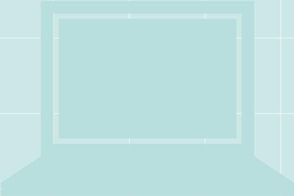
Silicones for Resin Modification

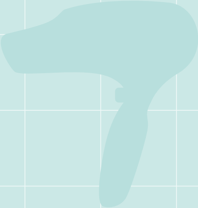
CONTENTS

Shin-Etsu Silicone



Silicones for Resin Modification

Silicones are highly functional resins that combine the characteristics of both inorganic and organic substances and exhibit an array of useful properties including heat resistance, cold resistance, weatherability, dielectric properties, release properties and water repellency.
By introducing silicones into other resins, the user can create new resin materials with enhanced functionality that includes not only heat resistance, weatherability and flame resistance, but improved impact resistance, lubricity and flexibility.
With their enhanced functionality, these high-performance composite resins are lightweight and have excellent fabricating characteristics and are used in a myriad of fields including electric and electronics applications, automotive applications, electrical wire, and construction.
Silicones for resin modification are available in many forms such as silanes and silane coupling agents, resins, oligomers, silicone fluids, modified silicone fluids and powders, so the user can choose the right type of product for the intended application and usage conditions.



This publication contains relevant articles featured in the Silicone Review, a publication of silicone-related news, gathered into a single collection.

Silanes and Resins

In this issue, we focus on silane coupling agents for resin modification, whose molecules contain two or more reactive groups which react with inorganic and organic materials, and look at their hydrolysis-condensation products, i.e. silicone resins and silicone alkoxy oligomers. As they bind to resins, these products impart adhesiveness, heat resistance, flame resistance and other properties to the resins, and can thus be used to create materials with enhanced functionality.

Introduction

Silane coupling agents are compounds which contain within their molecules a minimum of two different reactive groups, one of which binds chemically to inorganic materials and the other of which binds chemically to organic materials. Silane coupling agents, and the silicone resins and silicone alkoxy oligomers which are their hydrolysis-condensation products, contain reactive groups and polar functional groups within their structures, which means they can be used to modify organic resins. Silane coupling agents exhibit moisture-initiated crosslinking (moisture cure) properties and adhesiveness to inorganic and metallic materials, while silicone resins exhibit properties which include heat resistance and flame resistance. These properties can be imparted to other resins.

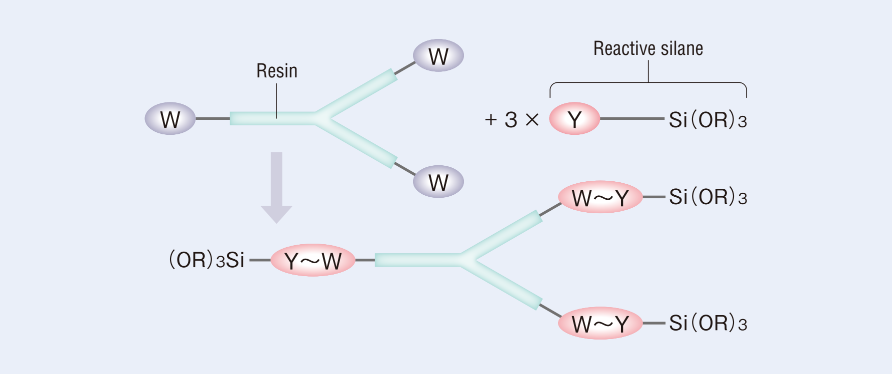
1. Synthesis of crosslinkable polymers using reactive organic group-containing silane coupling agents

The alkoxy groups in a silane coupling agent react with water in the presence of a catalyst to form stable siloxane bonds as shown in **Equation 1**.

Equation 1: Crosslinking mechanism

$$2\times\equiv Si—OR+2H_2O \rightarrow 2\times\equiv Si—OH+2ROH$$
$$\rightarrow \equiv Si—O—Si\equiv +H_2O+2ROH$$

Figure 1



Thus, an organic resin that has been modified by the organic reactive groups in the silane coupling agent, and functionalized with alkoxysilyl groups will have good crosslinking characteristics. And because it contains alkoxy groups, which have good affinity for inorganic and metallic materials, the modified resin will exhibit good adhesion to various substrates. Moreover, because the siloxane bonds formed via the crosslinking reaction are chemically stable, the crosslinkable polymer should exhibit improved heat resistance as the resin properties are enhanced.

As the following shows, there are several methods for introducing alkoxysilyl groups into an organic resin using a silane coupling agent.

1-1. Synthesis of crosslinkable polymers via chemical reaction

A synthesis model based on chemical reaction is shown in Figure 1. By reacting a resin containing an organic group W with a silane coupling agent containing an organic functional group Y which reacts with W, it is easy to obtain an organic resin functionalized with alkoxysilyl groups.

We find many examples of such reactions **(Table 1)**, including the reaction of isocyanate group-containing resins with amino group-containing or mercapto group-containing silane coupling agents, or hydroxyl group-containing resins with acid anhydride-containing silane coupling agents. These reactions are used in the modification of high-function resins such as moisture-cure liquid rubbers and sealing agents, and more recently polyimides and other materials for electronic applications.

Table 1: Reactive organic group-containing silane coupling agents

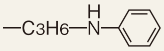
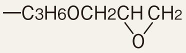
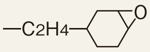
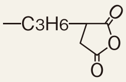
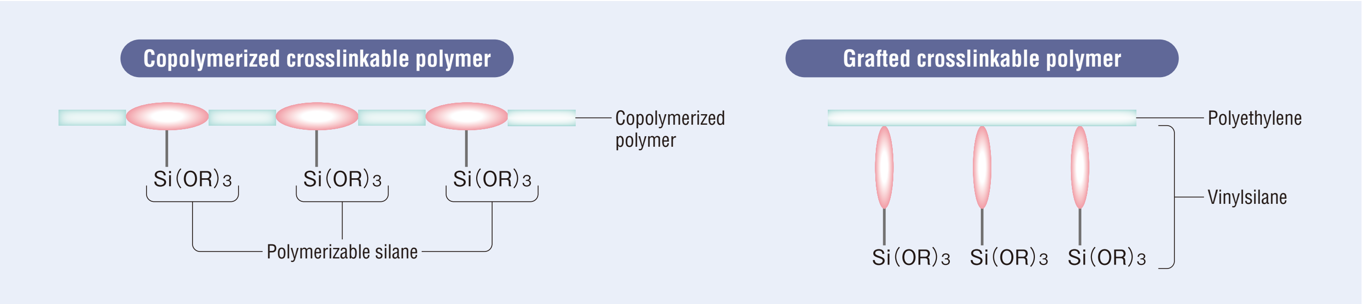
Functional group category	Reactive group (Y)	Product name	Alkoxy groups	Reactive groups in applicable resin (W)
Amino	$—C_3H_6NH_2$	**KBM-903**	Methoxy	Isocyanate groups, Epoxy groups
		KBE-903	Ethoxy	
		**KBM-573**	Methoxy	
Epoxy	 $—C_3H_6OCH_2\overset{}{CH}—CH_2$ (epoxide O bridging CH and CH_2)	**KBM-403**	Methoxy	Amino groups, Hydroxyl groups, Carboxyl groups
		KBE-402	Ethoxy	
		KBE-403	Ethoxy	
		**KBM-303**	Methoxy	
Mercapto	$—C_3H_6SH$	**KBM-802**	Methoxy	Isocyanate groups
		KBM-803	Methoxy	
Isocyanate	$—C_3H_6NCO$	**KBE-9007**	Ethoxy	Amino groups, Hydroxyl groups, Mercapto groups
Acid anhydride		**X-12-967C**	Methoxy	Amino groups, Hydroxyl groups

Figure 2



1-2. Synthesis of crosslinkable polymers via copolymerization

By copolymerizing a silane coupling agent which contains unsaturated groups (e.g. vinyl groups, styryl groups, (meth)acrylic groups) with a radical-polymerizing monomer (e.g. (meth)acrylate, styrene, vinyl ester, PVC, ethylene, propylene), we can obtain a resin which contains alkoxysilyl groups in its side chains **(Figure 2, Table 2)**. Crosslinkable copolymers obtained through such copolymerization are now in practical use as a base for weather resistant paints.

1-3. Synthesis of crosslinkable polymers via grafting

Vinyl group-containing silane coupling agents will, in the presence of an organic peroxide, initiate a grafting reaction with aliphatic olefin polymers including polyethylene and polypropylene to give a polyolefin polymer which contains alkoxysilyl groups in its side chains **(Figure 2)**. The vinylsilane-grafted polyethylene obtained via this method is used as moisture-cure polyethylene for wire coating and in other industrial applications. Because it can cure at a temperature below the softening point of the polymer, the cured material retains its shape and also shows improved resistance to thermal aging, adhesiveness and other properties.

2. Resin modification using nonreactive polar organic group-containing silane coupling agents

Unlike the aforementioned silane coupling agents which contain reactive groups that form chemical bonds directly, there also exist silane coupling agents which contain nonreactive polar groups and manifest a modifying effect through secondary interaction as typified by hydrogen bonding. Examples include ureido group-containing silane coupling agents and isocyanurate group-containing silane coupling agents **(Table 3)**. Their polar structure gives them excellent miscibility with highly polar resins such as polyamide, polyimide, polyester, polycarbonate and polyurethane, while improving adhesion to inorganic and metallic materials. And isocyanurate group-containing silane coupling agents can, thanks to their skeleton of isocyanurate rings, impart gas permeability resistance.

3. Resin modification using silicone resins and silicone alkoxy oligomers

By nature of their main skeleton of three-dimensional siloxane bonds, silicone resins exhibit high hardness and have excellent weatherability and flame resistance. One group of silicone resins known collectively as silicone alkoxy oligomers (below shortened to “oligomers”) are characterized by relatively low molecular weights, and their molecules are end-capped with alkoxysilyl groups. As the degree of polymerization increases, methyl silicone resins tend to have lower miscibility with other resins. Thus, oligomers are often used. Methyl phenyl silicone resins have phenyl groups introduced into the side chains for enhanced miscibility. There are many such products on the market today, ranging from highly polymerized resins to oligomers.

Resin modification methods can be divided into two categories: the chemical bonding method, whereby organic groups in the resin are reacted directly with organic groups in the silicone resin; and the integral blend method, whereby the silicone resin is simply mixed into the resin.

3-1. Chemical bonding method

This resin modification method uses methyl silicone resins and methyl phenyl silicone resins which contain alkoxysilyl and silanol groups, as well as oligomers which contain reactive organic groups. This generally involves a reaction with a hydroxyl

Table 2: Polymerizable organic group-containing silane coupling agents

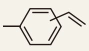
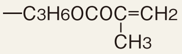
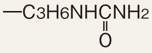
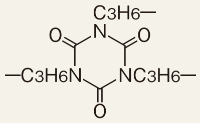
Functional group category	Reactive group (Y)	Product name	Alkoxy groups
Vinyl	$-CH=CH_2$	**KBM-1003**	Methoxy
		KBE-1003	Ethoxy
Styryl		**KBM-1403**	Methoxy
Methacrylate	 $-C_3H_6OCOC(CH_3)=CH_2$	**KBM-502**	Methoxy
		KBM-503	Methoxy
		KBE-502	Ethoxy
		KBE-503	Ethoxy
Acrylate	$-C_3H_6OCOCH=CH_2$	**KBM-5103**	Methoxy

Table 3: Nonreactive polar organic group-containing silane coupling agents

Functional group category	Reactive group (Y)	Product name	Alkoxy groups
Ureido	 $-C_3H_6NHC(=O)NH_2$	**KBE-585**	Ethoxy
Isocyanurate		**KBM-9659**	Methoxy

Crosslinked polyethylene: heat resistance test

group-containing resin in the presence of a catalyst, as shown in **Equation 2**. There are other possible reactions, such as reacting an isocyanate group-containing resin with a mercapto group-containing oligomer, or an epoxy group-containing resin with an amino group-containing oligomer **(Table 4)**. Typical applications involve the modification of acrylic, epoxy or polyester resins to produce a base for paints which offer improved weatherability, heat resistance and chemical resistance.

Equation 2: Crosslinking mechanism

$$\equiv \mathrm{Si-OR+HO-C}\sim\sim \rightarrow \equiv \mathrm{Si-O-C}\sim\sim \mathrm{+ROH}$$

3-2. Integral blend method

This method of resin modification involves the use of a methyl phenyl silicone resin which does not contain reactive organic groups **(Table 5)**. The resin is added by melt-mixing with a thermoplastic resin such as polycarbonate (PC), thereby imparting flame resistance without losing the inherent molding properties, impact strength and moisture resistance of the PC resin **(Table 6, Figure 3)**.

Table 4: Silicone alkoxy oligomers

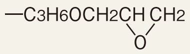
Functional group category	Reactive group	Product name	Alkoxy groups	Features
Methyl	Alkoxysilyl groups	**KC-89S**	Methoxy	Low DP (degree of polymerization)
		KR-500	Methoxy	Medium DP
		X-40-9225	Methoxy	High DP
Methyl/Phenyl	Alkoxysilyl groups	**KR-510**	Methoxy	High hardness
		KR-9218	Methoxy	Medium hardness
		X-40-9227	Methoxy	Improves softness
		KR-213	Methoxy	High phenyl content
Epoxy	 $-C_3H_6OCH_2CH(O)CH_2$	**X-41-1053**	Methoxy/Ethoxy	Epoxy equivalent 830 g/mol
Methyl/Epoxy		**KR-516**	Methoxy	Epoxy equivalent 280 g/mol
Mercapto	$-C_3H_6SH$	**X-41-1805**	Methoxy/Ethoxy	Mercapto equivalent 800 g/mol
Methyl/Mercapto		**X-41-1810**	Methoxy	Mercapto equivalent 450 g/mol
Methyl/Acrylate	$-C_3H_6OCOCH=CH_2$	**KR-513**	Methoxy	Acrylate equivalent 210 g/mol

Table 5: Silicone resins

Functional group category	Product name	Alkoxy groups	Features
Methyl/Phenyl	**KR-480**	—	Solid resin, softening point: 95°C

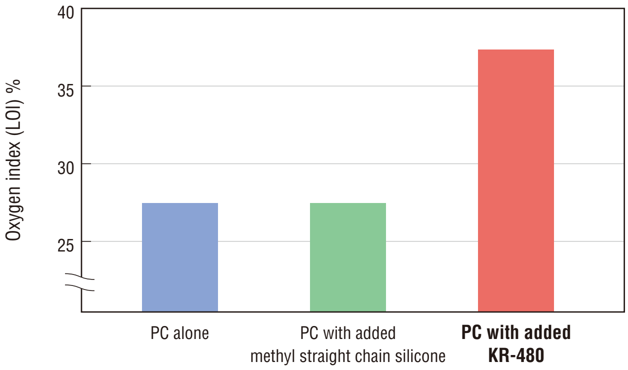
Table 6: Properties of polycarbonate with added KR-480

Item		PC alone	PC with added brominated flame retardant	**PC with added KR-480**
Bend strength	kgf/cm^2	960	970	930
Flexural modulus	kgf/mm^2	230	230	220
Impact strength	kgf·cm/cm	97	45	80
Heat deflection temperature	°C	138	137	134
Rockwell hardness		63	66	60
Melt flow index	g/min	10.4	10.7	11.8
Flame resistance UL94*		V-2	V-0	V-0

* Test strip thickness: 1/16 in.

(Not specified values)

Figure 3: Flame resistance of polycarbonate with silicone added



Conclusion

As the required characteristics for resins become more sophisticated in many fields, the use of engineering plastics and other high function resins for molded items and paints is on the rise. Shin-Etsu will continue to fill market needs by developing products that can be used for modification of these new resin materials. We are developing silanes and silicone resins functionalized with new reactive groups and products which can impart properties that were not possible previously.

● **Information current as of October 2010.**

Silicone Oligomers

Silicone oligomers are attracting attention as a category of products that can be used in applications where silane coupling agents and silicone resins could not. In this edition, we will discuss these silicone oligomers —a group of products having medium molecular weights and containing reactive functional groups.

Introduction

In order of increasing molecular weight, compounds can be grouped as follows: monomers, oligomers and polymers. Those that fall in the middle are called oligomers. Although oligomers are not defined by a specific degree of polymerization, they are typically dimers and trimers with molecular weights up to around 1,000.

Silicones are a diverse group of materials that can also be divided into categories, from monomers such as alkoxysilanes and silane coupling agents, whose molecules contain a single silicon atom, to polymers such as resins, fluids and rubbers. Those that fall somewhere in the middle are called silicone oligomers **(Fig. 1)**.

Silicone oligomers dissolve well in organic resins and consist of 100% active content that can be involved in chemical reactions. They can thus be used as reactive diluents, helping users avoid the use of solvents. In addition, they contain virtually no silanols and have long shelf lives. Silicone oligomers can be used as the main component to produce coatings that are extremely hard and weatherable, or combined with organic resins to create hybrid materials with improved heat resistance. Indeed, the list of applications for silicone oligomers continues to grow.

Whereas the molecules of “straight” and “modified” silicone fluids are built on a backbone of straight-chain siloxy units, the Type A and Type AR silicone oligomers (which contain alkoxysilyl groups) and Type R silicone oligomers (which contain reactive functional groups) we will discuss here are built on a backbone of branched siloxy units or siloxy units that branch after curing **(Fig. 2)**. This gives the molecules a more three-dimensional structure, and gives silicone oligomers their improved curability and improved miscibility with organic resins.

1. Alkoxy oligomers (Type A)

Reactive groups: Not containing
Alkoxysilyl groups: Containing

Type A alkoxy oligomers **(Table 1)** contain only alkoxysilyl groups.

One group of Type A products, methyl oligomers, contain methyl groups as a non-functional organic substituent. Methyl oligomers have high hydrolytic reactivity, and when used with the proper curing agent (catalyst), can be used as coating agents that cure with ambient moisture at room temperature. The curing agents for these products are typically titanium based.

Crosslinking mechanism

$$2\ \equiv\text{Si-OR} + 2\ H_2O \rightarrow 2\ \equiv\text{Si-OH} + 2\ \text{ROH}$$
$$\rightarrow \equiv\text{Si-O-Si}\equiv + H_2O + 2\ \text{ROH}$$

Methylphenyl oligomers, which contain both methyl and phenyl groups, have good miscibility with organic resins such as acrylics, epoxies and polyesters. For this reason, methylphenyl oligomers are often combined with these resins to create hybrid materials or used as reactive diluents.

Crosslinking mechanism

$$\equiv\text{Si-OR} + \text{HO-C-(Organic resins)}$$
$$\rightarrow \equiv\text{Si-O-C-(Organic resins)} + \text{ROH}$$

Copolymers, obtained through reactions involving the alkoxysilyl groups, are used to produce paints with excellent weatherability, heat resistance and chemical resistance.

In organic resin modification applications, alkyl titanates, organic acids and amine compounds are often used as reaction catalysts (promoters). But because the oligomers have a tendency to self-condense in such cases, the reaction conditions must be carefully controlled.

2. Alkoxy oligomers (Type AR)

Reactive groups: Containing
Alkoxysilyl groups: Containing

Type AR alkoxy oligomers **(Table 2)** contain both alkoxysilyl groups and reactive functional groups. Shin-Etsu offers a range of alkoxy oligomers that contain epoxy, mercapto, acrylate or methacrylate groups as the organic functional group.

Silane coupling agents are commonly added to organic resins to improve their adhesion to inorganic materials. However silane coupling agents can evaporate during the heat-cure process, which means they may not work to best effect. In cases where this is a problem, organic functional group-containing oligomers formulated to give them lower volatility can be quite effective. An example of such a product is KR-513, shown in **Fig. 3**.

The organic functional groups in this oligomer can be reacted with other organic resins to produce modified resins whose molecules will contain alkoxysilyl groups. This method has been used to create a variety of moisture-cure organic resins.

When alkoxysilyl groups are hydrolyzed, silanol groups are produced. Because these silanol groups are hydrophilic, alkoxysilyl groups are pushed to the surface during the curing process. Then, through hydrolysis, silanol groups will form on the surface such that the cured coating will have improved hydrophilic anti-fouling properties **(Fig. 4)**.

Figure 1: Position of silicone oligomer

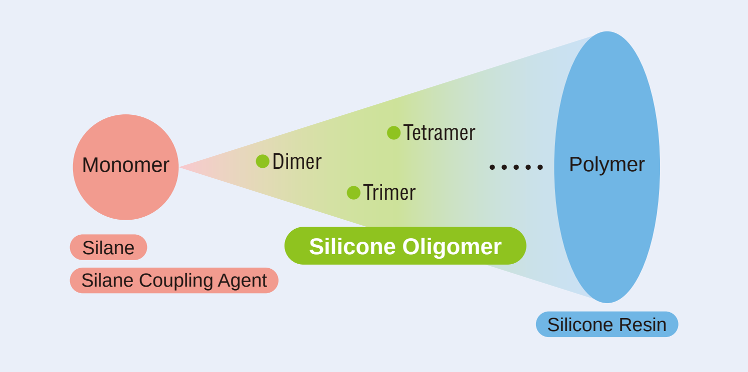


Figure 2: Classification of silicone oligomers

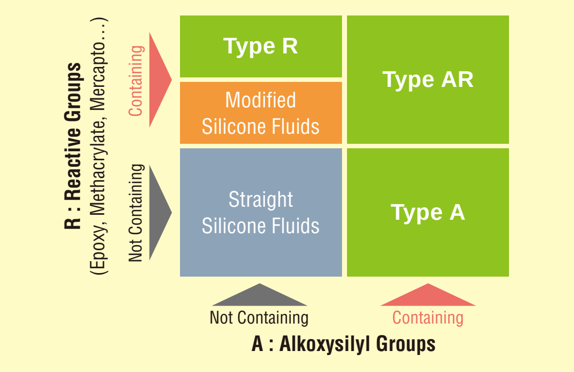


Table 1: Alkoxy oligomers (Type A)

Product name	Organic substituent group	Alkoxy group	Viscosity 25°C mm²/s	Refractive index 25°C	Alkoxy group content wt%	SiO2 content wt%	Features
KC-89S	Methyl	Methoxy	5	1.394	45	59	Low DP (degree of polymerization)
KR-500	Methyl	Methoxy	25	1.403	28	63	Medium DP
X-40-9225	Methyl	Methoxy	100	1.407	24	67	High DP
X-40-9246	Methyl	Methoxy	80	1.407	12	72	Improves flexibility
X-40-9250	Methyl	Methoxy	160	1.407	25	73	Improves flexibility, thick coatings
KR-401N	Methyl/Phenyl	Methoxy	20	1.432	33	56	Low phenyl content, Curability
X-40-9227	Methyl/Phenyl	Methoxy	15	1.460	15	59	Improves softness
KR-510	Methyl/Phenyl	Methoxy	100	1.509	17	44	High hardness
KR-9218	Methyl/Phenyl	Methoxy	40	1.529	15	40	Forms medium hardness coatings
KR-213	Methyl/Phenyl	Methoxy	16	1.525	20	38	High phenyl content

(Not specified values)

Table 2: Alkoxy oligomers (Type AR)

Product name	Organic substituent group	Alkoxy group	Viscosity 25°C mm²/s	Refractive index 25°C	Alkoxy group content wt%	Features
X-41-1053	Epoxy	Methoxy/Ethoxy	12	1.414	50	Epoxy equivalent 830 g/mol
X-41-1059A	Epoxy	Methoxy/Ethoxy	30	1.434	42	Epoxy equivalent 350 g/mol
X-24-9590	Epoxy	Methoxy	354	1.448	9.5	Epoxy equivalent 592 g/mol
KR-516	Epoxy/Methyl	Methoxy	50	1.441	17	Epoxy equivalent 280 g/mol
X-41-1805	Mercapto	Methoxy/Ethoxy	30	1.418	50	Mercapto equivalent 800 g/mol
X-41-1818	Mercapto	Ethoxy	14	1.417	60	Mercapto equivalent 850 g/mol
X-41-1810	Mercapto/Methyl	Methoxy	5	1.422	30	Mercapto equivalent 450 g/mol
KR-513	Acrylate/Methyl	Methoxy	35	1.450	20	Acrylate equivalent 210 g/mol

(Not specified values)

Table 3: General properties of X-40-2670 (Type R)

Product name	Organic substituent group	Alkoxy group	Viscosity 25°C mPa·s	Refractive index 25°C	Alkoxy group content wt%	Features
X-40-2670	Epoxy	Not containing	3,000	1.487	—	Epoxy equivalent 200 g/mol

(Not specified values)

Exterior coatings for vehicles

Figure 3: Comparison of volatile content of silicone oligomer (KR-513) and silane coupling agent (KR-5103)

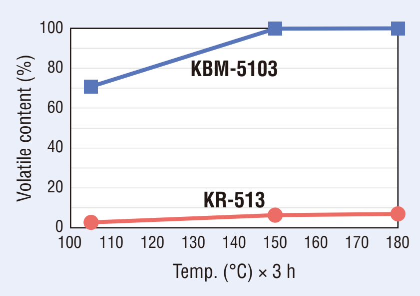
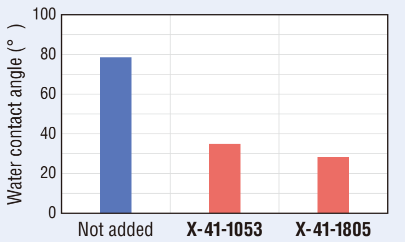
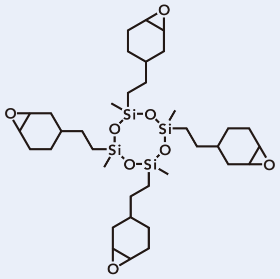


Figure 4: Hydrophilicity test results for coatings with oligomer added



Test conditions:
Fluoropolymer paint/Amt. of oligomer added=5 phr
Water contact angle measured after 16 hr immersion in 2.5% sulfuric acid solution.

Figure 5: Basic structure of X-40-2670



3. Silicone oligomers containing reactive groups (Type R)

Reactive groups: Containing
Alkoxysilyl groups: Not containing

Type R oligomers contain only reactive functional groups.

Modified silicone fluids with relatively low molecular weights are comparable to the reactive group-containing oligomers in this category. Since the molecules of these modified silicone fluids are built on a backbone of straight-chain dimethylsiloxy units and due to their wide molecular weight distribution, they have been known to have poor miscibility with organic resins. But Type R oligomers are compounds that have been developed with improved miscibility. This has been achieved by reducing their molecular weights and controlling the molecular weight distribution or, in some cases, producing them in a single molecular weight.

One such example is the silicone oligomer containing alicyclic epoxy groups X-40-2670 **(Table 3, Fig. 5)**. It has good miscibility with regular epoxies and is used as the main component of anhydride-cure and light/heat cationic-cure products. Resins produced using X-40-2670 have high glass transition points (high Tg), yet show minimal cure shrinkage as well as excellent heat resistance and transparency. Such resins are being used to a growing extent in optical applications and as binders.

4. Oligomer coatings

Alkoxy oligomers have also been used to create a variety of solventless coating agents, which are now available on the commercial market. These products are formulated with the optimal curing agents already in, which means they are easy to use and no mixing is required. When applied to metal, stone, wood and plastic materials, these products cure at room temperature in a prescribed time to form coatings of varying degrees of hardness. They can provide effective surface protection for a variety of materials and improve weatherability and water repellency **(Table 4)**.

Conclusion

Until recently, alkoxy oligomers have been made by controlling the partial hydrolysis of alkoxy silanes such that molecular weights are kept in a medium range and the material does not become a silicone resin. The alkoxy oligomers (both new and older) and the silicone oligomer containing reactive functional groups presented in this issue were developed to satisfy more sophisticated user needs. We expect these materials will be used more and more in the development of adhesives, resin modifiers and powder surface treatments for the electronics, aviation and other industries.

●This is an edited version of the original article released on Jan. 2014.

Table 4: Coating products curable under room temperature

Product name	Organic substituent group	Viscosity 25°C mm²/s	Refractive index 25°C	Tack free time min	Pencil hardness/ Days cured	Features
KR-400	Methyl	1.2	1.390	30 to 60	5H/2→8H/7	High hardness
X-40-2327	Methyl	0.9	1.382	5 to 10	5H/1	Rapid cure; Can be applied over other coatings
KR-401	Methyl/Phenyl	22	1.435	30 to 60	3H/7	Flexural & impact resistance

✻ Substrate: Polished steel sheet. Coating = 10 μm, cured at 25°C/70%RH.
(Tack-free time varies depending on temperature and humidity)

(Not specified values)

Fluids and Secondary Products

**An array of compounding techniques are employed to enhance the properties of various resins.
Compounding with silicone is a common technique, as it can improve heat resistance, weatherability, lubricity, impact resistance and other properties. Hence, today silicones are compounded with many resins.
In this edition, we introduce some silicones developed specifically for modification of organic resins.**

Introduction

Silicones exhibit many desirable properties, including excellent heat resistance, cold resistance, weatherability, lubricity, easy release, water repellency, flame retardancy, flexibility, and good electrical properties. By incorporating silicones, organic resins can be improved in these areas. A silicone can be introduced in different ways: a blend-in silicone can be dispersed evenly in the resin, or a silicone modifier can be reacted directly with the resin.

1. Blend-in silicones

By nature, silicone generally has poor miscibility with organic resins. As a result, a silicone may be blended directly into a resin, but it can be difficult to achieve uniform dispersion. To solve this problem, silicone master pellets **(Table 1)** can be used. These are manufactured by evenly dispersing a high concentration of high molecular weight silicone gum in an organic resin. By blending these silicone master pellets directly with the resin pellets and then molding, it is easy to obtain a resin in which the silicone is evenly dispersed.

Silicone rubber powders **(Table 2)** are another option. These are manufactured in a form that facilitates easy dispersion of the silicone rubber in the resin. One type, called silicone hybrid powders, features a silicone resin coating applied to the surface of silicone rubber powder grains. This improves their agglomeration properties compared to regular silicone rubber powders, for improved dispersion in resins.

There are also silicone emulsions **(Table 3)**, which can be blended directly when manufacturing resins using an emulsion polymerization process. These are made by emulsifying silicone gum in water. The emulsion particles are small, which translates to improved dispersibility in resins.

By blending these silicone master pellets, silicone rubber powders and silicone emulsions with resins at a ratio of 0.1–5%, the user can impart lubricity, easy release, anti-blocking properties, impact resistance, stress relaxation and coloring properties.

2. Silicone modifiers

By employing silicones in chemical reactions with organic resins, we can obtain silicone-modified resins in which the silicone structure is incorporated into the structure of the resin. These reactions involve the use of silicones which contain functional groups that react with organic groups in the resins. Dual-end reactive silicone fluids are silicones with functional groups on both ends of the molecule, while single-end reactive silicone fluids are silicones with functional groups on one end only. When dual-end types are used in the reaction, the silicone chains attach to the resin structure as a block to produce silicone block copolymers. When single-end types are used, the result is a silicone graft copolymer, in which the silicone chains hang from the resin side chains **(Figure 1)**.

If a block copolymer is used for silicone modification, it is possible to improve a resin's physical properties, including heat resistance, cold resistance, weatherability, impact resistance and flexibility. Meanwhile, if a graft copolymer is used, it is possible to improve a resin's surface characteristics, including lubricity, release properties, wear resistance and water repellency.

Examples of silicone-modified resins in practical use include acrylic, urethane, epoxy, polyimide, polyether and polycarbonate resins. Modification of these resins requires the use of different types of functional groups, which are contained in reactive silicone fluids. (Meth)acrylate groups are required for acrylic resins, hydroxyl groups for urethane resins, epoxy groups for epoxy

Table 1: Silicone master pellets

Base resin	Product name	Silicone content %
PP (polypropylene)	**X-22-2101**	50
LDPE (low density polyethylene)	**X-22-2125H**	50
EVA (ethylene vinyl acetate copolymer)	**X-22-2138B**	40
POM (polyacetal)	**X-25-5006**	40
ABS	**X-22-2184-30**	30

(Not specified values)

Table 2: Silicone rubber powders

Type	Product name	Avg. particle size μ
Rubber	**KMP-597**	5
	KMP-598	13
Hybrid (resin-coated rubber)	**KMP-600**	5
	KMP-601	12

(Not specified values)

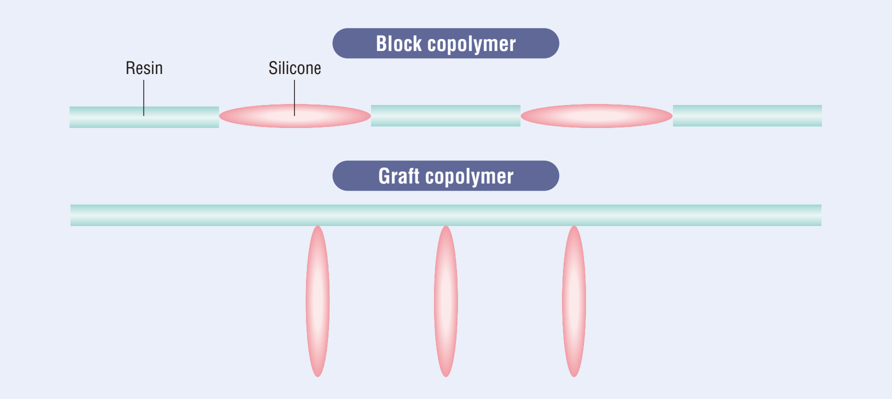
Table 3: Silicone emulsions

Product name	Non-volatile content %	Particle size nm	Ionicity
KM-9703	45	280	Anionic
X-52-8026C	32	180	Anionic

(Not specified values)

Silicone master pellets

Fig. 1: Structure of block copolymer and graft copolymer



resins, amino groups for polyimide resins, hydroxyl or carboxyl groups for polyester resins, and phenol groups for polycarbonate resins. The functional groups that can be reacted with organic resins include amino groups, epoxy groups, hydroxyl groups, phenol groups, methacrylate groups, carboxyl groups and mercapto groups. Silicones containing these groups are available as dual-end types **(Table 4)** or single-end types **(Table 5)**, and products are available which exhibit varying degrees of silicone polymerization.

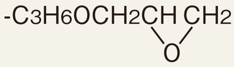
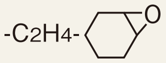
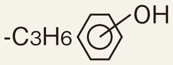
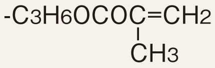
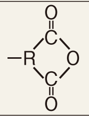
While silicones typically have poor miscibility with organic resins, there are products on the market which offer improved miscibility through the introduction of phenyl groups or polyether groups into the structure of a reactive silicone. Improving miscibility helps to improve the reaction between the resin and silicone, such that the modifying effect can be achieved using a smaller amount. In addition, by incorporating different types of reactive groups, manufacturers have developed products that can be used for multi-modification of resins, which is not possible with conventional products **(Table 6)**.

Conclusion

Shin-Etsu will continue our efforts to meet the needs of the market for silicones for resin modification, which can imbue organic resins with useful new properties. We are developing products with new structures, including silicones which contain reactive groups, silicones containing heterogeneous functional groups, and branched silicones. We are also working to develop higher purity formulas for reactive silicones.

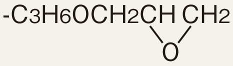
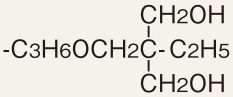
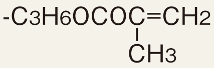
● **Information current as of Jul. 2010.**

Table 4: Dual-end reactive silicone fluids

Reactive group	Product name	Viscosity mm^2/s	Reactive group equivalent weight g/mol
$-C_3H_6NH_2$	**KF-8010**	12	430
	X-22-161A	25	800
	X-22-161B	55	1,500
	KF-8012	90	2,200
	**KF-105**	15	490
	X-22-163A	30	1,000
	X-22-163B	60	1,800
	X-22-163C	120	2,700
	**X-22-169AS**	30	500
	X-22-169B	70	1,700
$-C_3H_6OC_2H_4OH$	**KF-6000**	35	470
	KF-6001	45	900
	KF-6002	70	1,600
	KF-6003	110	2,500
	**KF-2200**	100	1,600
 $-C_3H_6OCO\underset{CH_3}{C}=CH_2$	**X-22-164A**	25	860
	X-22-164B	55	1,600
	X-22-164C	90	2,400
$-C_2H_4COOH$	**X-22-162C**	220	2,300
	**X-22-168AS**	160	500
	X-22-168A	140	1,000
	X-22-168B	180	1,600
$-C_3H_6SH$	**X-22-167B**	55	1,700
	X-22-167C	90	2,300

(Not specified values)

Table 5: Single-end reactive silicone fluids

Reactive group	Product name	Viscosity mm^2/s	Reactive group equivalent weight g/mol
	**X-22-173BX**	30	2,500
	X-22-173DX	60	4,700
$-C_3H_6OC_2H_4OH$	**X-22-170BX**	40	2,800
	X-22-170DX	65	4,700
 $-C_3H_6OCH_2\overset{CH_2OH}{\underset{CH_2OH}{C}}-C_2H_5$	**X-22-176DX**	130	3,200
	X-22-176GX-A	400	14,000
 $-C_3H_6OCO\underset{CH_3}{C}=CH_2$	**X-22-174ASX**	9	900
	X-22-174BX	27	2,300
	KF-2012	60	4,600
	X-22-2426	200	12,000
	X-22-2475	5	420

(Not specified values)

Table 6: Reactive silicone fluids containing heterogeneous functional groups

Reactive group	Heterogeneous substitution group	Product name	Viscosity mm^2/s	Reactive group equivalent weight g/mol
Hydroxy	Polyether	**X-22-4272**	270	1,100
		X-22-4952	100	1,200
		KF-6123	400	1,200
Amino	Polyether	**X-22-3939A**	3,300	1,700
	Phenyl	**X-22-1660B-3**	550	2,200
	Vinyl	**X-22-9412**	14	430
Epoxy	Polyether	**KF-1002**	5,000	4,500
		X-22-4741	380	2,500
	Phenyl	**X-22-2000**	170	600
	Aralkyl	**KF-1005**	2,500	250

(Not specified values)

Silicone Powder

Silicone powders feature the characteristics of silicone and are used in applications ranging from plastics and paints to personal care products. Silicone powders are an essential component for manufacturers wanting to enhance the functionality of their products.

Introduction

Shin-Etsu has developed a wide array of silicone powders, making good use of the properties that silicones have to offer **(Table 1)**. In this edition, we present silicone rubber powders, silicone resin powders, and our independently developed hybrid silicone powders and silica powders.

1. Silicone rubber powders

Silicone rubber powders are fine-grained silicone rubber with a structure of crosslinked straight chain dimethylpolysiloxane **(Photo 1)**. Compared to common rubbers, silicone rubbers have superior weatherability and heat and cold resistance, and exhibit rubber elasticity over a wide temperature range (-50° to 250° C). Silicone rubber powders can be added to synthetic rubbers to improve their sliding properties, abrasion resistance, releasability, heat resistance and cold resistance. And due to their exceptional flexibility, they can be added to synthetic resins to improve their impact resistance.

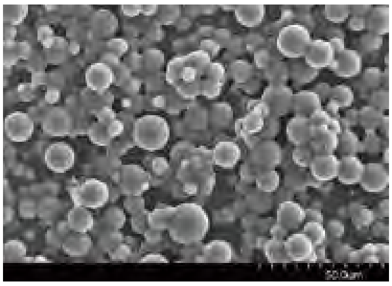
As an example, we show the effects when silicone rubber powder is added to polystyrene resin **(Table 2)**.

2. Silicone resin powders

Silicone resin powders have a crosslinked three-dimensional network structure in which the siloxane bonds are expressed as $(CH_3SiO_{3/2})$n. They are polymethylsilsesquioxane in powdered form. Compared to common organic polymers, silicone resin powders have superior heat resistance. In thermogravimetric analysis, they show almost no change in weight even at 400° C, and do not melt during heating. This is due to the highly crosslinked network structure of polymethylsilsesquioxane, and is partly why silicone resin powders do not dissolve or swell in organic solvents including alcohols, ketones, esters, or petroleum fractions.

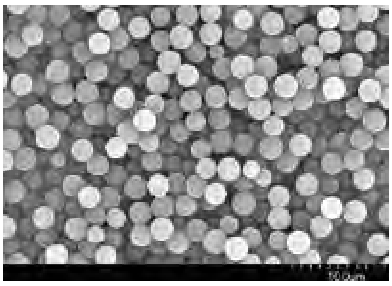
As you can see from **Photo 2**, the particle size distribution is narrow. Unlike silicone rubber powders, silicone resin powders are hard substances with no elasticity. This property gives them superior sliding properties. Silicone resin powders can be added to plastic films, paints, inks, personal care products, coating agents, waxes, rubbers and other materials to improve their sliding properties. And because their refractive indices differ from those of common organic polymers **(Table 3)**, silicone resin powders can be used to impart plastics with light diffusing properties. Their use as a light diffusing agent has increased in recent years. KMP-702 was developed with an emphasis on high optical transmittance with such applications in mind.

Photo 1



Electron micrograph of KMP-598 silicone rubber powder

Photo 2



Electron micrograph of KMP-590 silicone rubber powder

Table 1: Silicone powder types

Type	Product name	Shape	Avg. particle size μm	Particle size distribution μm	True specific gravity	Water content %
Rubber	**KMP-597**	Spherical	5	1 to 10	0.97	0.1
	KMP-598	Spherical	13	2 to 30	0.97	0.1
	X-52-875	Amorphous	30	1 to 100	0.97	0.1
Resin	**KMP-590**	Spherical	2.0	1 to 4	1.3	1
	KMP-706	Spherical	2.0	1 to 4	1.3	1
	KMP-701	Spherical	3.5	1 to 6	1.3	1
	X-52-854	Spherical	0.7	0.2 to 5	1.3	1
	X-52-1621	Spherical	5.0	1 to 8	1.3	1
Hybrid	**KMP-600**	Spherical	5	1 to 15	0.99	0.1
	KMP-601	Spherical	12	2 to 25	0.98	0.1
	KMP-602	Spherical	30	4 to 60	0.98	0.1
	KMP-605	Spherical	2	0.7 to 5	0.99	0.1
	X-52-7030	Spherical	0.8	0.2 to 2	1.01	0.1
	KSP-100✻	Spherical	5	1 to 15	0.99	0.1
	KSP-101✻	Spherical	12	2 to 25	0.98	0.1
	KSP-102✻	Spherical	30	4 to 60	0.98	0.1
	KSP-105✻	Spherical	2	0.7 to 5	0.99	0.1
	KSP-300✻	Spherical	5	1 to 15	1.1	0.1
Silica	**X-52-7042**	Spherical	4	0.5 to 15	2.2	0.1 max.
	X-52-7043	Spherical	10	0.5 to 15	2.2	0.1 max.
	X-24-9163A	Spherical	0.1	0.1	1.8	2

✻ For personal care products. KSP-300 contains phenyl groups. (Not specified values)

Table 2: Effects of adding silicone rubber powder
(polystyrene resin, impact resistance and abrasion resistance test results)

X-52-875 Amt. added (Parts by weight/ 100 parts of Polystyrene)	Impact resistance test✻1 Breakage %		Abrasion resistance test✻2 Abrasion amount mg	
	Drop height 40 cm	Drop height 55 cm	Abrasion pressure 15.5 kg/cm²	Abrasion pressure 25.4 kg/cm²
0 (Blank)	100	100	54 (after 2 min)	—
5	0	0	6	12
10	0	0	Less than 1	Less than 1

✻1 A 62 g steel ball is dropped on a molded sheet (30 mm × 30 mm × 2 mm), which is then examined for breakage.
✻2 Using a carbon steel cell (inner diameter: 20.2 mm; Outer diameter: 25.6 mm) rotating at 200 rpm, rotational friction is applied to a molded sheet. After 10 minutes, the abrasion amount is measured.

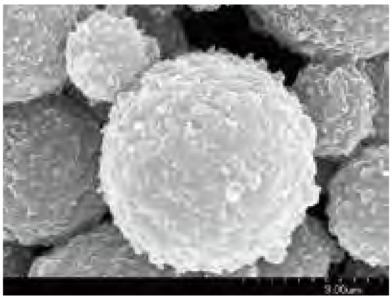
Table 3: Refractive indices of silicone resin powder and synthetic resins

Synthetic resin	Refractive index
KMP-590	1.43
Polymethyl methacrylate	1.49
Polycarbonate	1.59
Polystyrene	1.59

Table 4: Moisture absorption of X-52-7042 and X-52-7043 silica powders
(Change in moisture content caused by humidification)

Process No.	Process description	Processing conditions	Water content ppm	
			X-52-7042	**X-52-7043**
①	Drying before humidification	105°C/3 h	250	170
②	Humidification	①→35°C/85% Humidity/24 h	270	270
③	Re-drying	②→250°C/10 min	250	250

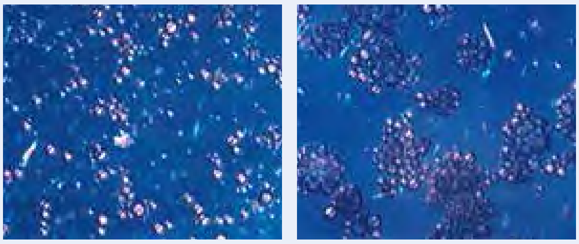
Photo 3



Electron micrograph of KMP-600 hybrid silicone powder

Photo 4

Dispersion of hybrid silicone powder in liquid epoxy resin



KMP-601 hybrid silicone powder

Silicone rubber powder

3. Hybrid silicone powders

Hybrid silicone powders consist of spherical rubber powder grains coated with silicone resin. In electron micrographs, you can see that the silicone rubber particles are coated with spherical silicone resin **(Photo 3)**.

As discussed above, silicone rubber powders excel in flexibility and impact resistance. When used in formulations for personal care products, their rubber elasticity means they can impart a unique feel to the product when it is used. However, powders of smaller particle size are especially subject to strong agglomeration, and to achieve primary particle distribution, it is necessary to knead the mixture with high shear force. This made formulation problematic. And in synthetic resins, dispersion was often insufficient even after thorough mixing and kneading.

Hybrid silicone powders eliminate these shortcomings, and the key to this can be found in their structure, i.e. silicone rubber powder grains coated with silicone resin powder. Hybrid silicone powders resist agglomeration **(Fig. 1)**, show outstanding dispersion onto substrates **(Photo 4)**, have a soft and slippery feel, and have excellent impact resistance – in other words, they exhibit features of both silicone rubber powder and silicone resin.

One of our hybrid silicone powders, KSP-300, was developed using a silicone rubber that contains phenyl groups for enhanced resistance to swelling in dimethyl silicone fluid **(Fig. 2)**.

4. Silica powders

Silica powders X-52-7042 and X-52-7043 were developed as anti-blocking agents for plastic film, and consist of relatively large, spherical silica particles **(Photo 5)**. Compared to common silica, these powders contain less moisture and have low moisture absorption properties **(Table 4)**, and they can be used in resin compounding and molding without risk of foaming. Compared to silicone resin powders, X-52-7042 and X-52-7043 have high refractive indices (near those of typical organic polymers), so they maintain high transparency.

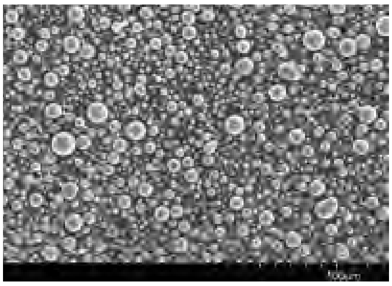
Sol-gel silica powder X-24-9163A consists of hydrophobized submicron spherical silica particles. As you can see from **Photo 6**, the particle size distribution is narrow. And thanks to an advanced hydrophobization process, X-24-9163A has excellent dispersibility and lubricity despite its submicron grain size, and can be dispersed even in organic solvents with just a small rise in viscosity.

Conclusion

Demand throughout the industrial sector for functional filling agents is only expected to rise. Shin-Etsu is committed to ongoing technological development with respect to silicone powders, to meet the increasingly sophisticated needs of the market.

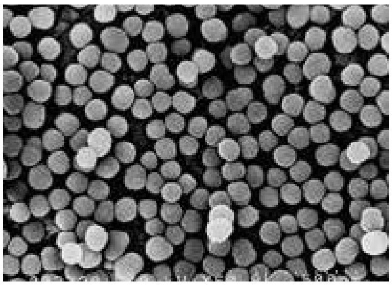
● Information current as of Oct. 2009.

Photo 5



Electron micrograph of X-52-7042 silica powder

Photo 6



Electron micrograph of X-24-9163A silica powder

Figure 1: Agglomeration of hybrid silicone powder
(Amount passing through mesh when shaken for 90 seconds by a shaker device)

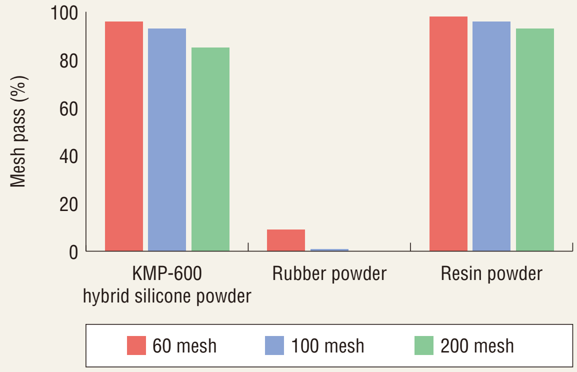
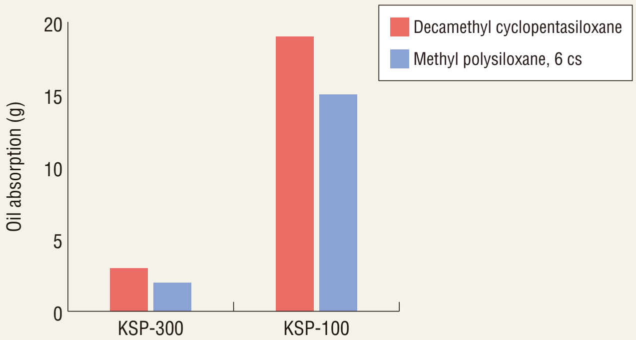


Figure 2: Swelling of KSP-300 in dimethyl silicone
(Oil absorption)



Five grams of hybrid powder are blended into 50 g of silicone fluid. After shaking, the mixture is stored for three days at room temperature, then the solid and liquid portions separated using a pressure filter apparatus. Oil absorption (g) = [Weight (g) of solid portion after solid/liquid separation] – 5 (g)

Shin-Etsu Chemical Co., Ltd.

Silicone Division

Marunouchi Eiraku Bldg., 4-1, Marunouchi 1-chome, Chiyoda-ku, Tokyo 100-0005, Japan

Sales and Marketing Department Ⅰ

< Fluids >
Phone : +81-(0)3-6812-2406 Fax : +81-(0)3-6812-2414

Sales and Marketing Department Ⅱ

< Silanes & Resins >
Phone : +81-(0)3-6812-2407 Fax : +81-(0)3-6812-2414

Sales and Marketing Department Ⅲ

< Rubber & LIMS >
Phone : +81-(0)3-6812-2408 Fax : +81-(0)3-6812-2415
< Designed Products >
Phone : +81-(0)3-6812-2409 Fax : +81-(0)3-6812-2415

Sales and Marketing Department Ⅳ

< RTV Rubber & Grease · Oil compounds >
Phone : +81-(0)3-6812-2410 Fax : +81-(0)3-6812-2415
< Sealant >
Phone : +81-(0)3-6812-2411 Fax : +81-(0)3-6812-2415

- The data and information presented in this catalog may not be relied upon to represent standard values. Shin-Etsu reserves the right to change such data and information, in whole or in part, in this catalog, including product performance standards and specifications without notice.
- Users are solely responsible for making preliminary tests to determine the suitability of products for their intended use. Statements concerning possible or suggested uses made herein may not be relied upon, or be construed, as a guaranty of no patent infringement.
- For detailed information regarding safety, please refer to the Safety Data Sheet (SDS).
- The silicone products described herein have been designed, manufactured and developed solely for general industrial use only; such silicone products are not designed for, intended for use as, or suitable for, medical, surgical or other particular purposes. Users have the sole responsibility and obligation to determine the suitability of the silicone products described herein for any application, to make preliminary tests, and to confirm the safety of such products for their use.
- Users must never use the silicone products described herein for the purpose of implantation into the human body and/or injection into humans.
- Users are solely responsible for exporting or importing the silicone products described herein, and complying with all applicable laws, regulations, and rules relating to the use of such products. Shin-Etsu recommends checking each pertinent country's laws, regulations, and rules in advance, when exporting or importing, and before using the products.
- Please contact Shin-Etsu before reproducing any part of this catalog. Copyright belongs to Shin-Etsu Chemical Co., Ltd.

Shin-Etsu Silicones of America, Inc.

1150 Damar Drive, Akron, OH 44305, U.S.A.
Phone : +1-330-630-9860 Fax : +1-330-630-9855

Shin-Etsu do Brasil Representação de Produtos Químicos Ltda.

Rua Coronel Oscar Porto, 736 - 8°Andar - Sala 84,
Paraíso São Paulo - SP Brasil CEP: 04003-003
Phone : +55-11-3939-0690 Fax : +55-11-3052-3904

Shin-Etsu Silicones Europe B.V.

Bolderweg 32, 1332 AV, Almere, The Netherlands
Phone : +31-(0)36-5493170 Fax : +31-(0)36-5326459

Germany Branch
Rheingaustrasse 190-196, 65203 Wiesbaden, Germany
Phone : +49-(0)611-962-5366 Fax : +49-(0)611-962-9266

Shin-Etsu Silicone Taiwan Co., Ltd.

Hung Kuo Bldg. 11F-D, No. 167, Tun Hua N. Rd.,
Taipei, 105406 Taiwan, R.O.C.
Phone : +886-(0)2-2715-0055 Fax : +886-(0)2-2715-0066

Shin-Etsu Silicone Korea Co., Ltd.

GT Tower 15F, 411, Seocho-daero, Seocho-gu,
Seoul 06615, Korea
Phone : +82-(0)2-590-2500 Fax : +82-(0)2-590-2501

Shin-Etsu Singapore Pte. Ltd.

4 Shenton Way, #10-03/06, SGX Centre Ⅱ, Singapore 068807
Phone : +65-6743-7277 Fax : +65-6743-7477

Shin-Etsu Silicones India Pvt. Ltd.

Unit No. 403A, Fourth Floor, Eros Corporate Tower,
Nehru Place, New Delhi 110019, India
Phone : +91-11-43623081 Fax : +91-11-43623084

Shin-Etsu Silicones (Thailand) Ltd.

7th Floor, Harindhorn Tower, 54 North Sathorn Road,
Bangkok 10500, Thailand
Phone : +66-(0)2-632-2941 Fax : +66-(0)2-632-2945

Shin-Etsu Silicone International Trading (Shanghai) Co., Ltd.

29F Junyao International Plaza, No.789,
Zhao Jia Bang Road, Shanghai 200032, China
Phone : +86-(0)21-6443-5550 Fax : +86-(0)21-6443-5868

Guangzhou Branch
Room 2409-2410, Tower B, China Shine Plaza, 9 Linhexi Road,
Tianhe, Guangzhou, Guangdong 510610, China
Phone : +86-(0)20-3831-0212 Fax : +86-(0)20-3831-0207

The Development and Manufacture of Shin-Etsu Silicones are based on the following registered international quality and environmental management standards.

Gunma Complex	ISO 9001 (JCQA-0004	ISO 14001 JCQA-E-0002)
Naoetsu Plant	ISO 9001 (JCQA-0018	ISO 14001 JCQA-E-0064)
Takefu Plant	ISO 9001 (JQA-0479	ISO 14001 JQA-EM0298)

https://www.shinetsusilicone-global.com/

This is an edited version of the product data released on Jan. 2017.