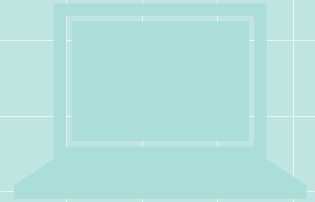


Silicones for Resin Modification



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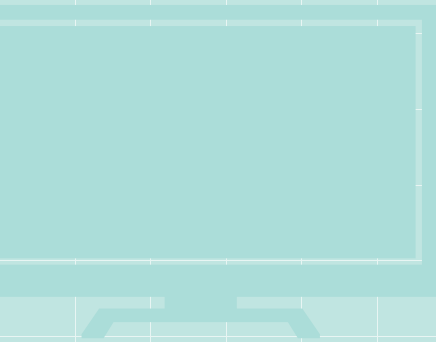
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Silicones for Resin Modification

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.



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.

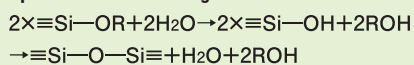
Introduction

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

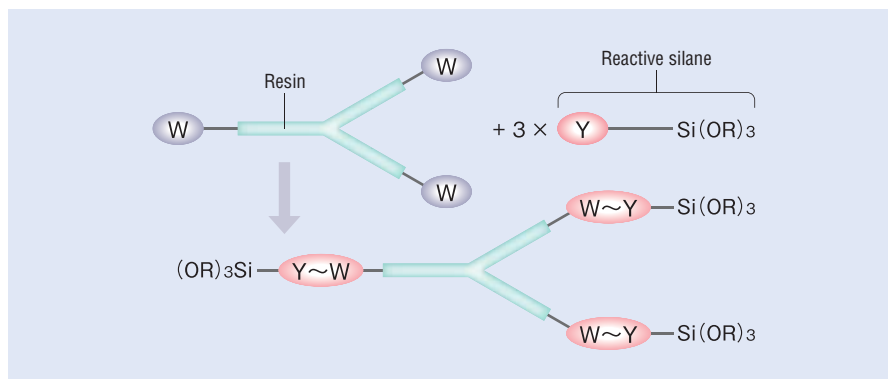
The alkoxy groups in a silane coupling agent react with water in the presence of a catalyst to form stable siloxane bonds as shown in Equation 1.

Equation 1: Crosslinking mechanism



Thus, an organic resin that has been modified by the organic reactive groups in the silane coupling agent, and functionalized with alkoxy groups will have good crosslinking

Figure 1



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 alkoxy 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

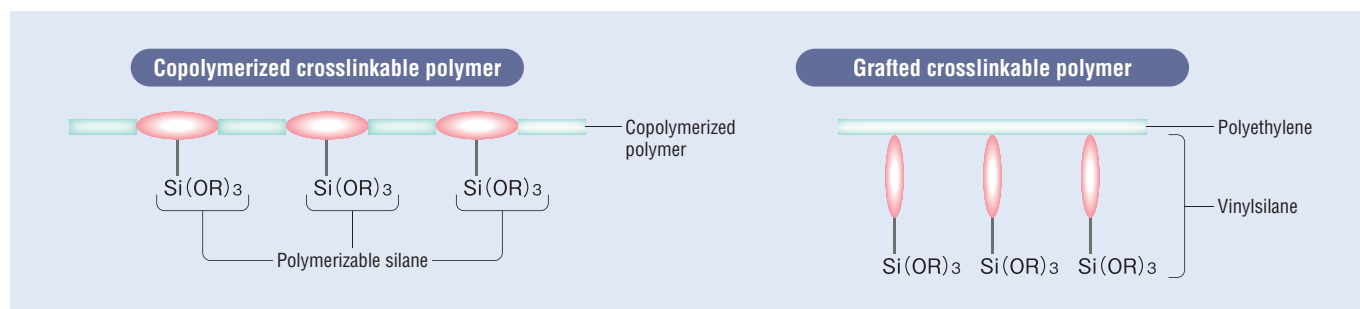
reaction is shown in Figure 1. By reacting a resin containing an organic group W with a silane coupling agent containing an organic functional group Y which reacts with W, it is easy to obtain an organic resin functionalized with alkoxy groups.

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 ₃ H ₆ NH ₂	KBM-903	Methoxy	Isocyanate groups, Epoxy groups
		KBE-903	Ethoxy	
	-C ₃ H ₆ -N ₂ -C ₆ H ₅	KBM-573	Methoxy	
Epoxy	-C ₃ H ₆ OCH ₂ CH ₂ CH ₂	KBM-403	Methoxy	Amino groups, Hydroxyl groups, Carboxyl groups
		KBE-402	Ethoxy	
		KBE-403	Ethoxy	
	-C ₂ H ₄ -C ₆ H ₈ O	KBM-303	Methoxy	
Mercapto	-C ₃ H ₆ SH	KBM-802	Methoxy	Isocyanate groups
		KBM-803	Methoxy	
Isocyanate	-C ₃ H ₆ NCO	KBE-9007	Ethoxy	Amino groups, Hydroxyl groups, Mercapto groups
Acid anhydride	-C ₃ H ₆ -C ₄ H ₄ O ₂	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 alkoxy-silyl 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 alkoxy-silyl 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 alkoxy-silyl 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 alkoxy-silyl 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 ₃ H ₆ OCOC(=CH ₂) CH ₃	KBM-502	Methoxy
		KBM-503	Methoxy
		KBE-502	Ethoxy
		KBE-503	Ethoxy
Acrylate	—C ₃ H ₆ OCOCH=CH ₂	KBM-5103	Methoxy

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

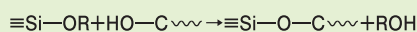
Functional group category	Reactive group (Y)	Product name	Alkoxy groups
Ureido	—C ₃ H ₆ NHC(=O)NH ₂	KBE-585	Ethoxy
Isocyanurate		X-12-965	Methoxy



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



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).

Figure 3: Flame resistance of polycarbonate with silicone added

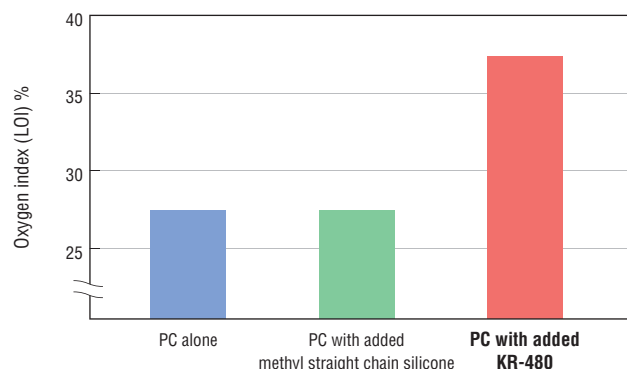


Table 4: Silicone alkoxy oligomers

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	Low hardness
		KR-213	Methoxy	High phenyl content
Epoxy	$-\text{C}_3\text{H}_6\text{OCH}_2\text{CH}(\text{O})\text{CH}_2$	X-41-1053	Methoxy/Ethoxy	Epoxy equivalent 830 g/mol
Methyl/Epoxy		X-41-1056	Methoxy	Epoxy equivalent 350 g/mol
Mercapto	$-\text{C}_3\text{H}_6\text{SH}$	X-41-1805	Methoxy/Ethoxy	Mercapto equivalent 800 g/mol
Methyl/Mercapto		X-41-1810	Methoxy	Mercapto equivalent 450 g/mol
Methyl/Amino	$-\text{C}_3\text{H}_6\text{NH}_2$	X-40-2651	Methoxy	Self-forming rubber film
Methyl/Methacrylate	$-\text{C}_3\text{H}_6\text{OCOC}(\text{CH}_3)=\text{CH}_2$	X-40-9272B	Methoxy	Methacrylate equivalent 290 g/mol
Methyl/Acrylate	$-\text{C}_3\text{H}_6\text{OCOCH}=\text{CH}_2$	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)

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 Alkoxy Oligomers

Silicone resins form coatings of exceptional hardness, weatherability and flame resistance, and are used in applications in a variety of fields. One drawback is that curing requires high temperatures and considerable time. Silicone alkoxy oligomers were developed in response to user needs, for products that had better curing properties or were solvent free. Silicone alkoxy oligomers have the potential for application to a wider array of fields in which silicone resins could not be used.

Introduction

A silicone resin is a silicone with a three-dimensional network structure consisting primarily of tetra-functional siloxane units. When cured, the material forms a coating with high hardness and excellent weatherability and flame resistance.

Organic substituent groups can impart water repellency or hydrophilicity, properties which make silicone resins useful in applications including construction materials and electronic materials.

Conventional products typically consist of a silanol group-containing resin dissolved in an organic solvent, and cure through a process of dehydration/condensation of the silanol groups. But this curing process requires high temperatures and considerable time, meaning that the range of suitable applications is somewhat limited. Many users indicated a need for materials that had better curing properties and were solvent free.

In this issue, we discuss silicone alkoxy oligomers: a type of resin in which the drawbacks of conventional resin products

have been overcome, opening up the potential for use in new applications in fields in which conventional products could not be used.

Silicone alkoxy oligomers

Silicone alkoxy oligomers are a type of silicone resin of relatively low molecular weight, and whose molecule ends are capped with alkoxysilyl groups ($\equiv\text{Si-OR}$).

In these materials, typically the active ingredient is 100%, a condition which makes for an exceptionally stable liquid. Contact with moisture or humidity in the air initiates the hydrolysis of the alkoxy groups to start the crosslinking reaction. This characteristic makes these materials attractive for users hoping to eliminate solvents from their work processes.

At present, silicone alkoxy oligomers are primarily used in the following applications:

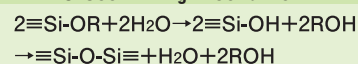
1. High-weatherability coating agents
2. Modifiers for heat-resistant plastics
3. Coupling agents for organic-inorganic composite materials
4. Surface modification agents

It is important to select the right type of silicone alkoxy oligomer for the particular intended use. Shin-Etsu offers a lineup of products incorporating different functional groups, so users can find the ideal alkoxy oligomer for their specific applications.

● Methyl oligomers

Whereas UV light breaks down organic substances, silicone resins that feature methyl groups as the organic substituent group do not absorb UV rays and resist degradation by light and ozone. Their three-dimensional crosslinked siloxane skeleton has high binding energy and they form coatings that are highly resistant even to acid rain. These oligomers are thus the best suited for use as high-weatherability coating agents. Methyl oligomers have excellent hydrolysis reaction properties, and when used with the proper curing catalyst can be used as coating agents which cure at normal temperature and humidity.

Crosslinking mechanism



A range of methyl oligomers exist today. Products are available in several grades of different molecular weight distributions, and materials have been developed which can improve flexibility (anti-cracking properties), enable application of thicker films, or impart other functions (Table 1).

Using these oligomers in combination with curing catalysts, the user can obtain a coating with the desired properties.

The titanium based curing catalysts D-20 and D-25 are commonly used, with D-25 frequently chosen for its greater ease of blending (Table 2).

● Methyl phenyl oligomers

Oligomers which contain phenyl groups have good miscibility with organic resins such as acrylic, epoxy and polyester, and are thus used as intermediates for resin modification or as reactive diluents (Table 3).

Reaction mechanism

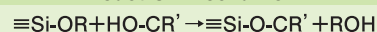


Table 1: Methyl silicone alkoxy oligomers

Product name	Alkoxy groups	Viscosity at 25°C, mm ² /s	Refractive index, 25°C	Alkoxy group content, wt %	Features
KC-89S	Methoxy	5	1.394	45	Low polymer, High hardness
KR-500	Methoxy	25	1.403	28	Medium polymer
X-40-9225	Methoxy	100	1.407	24	High polymer, Improves flexibility
X-40-9246	Methoxy	70	1.407	12	Improves flexibility
X-40-9250	Methoxy	120	1.407	25	Enables flexible, thick coatings

(Not specified values)

Table 2: Variation in coating properties depending on the methyl silicone alkoxy oligomer/catalyst combination

Product name	Curing catalyst (Amt. added, %)	Coating, μm	Tack-free time, min	Pencil hardness	Flexural & impact resistance
KR-500	D-25 (2)	25	30	H	Fair
KR-500	D-25 (5)	25	20	2H	Fair to poor
KR-500	DX-9740 (5)	25	100	5H	Poor
X-40-9225	D-25 (5)	40	60	H	Good
KR-500/X-40-9250=80/20	D-25 (2)	60	60	F	Good

* Substrate: Polished steel sheet. Drying conditions: 25 °C/70% RH/7 days (Tack-free time varies depending on temperature & humidity.) (Not specified values)

Table 3: Methyl phenyl silicone alkoxy oligomers

Product name	Alkoxy groups	Viscosity at 25°C, mm ² /s	Refractive index, 25°C	Alkoxy group content, wt %	Features
KR-9218	Methoxy	40	1.529	15	Forms medium hardness coatings
KR-213	Methoxy	16	1.525	20	High phenyl content
KR-510	Methoxy	100	1.509	17	High hardness, low cost
X-40-9227	Methoxy	15	1.460	15	Improves softness
X-40-9247	Methoxy	90	1.505	16	High hardness, low volatile content

(Not specified values)



Chimney stack with heat-resistant protective coating

Figure 1: Weatherability test results for modified resin coatings

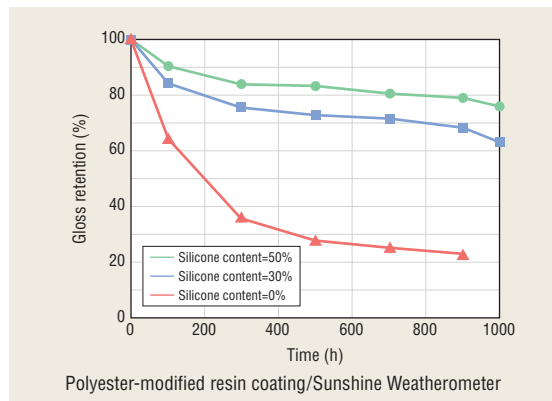
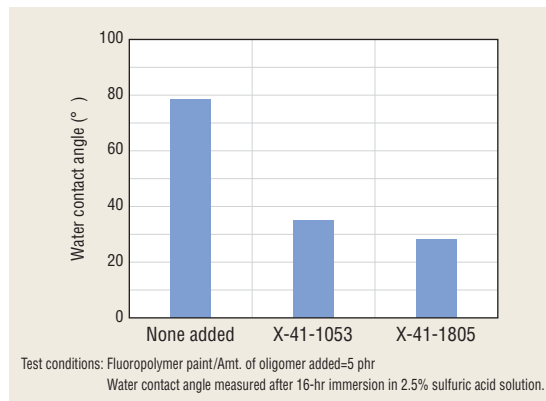


Figure 2: Hydrophilicity test results for coatings with oligomer added



In applications involving modification of organic resins, the reaction catalysts used are typically alkyl titanates, organic acids or amine compounds. But in these reactions, the oligomers have a tendency to undergo a self-condensation reaction, meaning that the reaction conditions must be kept relatively mild. Hydroxyl and other active groups in the organic resin react with alkoxysilyl groups to produce copolymers which are useful as a resin component for manufacturing paints which have excellent weatherability, heat resistance and chemical resistance (Fig. 1).

- Oligomers which contain organic functional groups
- Oligomers which contain no organic groups

Silane coupling agents are commonly added to organic resins as a means of improving their adhesion to inorganic substrates. In such applications, a potential problem is that the silane coupling agent may evaporate during the heat-curing process and thus not function effectively. Today the market offers a solution to this problem in the form of special oligomers that contain organic functional groups and feature pre-hydrolyzed silane coupling agents to give them lower volatility.

The Shin-Etsu lineup includes alkoxy oligomers which feature epoxy, mercapto, acrylate and amino groups as the organic functional groups (Table 4).

The organic functional groups in these oligomers react with other organic resins to produce modified resins which are functionalized with alkoxysilyl groups. This method is being employed in attempts to develop organic resins which cure based on a moisture-cure system.

Also noteworthy is the fact that the silanol groups formed through hydrolysis of the alkoxysilyl groups are hydrophilic. During the cure process, alkoxysilyl groups migrate to the surface, and when later hydrolyzed will form silanol groups on the surface and

thereby produce a cured coating which exhibits hydrophilic antifouling properties. Researchers have developed products based on this technology (Fig. 2).

The oligomers which contain no organic substituent groups form silica coatings with exceptional hardness, and are thus useful as coating agents for surface protection of manmade structures of stone and other materials.

● Room-temperature-cure coating agents

Also available on the market today are solvent-free coating agents consisting of alkoxy oligomer with the most suitable catalysts and other components already blended in. These products are easier to use as there is no need to mix them with a curing catalyst. They can be applied to metal, stone, wood, plastic and other materials, where they cure rapidly at room temperature to form cured coatings of varying degrees of hardness. On a variety of substrates, these

products offer effective surface protection and improve weatherability and water repellency (Table 5).

Conclusion

Silicone alkoxy oligomers are easy to work with, and users in various fields are experimenting with their use in new applications. We expect the range of applications for silicone alkoxy oligomers to continue to grow.

We expect organic functional group-containing oligomers to be used increasingly in applications in which the use of silane coupling agents has been problematic. Silicone alkoxy oligomers can also meet the needs of users who want to reduce the amount of alcohol released when using other products. Shin-Etsu will continue working to develop new products in this promising category.

● Information current as of Apr. 2009.

Table 4: Oligomers containing organic functional groups, and oligomers containing no organic groups

Product name	Organic substituent group	Alkoxy groups	Viscosity at 25°C, mm ² /s	Refractive index, 25°C	Alkoxy group content, wt %	Features
X-41-1053	Epoxy	Methoxy/Ethoxy	10	1.414	50	Epoxy equivalent 830 g/mol
X-41-1059A	Epoxy	Methoxy/Ethoxy	30	1.434	43	Epoxy equivalent 350 g/mol
X-41-1056	Epoxy/Methyl	Methoxy	50	1.442	17	Epoxy equivalent 280 g/mol
X-41-1805	Mercapto	Methoxy/Ethoxy	20	1.417	50	Mercapto equivalent 800 g/mol
X-41-1818	Mercapto	Ethoxy	15	1.416	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
X-40-2672B	Acrylate/Methyl	Methoxy	90	1.444	23	Acrylate equivalent 280 g/mol
X-40-9272B	Methacrylate/Methyl	Methoxy	10	1.433	32	Methacrylate equivalent 290 g/mol
X-40-2651	Amino/Methyl	Methoxy	25	1.405	7	Curing properties, rubbery coating
X-40-2308	(None)	Methoxy	5	1.388	65	Ultra high hardness
X-40-9238	(None)	Ethoxy	10	1.401	70	Ultra high hardness

(Not specified values)

Table 5: Room-temperature-cure coating agents

Product name	Organic substituent group	Viscosity at 25°C, mm ² /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 (X-40-175)	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.

(Not specified values)

(Tack-free time varies depending on temperature & humidity.)

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-22-2102	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

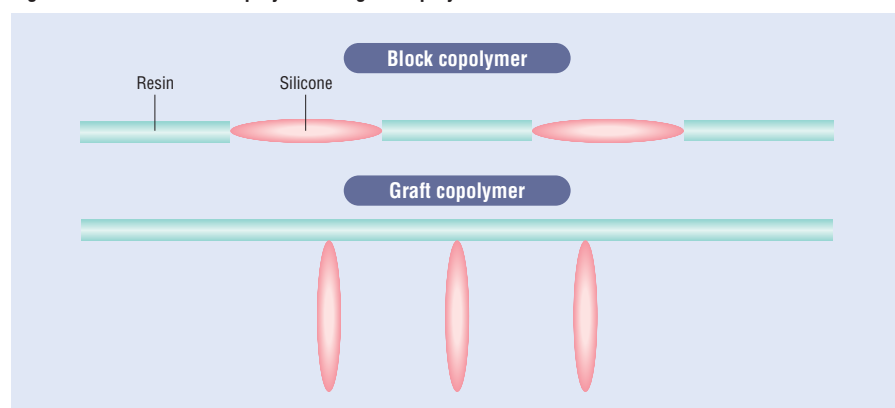
Product name	Non-volatile content, %	Particle size, nm	Ionicity
KM-9703	45	280	Anionic
X-52-8026C	32	180	Anionic

(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



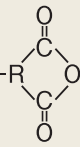
of a reactive silicone. Improving miscibility helps to improve the reaction between the resin and silicone, such that the modifying effect can be achieved using a smaller amount. In addition, by incorporating different types of reactive groups, manufacturers have developed products that can be used for 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 ₃ H ₆ NH ₂	KF-8010	12	430
	X-22-161A	25	800
	X-22-161B	55	1,500
	KF-8012	90	2,200
-C ₃ H ₆ OCH ₂ CH(CH ₂) ₂ O	KF-105	15	490
	X-22-163A	30	1,000
	X-22-163B	60	1,800
	X-22-163C	120	2,700
-C ₂ H ₄ - 	X-22-169AS	30	500
	X-22-169B	70	1,700
-C ₃ H ₆ OC ₂ H ₄ OH	X-22-160AS	35	470
	KF-6001	45	900
	KF-6002	70	1,600
KF-6003	110	2,500	
-C ₃ H ₆ - 	X-22-1821	100	1,600
-C ₃ H ₆ OCOC(=CH ₂)CH ₃	X-22-164A	25	860
	X-22-164B	55	1,600
	X-22-164C	90	2,400
-C ₂ H ₄ COOH	X-22-162C	220	2,300
	X-22-2290AS	160	500
-C ₃ H ₆ SH	X-22-167B	60	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
-C ₃ H ₆ OCH ₂ CH(CH ₂) ₂ O	X-22-173BX	30	2,500
	X-22-173DX	60	4,700
-C ₃ H ₆ OC ₂ H ₄ OH	X-22-170BX	40	2,800
	X-22-170DX	65	4,700
-C ₃ H ₆ OCH ₂ C(CH ₂ OH) ₂ C ₂ H ₅	X-22-176DX	130	3,200
	X-22-176GX-A	400	14,000
-C ₃ H ₆ OCOC(=CH ₂)CH ₃	X-22-174DX	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
		X-22-6266	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	610
Aralkyl	X-22-3000T	2,000	250	
Acrylic	Polyether	X-22-1602	300	1,200

(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.

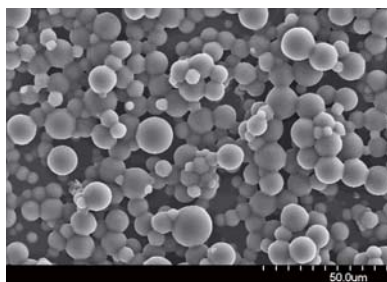
As an example, we show the effects when silicone rubber powder is added to polystyrene resin (Table 2).

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.

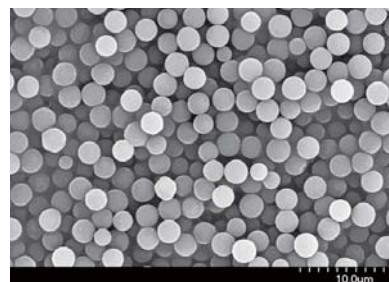
As you can see from Photo 2, the particle size distribution is narrow. Unlike silicone rubber powders, silicone resin powders are hard substances with no elasticity. This property gives them superior sliding properties. Silicone resin powders can be added to plastic films, paints, inks, personal care 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-702	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/cm ²	Abrasion pressure 25.4 kg/cm ²
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.

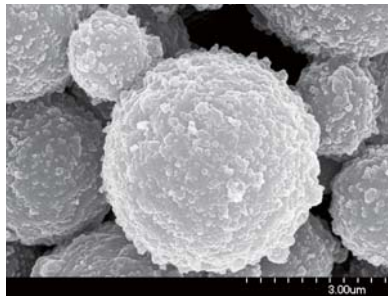
Table 3: Refractive indices of silicone resin powder and synthetic resins

Synthetic resin	Refractive index
KMP-702	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)

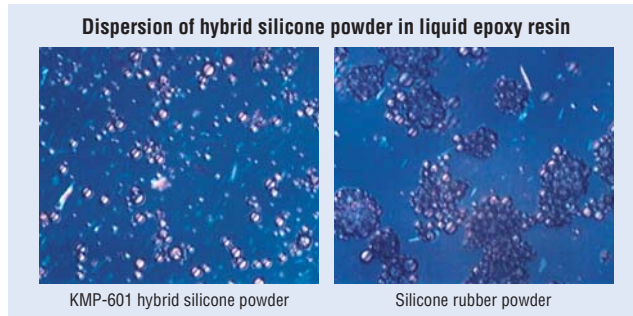
Process No.	Process description	Processing conditions	Water content, ppm	
			X-52-7042	X-52-7043
①	Drying before humidification	105°C/3h	250	170
②	Humidification	① → 35°C/85% Humidity/24h	270	270
③	Re-drying	② → 250°C/10min	250	250

Photo 3



Electron micrograph of KMP-600 hybrid silicone powder

Photo 4



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

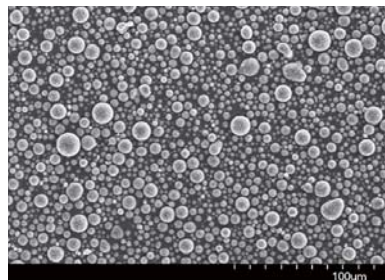
of hydrophobized submicron spherical silica particles. As you can see from Photo 6, the particle size distribution is narrow. And thanks to an advanced hydrophobization process, X-24-9163A has excellent dispersibility and lubricity despite its submicron grain size, and can be dispersed even in organic 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)

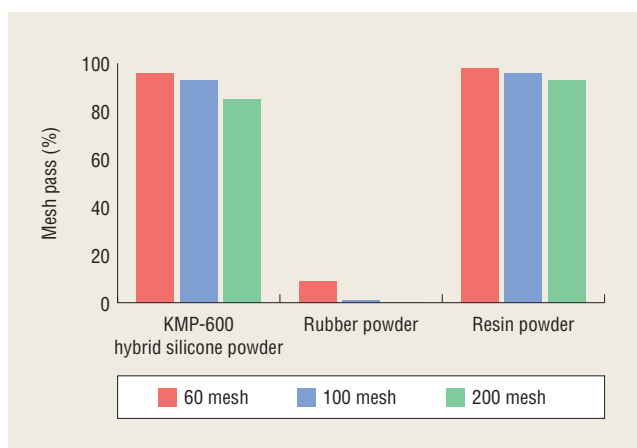
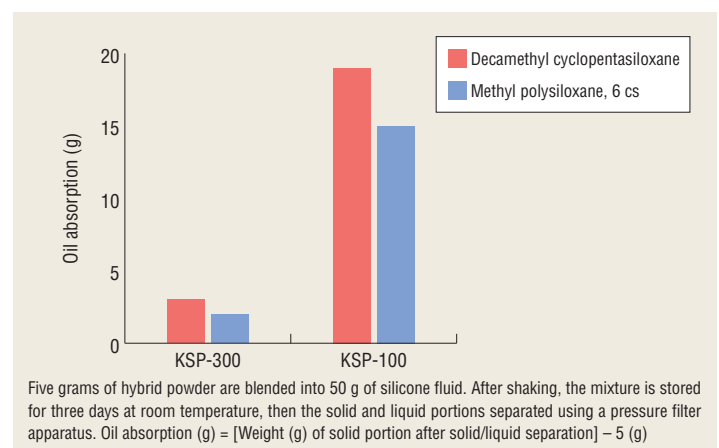


Figure 2: Swelling of KSP-300 in dimethyl silicone
(Oil absorption)



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