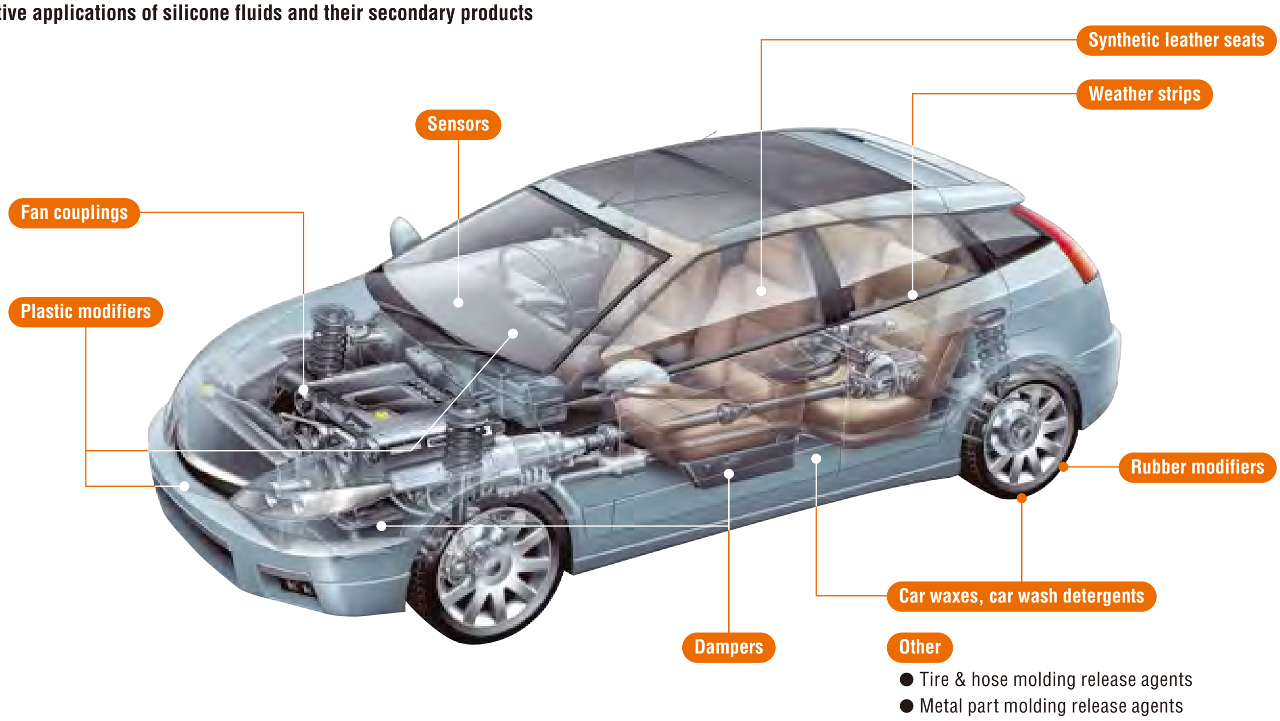
Parameter \ Product name	X-22-1877	X-52-8051	SILCAST-U
Appearance	Pale yellow transparent liquid	Creamy white liquid	Creamy white liquid
Active ingredient %	100	50	32
Features	Alkyl-aralkyl silicone	Alkyl-aralkyl silicone Weakly ionic emulsion	Alkyl silicone Weakly ionic emulsion

(Not specified values)

Conclusion

Automobiles are complex machines manufactured using advanced plastics and fabrics, and sophisticated mechanical, electric and electronic components. These parts have to last ten years or more. Most of the materials that are currently under development or that have been used for automotive applications have been developed in cooperation with automakers and auto parts manufacturers, and Shin-Etsu is simply not at liberty to discuss them in this publication.
Without question, specially designed silicones will continue to be used in places with unique requirements. Shin-Etsu is committed to development of materials that meet diverse user needs, and we look forward to hearing your ideas and requests in this regard.

Automotive applications of silicone fluids and their secondary products



Silicone Elastomers for Automotive Applications

With the quest for higher performance automobiles and the increased use of electronic components, the performance requirements for silicones and other raw materials are becoming ever more diverse and sophisticated. In this article, we will present liquid silicone rubbers designed for automotive applications, for the fixing and protection of parts, thermal interface, and other functions.

Introduction

As automobiles have become higher performance products, the use of electronic components has also increased. In some models today there are over 70 Electronic Control Units (ECU); silicone elastomers are used as sealing materials, adhesives and potting agents for these ECUs. Silicone elastomers provide exceptional durability and stable performance over a wide temperature range. In this article, we'll focus on car electronics as we present a number of liquid silicone rubber products.

1. Protecting components

In this section, we will discuss products designed for the protection of automotive components, including conformal coatings, potting materials and sealing materials, plus products designed to prevent sulfurization, which are attracting interest throughout the industry today.

Conformal Coatings

Conformal coatings are dielectric materials applied to electric and electronic components to protect from moisture, condensation and dust. Shin-Etsu has developed eco-friendly solventless products and low- and high-viscosity types. Different products can be applied in different spots, as needs dictate **(Table 1)**.

Potting Materials

Like conformal coatings, potting materials protect electronic components arranged on circuit boards from moisture, condensation and dust. Potting also helps reduce mechanical stress on electronic components caused by extreme temperatures and vibration. Regular silicone is called dimethyl silicone, and it features methyl groups attached to the side chains of the polymer. This type of silicone cannot be used in places where it will be directly exposed to gasoline or oils, but this weak point can be overcome by introducing trifluoropropyl groups into the side chains of the base polymer **(Table 2)**.

Case Seal Materials

Case seal materials are used for waterproofing, to protect the electronic components inside ECUs from damage. These silicones will be exposed to the outdoor elements for years, and thus must provide high bonding durability. What's more, by adding substances that capture acidic gases from auto exhausts, which include NOx and SOx, we have developed silicones that help ensure the performance of components over years of use **(Table 3)**.

2. Thermal Interface Materials

The transistors and ICs on circuit boards generate considerable heat. Silicones with high thermal conductivity are used to effectively radiate this heat. Because these silicones are applied directly to electric and electronic components, they have been designed with minimal amounts of low-molecular-weight siloxane, since this substance can cause faulty conduction at electrical contacts. Our lineup of thermal interface materials includes greases, adhesives and sheets. The properties of some typical thermal interface adhesives are shown in **Table 4**.

3. Fastening of parts

Many adhesives are used for the fastening of electronic parts and structural bonding. Some usage locations stay continually hot, while others are exposed to gasoline and other substances. Shin-Etsu has developed a lineup of adhesives to meet the requirements of diverse applications and manufacturing processes, so the user can select a product of the appropriate cure type for their specific needs **(see 4. Curing mechanisms)**.

Table 1: Conformal coatings

Parameter \ Product name	KE-1870	KE-1871	KE-3470	KE-3420
Viscosity mPa·s	400	800	70	700
Cure type	Addition	Addition	Condensation (acetone)	Condensation (acetone)
Cure conditions	150°C×0.5 h	150°C×0.5 h	23°C/50% RH × 7 days	23°C/50% RH × 7 days
Hardness, Durometer A	15	27	35	19
Volume resistivity TΩ·m	10	10	20	60
Relative dielectric constant, 50Hz	3.1	3.1	3	3
Dielectric dissipation factor, 50Hz	1.0×10^{-3}	1.0×10^{-3}	0.1×10^{-3}	3.0×10^{-3}

(Not specified values)

Electronic components potted with silicone gel

Table 2: Potting materials

Parameter \ Product name		KE-1056	FE-57	KE-1842	KE-200 CX-200
Cure type		Addition	Addition	Addition	Condensation (acetone)
Features		Cold-resistant, high penetration	Cold-resistant transparent gel	Low hardness	Rapid cure, good deep section curability
Appearance	Consistency	Liquid	Liquid	Low viscosity	Liquid
	Color	Slightly hazy	Light brown	White	Blue transparent, pale yellow translucent
Viscosity mPa·s		800	2000	4000	2800
Density g/cm3		0.98	1.28	1.00	1.01
Cure conditions		130°C×0.5 h	125°C × 2 h	120°C × 1 h	23°C × 72 h
Penetration		90	60	—	—
Hardness, Durometer A		—	—	13	25
Volume resistivity TΩ·m		8.0	0.02	1	60
Dielectric breakdown voltage kV		14	—	20	20
Relative dielectric constant, 50Hz		3.0	7.0	3.5	2.9
Dielectric dissipation factor, 50Hz		5×10^{-4}	1×10^{-2}	5×10^{-3}	3×10^{-3}

(Not specified values)

Table 3: Case seal materials

Parameter \ Product name		KE-1833	IO-SEAL-300	KE-1875
Cure type		Addition	Addition	Addition
Features		High heat-resistant	Releases less acidic gas	Reduced low-molecular-weight siloxane
Appearance (after cure)		Reddish brown	White	Black
Viscosity Pa·s		140	50	50*
Density g/cm^3		1.36	1.23	1.06
Hardness, Durometer A		33	31	26
Elongation at break %		350	270	380
Tensile strength MPa		3.4	2.8	2.5
Shear adhesive strength MPa	Glass	1.8	1.5	1.8
	Aluminum	1.8	1.5	1.8
	PBT	1.8	1.5	1.8
	PPS	1.8	1.5	1.8
Cure conditions		120°C × 1 h	100°C × 1 h	120°C × 0.5 h

✻ Shear viscosity 10^{-1} (Not specified values)

Table 4: Thermal interface adhesives

Parameter \ Product name		KE-3466	KE-3467	X-32-2020	KE-1867
Cure type		Condensation (acetone)		Addition	
Features		Reduced low-molecular-weight siloxane UL certified	Flame resistant, high thermal conductivity	Reduced low-molecular-weight siloxane	Reduced low-molecular-weight siloxane UL certified
Appearance	Consistency	Med. viscosity	High viscosity	High viscosity	Med. viscosity
	Color	White	White	Gray	Gray
Viscosity Pa·s		50	80	100	60
Density g/cm^3		2.80	2.95	2.83	2.92
Cure conditions		23°C/50% RH × 7 days	23°C/50% RH × 7 days	120°C × 1 h	120°C × 1 h
Hardness, Durometer A		88	90	78	75
Tensile strength MPa		3.1	3.6	1.8	2.1
Elongation at break %		30	30	30	60
Volume resistivity TΩ·m		2.9	2.5	1.0	1.2
Dielectric breakdown voltage kV/mm		24	25	23	23
Thermal conductivity W/m·K		1.9	2.4	1.9	2.2

(Not specified values)

4. Curing Mechanisms

There are four types of curing mechanisms for silicone elastomers, each with distinctive characteristics **(Table 5)**.

Addition-cure products

Generally, the cure temperature is around 120°C and cure time around one hour. Recently, manufacturers are working to develop products that cure more rapidly and at lower temperatures. Virtually no byproducts are released during the curing reaction.

Dual-cure products

A drawback of addition-cure products is that tin, nitrogen, phosphorus and sulfur compounds can interfere with curing. To address this, Shin-Etsu developed dual-cure products based on a combination of platinum addition/peroxide cure.

Condensation-cure products

These products cure by reacting with moisture in the air so that, unlike with addition-cure products, heating devices are unnecessary. These products are grouped according to the type of gas released in minute quantities during the cure reaction. Acetone-cure (i.e. acetone is released) and alcohol-cure types are used for electric and electronic applications. Generally, curing takes seven days, at 23±2°C and 50% relative humidity, but some products cure in as little as one to three days.

UV-cure products

These products cure rapidly through irradiation with UV light.

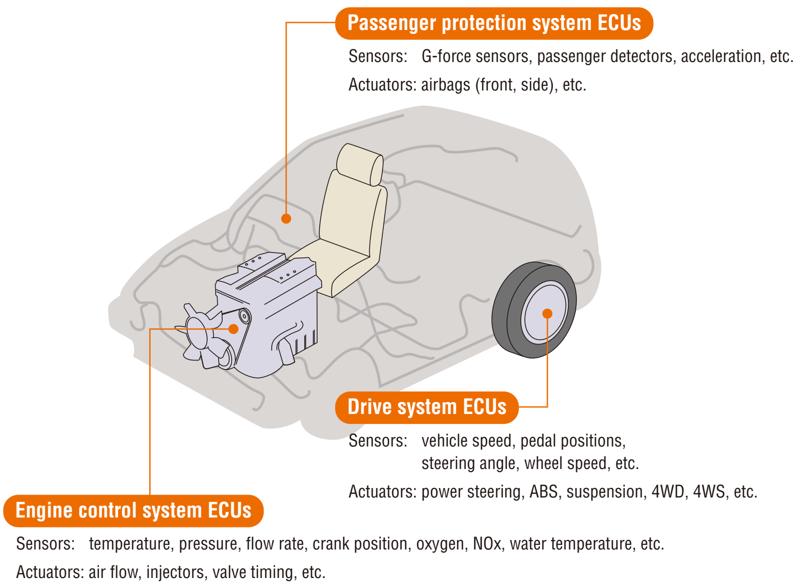
Conclusion

In the field of automotive components and materials, there is steadily growing demand for products that offer greater functionality and environmental performance. Shin-Etsu is committed to ongoing development of materials to meet this demand, and we'd like to hear from our customers regarding any ideas and requests they may have.

Table 5: Cure mechanism & characteristics

Cure mechanism			Cure temp.	Cure time	Advantages
Addition	1-component		80°C or higher	about 60 min	Rapid cure
	2-component		Room temp. or higher	1-3 days	Heating unnecessary (rapid cure)
Dual-cure			150°C or higher	about 60 min	Resists cure inhibition
Condensation	1-component	Alcohol	Room temp.	7 days	Heating unnecessary
		Acetone			
		Oxime			
		Acetic acid			
	2-component	Alcohol		1-3 days	
		Acetone			
UV-cure	Acrylic		Room temp.	20 sec	Heating unnecessary (rapid cure)
	Mercapto				

Application of silicone elastomers in the field of automotive electronics



Silicone Elastomers for Automotive Applications — Application to Airbags —

Of all automotive technologies, those designed to help keep drivers and passengers safe in the event of an accident are among the most critical. The properties of silicone materials have led to their use in numerous locations in modern vehicles. This article will look at the use of silicones in automobiles, with a particular focus on safety.

Introduction

There were over 850,000,000 cars on the world's roads in 2004. With growth in the Chinese market, this number is expected to reach 1.2 billion by the year 2020*1. In automobiles, silicone elastomers have long been used to manufacture spark plug boots and connector seals, and more recently for such components as intake manifold gaskets (fluorosilicone), turbo charger hoses and silicone wiper blades.

A look at the trends*1 in research and development of automotive materials reveals that, in addition to the quest for vehicles that are lighter and more efficient and for new sources of power – collectively aimed at reducing CO_2 emissions – automakers are also working to make vehicles safer. In the next section, we will discuss the connection between silicone elastomers and car airbags.

1. Airbags

The first airbags were installed in vehicles in the 1960s. Airbags were developed to reduce head injuries to passengers wearing seatbelts in the event of a crash, specifically by mitigating secondary impacts (primary impact is that of the vehicle hitting another object, and the secondary impact is that of the passenger's body hitting the steering wheel, instrument panel, windshield, etc.)*2.

In recent years, industry focus has shifted to auto airbags made of 6,6-nylon, 6-nylon, polyester and other fabrics coated with silicone rubber. The silicone rubber coating materials are typically dissolved types, which are millable or liquid silicones dissolved in a solvent, or emulsions. However, in the interest of enhancing the properties required for airbag applications and reducing environmental impact, manufacturers are gradually switching to solventless silicone materials **(Table 1)**.

Curtain airbags, which are fitted in spaces along the roof extending back from the front pillars, have to maintain inflation for a longer period than the airbags installed in the driver and front passenger seats. Curtain airbags are designed to protect the head and help keep passengers from being ejected from the vehicle in the event of an impact or rollover. The manufacture of curtain airbags requires liquid silicone rubber coating agents that have characteristics of low viscosity, high strength, high adhesiveness, moisture resistance, heat resistance, low-temperature flexibility, and stability over time.

2. Viscosity / strength

The strength of silicone rubbers can be enhanced by adding a larger proportion of silica filler or increasing the polymerization of the organopolysiloxane polymer. Normally, silicones are compounded with fumed silica to improve strength, because it is not possible to obtain strength sufficient for industrial products with siloxane polymers alone*3. See **Table 2** for the correlation between silica fill content and viscosity/tear strength.

Increasing the silica fill ratio has a mechanical "volume effect", and a physicochemical "surface effect" (improved adsorption of the organopolysiloxane molecules to the particle surface, and increased intermolecular force, or chemical bonding of organopolysiloxane molecules to silanols on the silica surface), resulting in increased tear strength **(Fig. 1)**.

Meanwhile, **Table 3** illustrates the relationship between viscosity and tear strength, as affected by organopolysiloxane polymerization. With increased polymerization of the polymer, high tear strength can be achieved, but it causes uneven crosslinking (maldistribution) known as "knock tear."

Table 1: Silicone rubber coating materials

Parameter \ Type	Millable/ Liquid silicone solution	Emulsion	Solventless silicone
Rubber strength	●	×	●
Environmental properties	×	●	●
Workability	×	●	●

Table 2: Correlation between silica fill content and viscosity/tear strength

Parameter \ Sample	Sample 1	Sample 2	Sample 3
Silica content	Low	Medium	High
Organopolysiloxane	Medium chain	Medium chain	Medium chain
Viscosity	Low	→	High
Tear strength	Low	→	High

Table 3: Correlation between polymerization of organopolysiloxane and viscosity/tear strength

Parameter \ Sample	Sample 4	Sample 5	Sample 6
Silica content	Medium	Medium	Medium
Organopolysiloxane	Short chain	Medium chain	Long chain
Viscosity	Low	→	High
Tear strength	Low	→	High

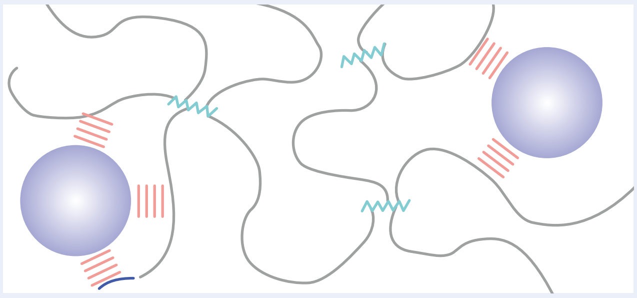
Figure 1: Reinforcing effect of silica particles

Reinforcement factor: 40 times (organopolysiloxane 0.2-0.3 MPa→10 MPa after reinforcement)

- **Mechanical "volume effect"**
- **Physicochemical "surface effect"**

• Improved adsorption of organopolysiloxane to the particle surface, increased intermolecular force.

• Chemical bonding of organopolysiloxane molecules to silanols on the silica surface



As **Tables 2 and 3** show, with increased strength there is an increase in viscosity. But to enable high-speed application of coating materials, researchers must develop low-viscosity/high-strength technologies.
Furthermore, when applying coating materials at high speed, the shear viscosity of the coating material is largely influenced by the application conditions. **Figure 2** shows the viscosity behavior of Sample 2 and Sample 3 (shown in **Table 2**) at different shear speeds. It is essential that the composition of the coating material be designed such that shear viscosity meets the requirements of the coating conditions.

3. Adhesiveness

The next important consideration for an airbag coating is the adhesion of the coating to the fabric. Silane coupling agents can be used to obtain the desired adhesive properties for proper adhesion to the fabric. The structure of a silane coupling agent is typically like that shown in the following structural formula*4.

$$\begin{array}{c} (CH_3)n \\ | \\ X{-}R{-}SiY_{3}{-}n \end{array}$$

"X" represents an organic functional group, and "Y" a hydrolyzable group.
The organic functional group "X" reacts with or promotes miscibility with organic materials. Various types of functional groups are synthesized.
Meanwhile, for the hydrolyzable group "Y", there are a number of possible functional groups, but the methoxy groups, ethoxy groups and alkoxy groups are most commonly used.
Silane coupling agents, whose molecules contain functional groups, thus act as an adhesive auxiliary agent for better adhesion to fabrics. This is thought to be the effect of hydrogen bonding, or wetting, or miscibilization **(Fig. 3)**.

Conclusion

In the field of automotive components and materials, there is steadily growing demand for products that offer greater functionality and environmental performance. Shin-Etsu is committed to ongoing development of materials to meet this demand, and we'd like to hear from our users regarding any ideas and requests they may have.

References:

*1 Shigeki Suzuki: Journal of the Society Of Rubber Industry, Japan, Vol. 80 172 (2007)
*2 http://www.nissan.co.jp/COMPASS/ISF/3rd/PAPER
*3 Kunio Ito: Silicone Handbook
*4 Hideyoshi Yanagisawa: Silane Coupling Ganryo Kyokai (Pigments Association)

Figure 2:

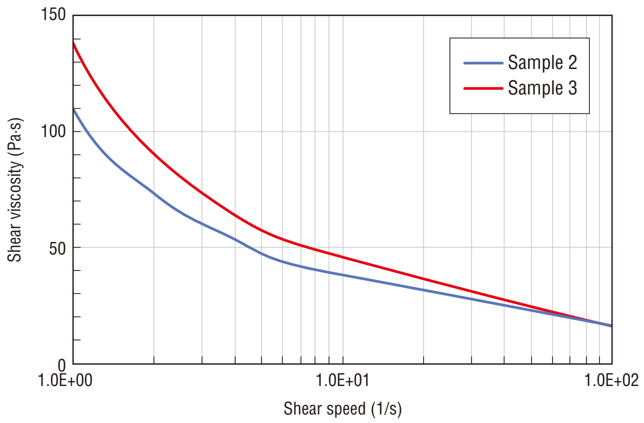
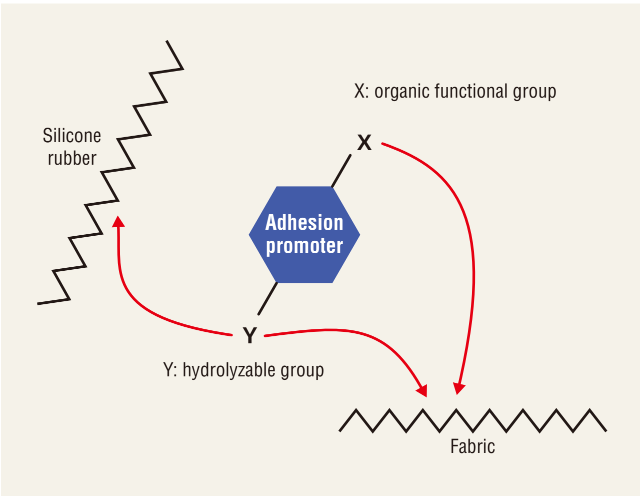


Figure 3:



Thermal Interface Materials for Automotive Applications

Car electronics has progressed on a course that should lead to improvements in performance in terms of safety, comfort and the environment. As electronic devices become smaller in size and higher in performance, thermal interface materials have become a more and more important theme. Among silicone materials for heat dissipation, this paper discusses those developed for automotive applications, for which performance requirements are especially strict.

Introduction

At the same time that the automobile grows more and more sophisticated in performance, extremely rapid progress is also being made in the electronification of automotive parts. And as electronic devices become more compact and more tightly integrated, the volumes of heat generated from them have risen dramatically. In consequence, materials that provide outstanding thermal performance have come into strong demand. Automobiles are used in extreme environments ranging from deserts to arctic regions, and are exposed to vibrations. It is imperative, therefore, that thermal interface materials show durability against heat, cold and vibrations. As a material that can satisfy these requirements, silicone is ideal, and silicone thermal interface materials have proven to be highly reliable in automotive applications. In light of this background, silicone thermal interface materials developed especially for automotive applications will be introduced.

1. Silicone Thermal Interface Materials

Silicone thermal interface materials start with a base of silicone polymer, which means they outperform other organic polymers in terms of heat and cold resistance, weatherability and electrical properties. These special silicone products excel in long-term reliability and are thus used as thermal interface materials in a wide array of applications. The products are available in sheet form and as paste compositions, and which is used will depend on the intended application **(Table 1)**.

2. Thermal Interface Grease

Initially, there were many cases in which automakers used thermal conductive grease that can be applied in mass-production methods based on automation. Recently, however, the performance requirements for such thermal conductive grease have been getting much stricter.
In addition to improvements in the rate of thermal conductivity, demand has arisen for thermal conductive grease that exhibits no bleed out or pump out phenomenon. Given that such grease is a simple mixture of polymer and thermal conductive filler, depending on how it is used, it can gradually manifest pump out due to cold or heat shocks or other conditions. Consequently, this type of grease has the disadvantage that its thermal performance sometimes suddenly becomes very poor. Nevertheless, given the product characteristics of this grease, it is extremely difficult to eliminate bleed out or pump out phenomenon altogether.
Nevertheless, this hurdle is being overcome thanks to recent advances in research.
Let us consider an example. **Table 2** presents the results of pump out tests performed on the very latest thermal conductive grease products to be developed and on conventional predecessors. In the conventional products, as the number of heat cycles advances, pump out and bleed out are slowly produced. In the very latest products, on the other hand, we see that there is absolutely no change in configuration from the initial state. Newly developed grease that exhibits this property does not require any additional heat processing after it has been applied as a coating, and it demonstrates highly stabilized performance. Another advantage of the latest grease products is that in comparison to conventional sheet-formed thermal materials, they are much softer, so there is no need for concern about damage to electronic devices resulting from stress.

3. Thermal Interface Sheets

Thermal interface sheets are categorized into three types: high-hardness rubber thermal interface sheets, low-hardness rubber thermal interface sheets, and phase-change materials that soften when heated. Here, we would like to introduce the latest products developed by Shin-Etsu.
The TC-CA Series was developed using Shin-Etsu's proprietary polymer technology

Table 1: Properties and Applications of Silicone Thermal Interface Materials

Property	Type	Applications
Sheet-shaped moldings	Thermal conductive sheet	Power transistor heat dissipation and insulation
		Power module heat dissipation and insulation
		Insulation and thermal conducting media in temperature sensing components
	Low-hardness thermal conductive sheet	Semiconductor device heat dissipation and insulation
	Phase change sheet	Thermal conducting media between heat-emitting elements and cooling materials
Pasty compositions	Thermal conductive grease	Power module heat dissipation
		Heat dissipation from heat-generating ICs
		Semiconductor device heat dissipation
	Thermal conductive gel, adhesive	For fixing heat dissipation from electronic components, for bonding

Table 2: Pump out tests

Cycle count	Newly developed product	Conventional product
Initial period (0 cycle)		
149 cycles		
457 cycles		

Photo 2: TC-SP-1.7 Series

Figure 1: Structure of TC-SP-1.7 Series

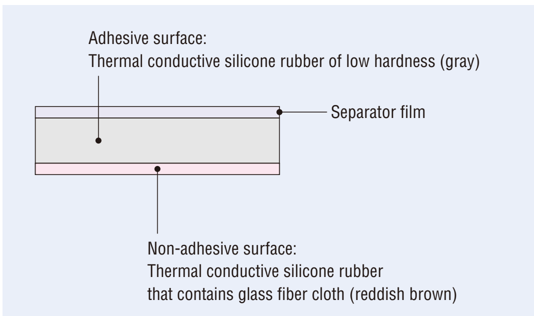


Photo 1: TC-CA Series

and filler compounding technology. These low-hardness rubber thermal interface sheets provide both high thermal conductivity and excellent electrical properties. Their low hardness also gives them good compressibility and stress-relieving properties, plus excellent processing characteristics, working properties and reworkability. Another major feature is their advantage in cost performance compared to conventional low-hardness products **(Photo 1, Table 3, Table 4)**.

The TC-SP-1.7 Series is a line of adhesive sheets which are ultra-soft adhesive sheets, which makes them and are thus highly effective as thermal interface materials. The non-adhesive face is reinforced with glass fiber, so the sheets have outstanding physical strength and dielectric reliability, and excel in ease of application and processing characteristics. Products in this series are now being used in the electrical systems of hybrid vehicles **(Photo 2, Figure 1, Table 5)**.

Products in the PCS-LT-30 Series are described as phase-change materials. They consist of an adhesive substance (polymer) that is solid at room temperature, but undergoes phase change (softens with heat) at high temperatures. The polymer is compounded with a high proportion of thermally conductive fillers and manufactured in sheets **(Table 6)**. These sheets outperform conventional products in various ways: 1) They can be applied to devices of varying heights, providing a "leveling effect" by filling gaps of uneven size **(Figure 2)**; 2) They provide improved resistance to pump-out (i.e. they don't become fluid even at high temperatures) **(Photo 3)**; and 3) They have good transfer properties for greater ease of use.

Table 3: General Properties

Parameter \ Product name	TC-100CAS-10 ("100" shows 1.0 mm in thickness.)	TC-100CAB-10 ("100" shows 1.0 mm in thickness.)	TC-100CAD-10 ("100" shows 1.0 mm in thickness.)	TC-100CAT-20 ("100" shows 1.0 mm in thickness.)
Appearance	Dark gray	Pink	Light reddish purple	Gray
Sheet size	300 × 400	300 × 400	300 × 400	300 × 400
Structure	Single layer	Single layer	Single layer	Single layer
Density g/cm^3	1.9	2.2	3.0	3.2
Hardness, Asker C	10*3	10*3	10*3	20
Dielectric breakdown voltage, 1mm kV	22	22	15	15
Thermal conductivity*1 W/m·K	1.8	2.3	3.2	4.5
Thermal resistance*2 °C/W	0.87	0.64	0.58	0.32
Flammability, UL94	V-0	V-0	V-0	V-0
Thickness mm	0.5, 1.0, 1.5, 2.0, 2.5 3, 4, 5, 6, 7, 8, 9,10	0.5, 1.0, 1.5, 2.0 2.5, 3, 4, 5	0.5, 1.0, 1.5, 2.0 2.5, 3, 4, 5	0.5, 1.0, 1.5, 2.0 2.5, 3, 4, 5
Operating temp. range °C	-40 to 150	-40 to 150	-40 to 180	-40 to 180

*1 Based on ISO-22007-2 *2 Based on Shin-Etsu method (Thickness: 1 mm) (Not specified values)
*3 Hardness 30 sheet can be supplied in case of less than 1.5 mm thickness.

Table 4: Conventional Products

Conventional products	TC-HSV-1.4	TC-THS	TC-TXS
Thermal conductivity* W/m·K	1.2	2.1	3.3

* Based on ISO-22007-2 (Not specified values)

Conclusion

Silicone thermal interface materials have come into widespread use in all types of equipment power supplies, as well as in computer CPUs and chip sets. In recent years, moreover, progress has been made in wide-area mounting of heat-dissipating components associated with car electronics. With demand in the hybrid and electric vehicle segments expected to grow in the coming years, Shin-Etsu will intensify efforts to develop new products and technologies based on ideas and insight gained from your feedback as users.

Photo3: Pump out in silicone versus olefin materials

Inserted with clip via glass plate at a tightening force of 0.9 kg and subjected to thermal application thermal compression bonding at 70°C per hour. Heat cycle was repeated once every 10 minutes (25 times) from 125 to 55°C and the spread of phase change sheet was checked.

Figure 2: Image of Phase-change

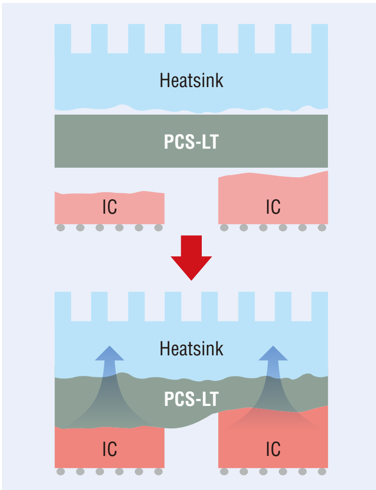


Table 5: General Properties of TC-SP-1.7 Series

Parameter \ Product name	Test method	TC-100SP-1.7
External appearance, Color tone	—	Gray/Reddish brown
Thickness mm	—	1.0
Density g/cm^3	JIS K 6249	2.32
Hardness*1, Asker C	—	2
Thermal conductivity W/m·K	ASTM E 1530	1.7
Thermal resistance*2 K/W	Shin-Etsu measurement method	1.00
Insulation breakdown voltage kV	JIS K 6249	20
Flame retardancy	UL94	V-0
Standard sheet thickness mm	—	0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 4.0, 5.0

*1 Measurements taken with 2 overlapping sheets of 6-mm sheet of low hardness. (Not specified values)
*2 Model heater (TO-3P type, 7 cm^2), applied power: 28 W/Load 29.4 kPa (300 gt/ cm^2)

Table 6: General Properties of Phase Change Material

Parameter \ Product name	PCS-LT-30
Color	Gray
Initial thickness μm	120
Bond line thickness*2, 3 μm	28
Density at 25°C g/cm^3	2.4
Softening point*4 °C	48
Thermal conductivity*1 W/m·K	3.0
Thermal resistance*1, 3 cm^2·K/W	0.11
Sheet size mm	300 × 400

*1 Measured by laser flash method. (Not specified values)
*2 Measured by Micro gauge.
*3 After 1 hour compression, 200 psi/100°C.
*4 Measured by Shin-Etsu method.

LIMS Materials for Automobiles

Liquid silicone rubber LIMS materials have attracted wide attention because they can facilitate stepped-up rationalization of formation processes. Advances are also being made in the use of such materials for automobiles. In particular, products have been developed in which siloxane of low molecular weight has been removed. This eliminates the need for secondary curing to remove such siloxane. Accordingly, LIMS materials can be expected to find more widespread applications in automobiles, for which there are very strict requirements for stabilized performance.

Introduction

Silicone elastomers are used in various automotive parts because they are advantageous in terms of heat resistance, low-temperature characteristics and electrical characteristics. Meanwhile, thanks to technological innovations in molding machines, metal molds and materials, conventional millable or high consistency rubber is being replaced with liquid-type LIMS (Liquid Injection Molding System) materials, which facilitate rationalization of molding.

The physical properties of cured substances obtained by LIMS molding are in no way inferior to those of millable rubber, and LIMS molding facilitates injection molding at low pressure. Moreover, with advances made in molding machines and metal molds, molding cycles have been shortened. Still another advantage is that products are flashless and runnerless, so waste produced during molding has declined.

This paper introduces materials recently developed using LIMS, for which there is no need for secondary curing.

1. Features of Liquid Silicone Rubber LIMS Material

1. Outstanding material characteristics

These materials offer a number of outstanding characteristics including high strength, heat resistance and electrical insulation. They also have excellent transparency, so they can be easily colored with pigments, resulting in vividly colored mold products.

2. Reduced processing times

Because liquid silicone rubber can be cured by means of addition reaction, the time periods required for curing and molding can be shortened.

3. Improved productivity

Molding can be executed at low injection pressure and precision components can be produced. High-quality molds can be realized at good efficiency and with no contaminants.

4. Automation of molding

This material facilitates flashless and runnerless molding. It also allows molding processes to be automated, since products can be easily demolded after curing.

5. Eco-friendly

Eco-friendly molding is made possible because there are no curing reaction byproducts and no need to dispose of molding waste materials.

2. Materials of Minimal Low-Molecular-Weight Siloxane

The silicone rubber products used around electrical and electronic equipment can damage electrical contact points through volatilization of any low-molecular-weight siloxane that remains in mold products **(Fig. 1)**. Normally, therefore, secondary curing is performed, using ovens, so as to remove low-molecular-weight siloxane before application.

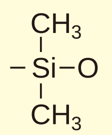
LIMS materials of minimal low-molecular-weight siloxane are a type of material in which low-molecular-weight siloxane has been reduced, without secondary curing, to a level comparable to that in millable rubber after it has been cured at 200°C for 4 hours **(Fig. 2)**.

Table 1 lists products for which secondary curing is not required (KE-2019 series).

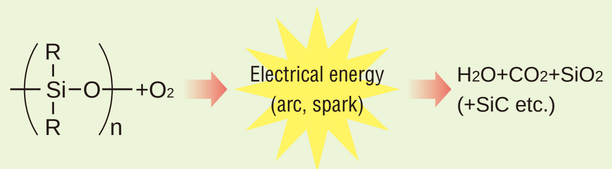
3. Applications to Harnesses

The harnesses used with vehicle-mounted electrical components make up an indispensable wiring system that transmits energy and diverse types of information. In the wake of recent advances toward high performance in automobiles, harnesses now come in a much wider array of types, and

Figure 1:Low-molecular-weight siloxane



Mechanism of silica production by low-molecular-weight siloxane



■ LIMS materials of minimal low-molecular-weight siloxane

Table 1: General purpose, high strength type

Parameter \ Product name		KE-2019-40A/B	KE-2019-50A/B	KE-2019-60A/B
Viscosity ($0.9S^{-1}$) at 23°C A/B	Pa·s	320/300	840/710	720/810
130°C:MDR T10/T90	s	23/52	27/69	38/65
Density	g/cm³	1.11	1.13	1.14
Hardness, Durometer A		42	52	62
Tensile strength	MPa	9.8	9.3	9.8
Elongation at break	%	655	538	470
Tearing strength, Angle shape	kN/m	35	44	47
Compression set, 150°C × 70 h	%	12	16	35
Low-molecular-weight siloxane ΣD_3-D_{10}	ppm	50	80	80

✻ Curing conditions (Non post cure): 150°C × 15 min. (Not specified values)

Table 2: Oil-bleed type

Parameter \ Product name		KE-2017-30A/B	KE-2017-40A/B	KE-2017-50A/B
Viscosity ($0.9S^{-1}$) at 23°C A/B	Pa·s	1840/1450	1800/1700	1700/1500
130°C:MDR T10/T90	s	41/77	36/76	32/75
Density	g/cm³	1.13	1.13	1.13
Hardness, Durometer A		33	42	52
Tensile strength	MPa	9.9	10.2	9.4
Elongation at break	%	740	650	490
Tearing strength, Angle shape	kN/m	20	33	38
Compression set, 150°C × 70 h	%	16	18	18
Low-molecular-weight siloxane ΣD_3-D_{10}	ppm	100	80	80

✻ Curing conditions (Non post cure): 150°C × 15 min. (Not specified values)

their performances greatly impact upon reliability **(Fig. 3)**.
Thanks to progress in car electronics, demand for harnesses has trended upward. At the same time, LIMS, which does not require secondary curing, is finding more widespread use in harnesses so as to bolster reliability and production efficiency. Listed in **Table 2** are oil-bleed type products used in harnesses.

4. Self-adhesive LIMS Materials

Self-adhesive LIMS materials, which do not adhere to metal dies but only to plastic, can be used with plastic to form integral molds. Additionally, they allow molding at low pressure, so they can yield moldings in which resin deformations are minimized. What is more, the level of precision in mold products can be easily elevated.

5. Prospective Benefits

Because low-molecular-weight siloxane has been minimized, metal dies will suffer much less contamination during molding and they will have to be cleaned far less frequently. LIMS materials are eco-friendly, since the volume of low-molecular-weight siloxane produced by volatilization during curing is minimal. What is more, fluctuations in contraction rates during molding have been reduced, making it possible to realize high-quality mold products.

Figure 2: Comparisons of low-molecular-weight siloxane volumes based on solvent extraction method

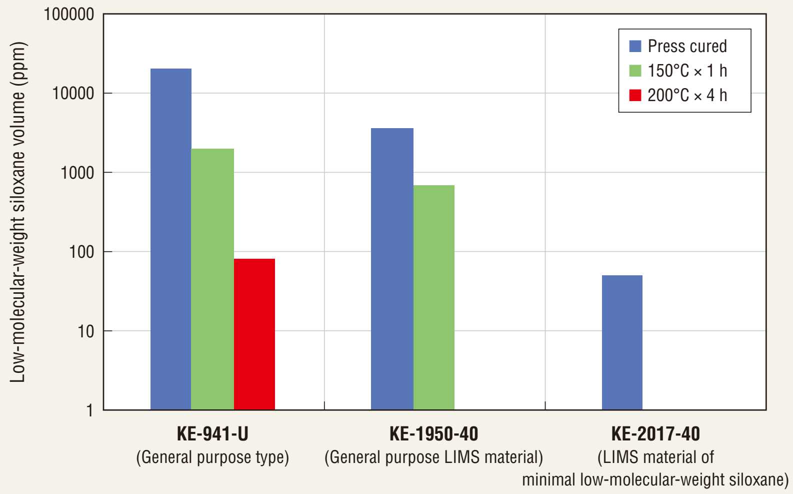
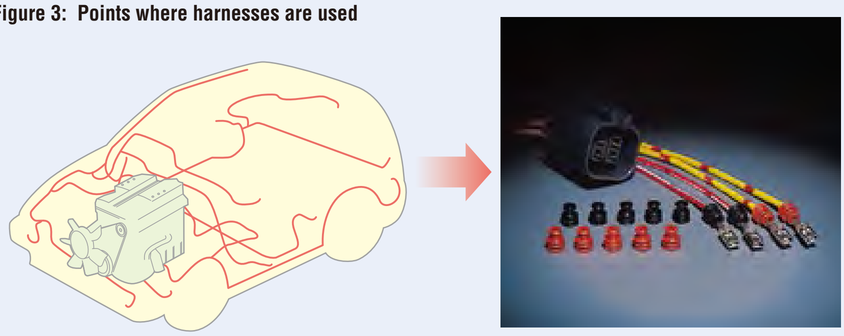


Figure 3: Points where harnesses are used



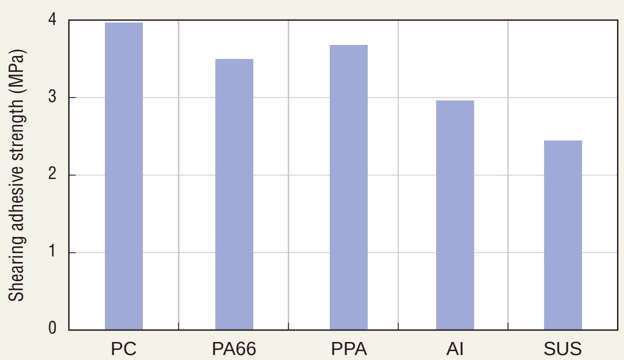
Waterproof connectors for harnesses

Table 3: Self-adhesive LIMS materials

Parameter \ Product name		KE-2096-40A/B	KE-2096-50A/B	KE-2096-60A/B
Viscosity (0.9S^{-1}) at 23°C A/B	Pa·s	540/620	610/840	550/800
130°C:MDR T10/T90	s	26/38	32/43	30/45
Density	g/cm^3	1.12	1.13	1.13
Hardness, Durometer A		36	50	61
Tensile strength	MPa	8.2	8.5	8.7
Elongation at break	%	670	470	430

✻ Curing conditions (Non post cure): 150°C × 5 min. (Not specified values)

Figure 4: Shearing adhesive strength on various materials (KE-2096-40A/B)



Conclusion

Eco-friendly products have been attracting more and more attention recently. Against this backdrop, great expectations have been put on LIMS materials because they eliminate the need for disposal of waste materials and the need for removal of low-molecular-weight siloxane through secondary curing.
LIMS materials can be expected to find applications in a diverse array of fields.

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