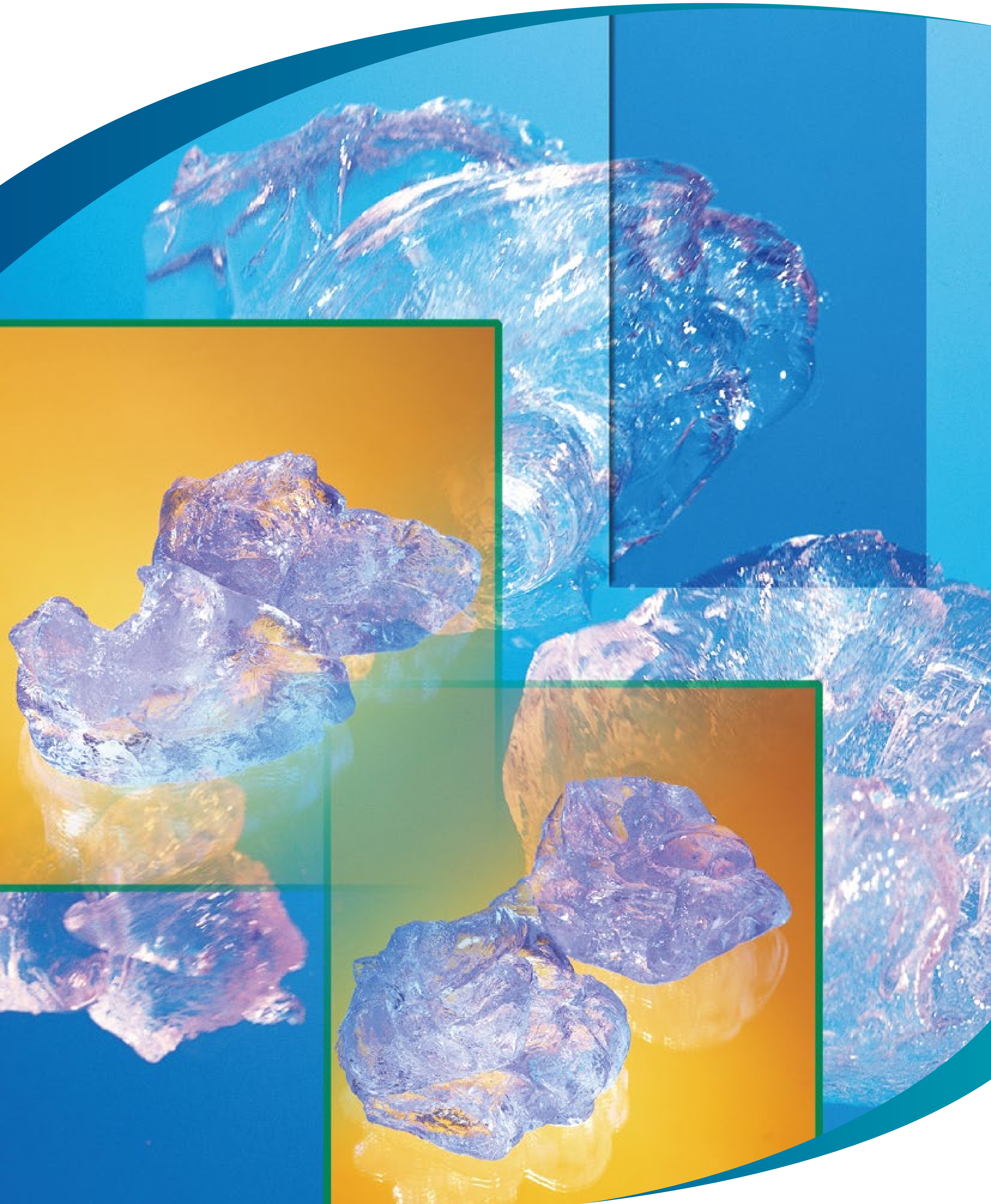
Characteristic properties of Silicone Rubber Compounds

Shin-Etsu Silicone



Meeting the increasingly diverse and sophisticated needs of industry with the unique properties of silicone rubbers

The main ingredients of Shin-Etsu's silicone rubber compounds are unique raw silicone rubber gum and high-purity silica. Silicone rubber compounds have characteristics of both inorganic and organic materials, and offer a number of advantages not found in other organic rubbers. Silicone rubbers have fine electrical properties, good chemical stability and flame retardancy, and superior resistance to heat and cold. They are thus used in nearly every industry to improve the quality and functionality of products including electric and electronic equipment, office automation equipment, automobiles, food products, household goods, and leisure products.

■ Contents

General properties of silicone

High binding energy

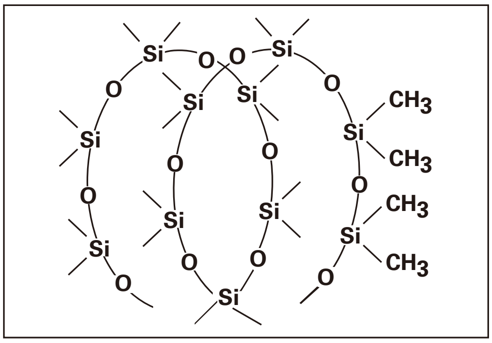
The siloxane bonds (–Si–O–Si–) that form the backbone of silicone (dimethyl polysiloxane) are highly stable. At 433 kJ/mol, their binding energy is higher than that of carbon bonds (C–C), at 355 kJ/mol. Thus, compared to common organic polymers, silicone rubbers have higher heat resistance and chemical stability, and provide better electrical insulation.

-Si—O—Si—O—Si-

- Heat resistance
- Flame retardancy
- Chemical stability
- Good weatherability
- Radiation resistance
- Electrical properties

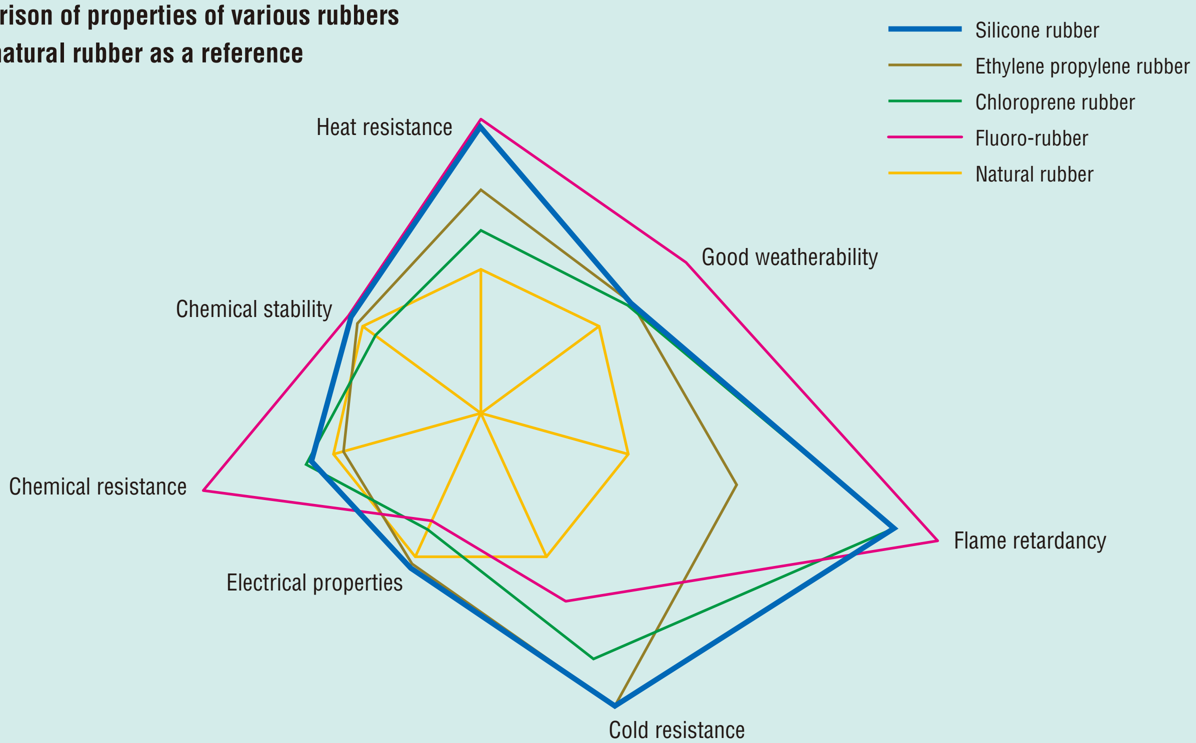
Intermolecular force is low, and coil formation capacity is high.

Silicone molecules are helical and intermolecular force is low, resulting in high elasticity, high compressibility, and excellent resistance to cold temperatures. Furthermore, the methyl groups located on the outside the coil structure can rotate freely. This characteristic gives silicone its distinctive interfacial properties, including water repellency and good releasability.



- Water repellency
- Releasability
- Cold resistance
- Good compression characteristics

Comparison of properties of various rubbers using natural rubber as a reference



Heat and cold resistance

Silicone rubber withstands high and low temperatures far better than organic rubbers. Silicone rubber can be used indefinitely at 150°C with almost no change in its properties. It withstands use even at 200°C for 10,000 hours or more, and some products can withstand heat of 350°C for short periods. Silicone rubbers are thus suitable as a material for rubber components used in high temperature environments.

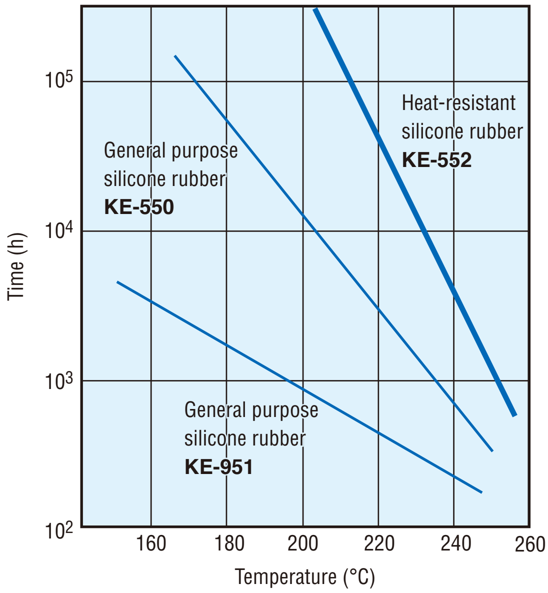
Silicone rubber also has excellent resistance to cold temperatures. The embrittlement point of typical organic rubbers is between -20° and -30°C, compared to -60° to -70°C for silicone rubbers. Even at temperatures at which organic rubbers turn brittle, silicone rubber remains elastic. Some products withstand extremely low temperatures of -100°C and below.

Generally speaking, silicone rubber hardens when heated in air, with decreasing elongation as it deteriorates; but in sealed conditions it softens as it deteriorates, and its operating life at high temperatures is shorter in sealed conditions than in air.

This softening results from the degradation of the siloxane polymer. Adjusting the silicone rubber formula, using a different curing agent, and/or post-curing can help prevent softening in hot, sealed conditions. Such products are also available.

Operating life of silicone rubber in high-temperature conditions

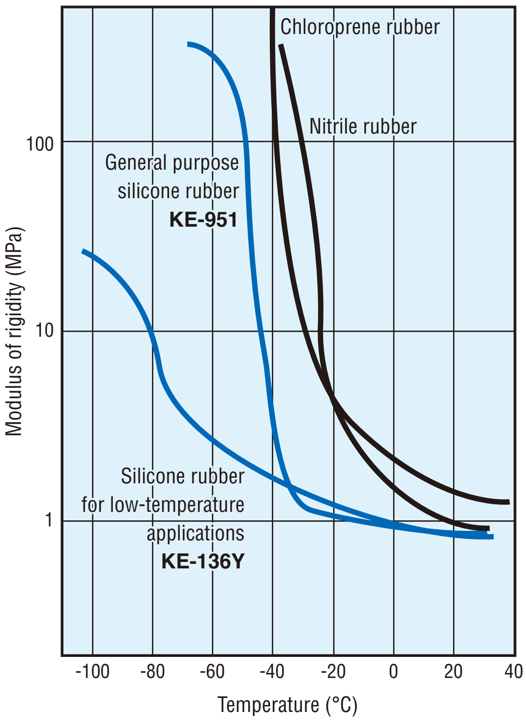
(Operating life defined as the time at which elongation at break is 1/2 that of the initial value)



Even among general purpose silicone rubbers, heat resistance varies depending on the rubber formula, curing agent, and other factors.

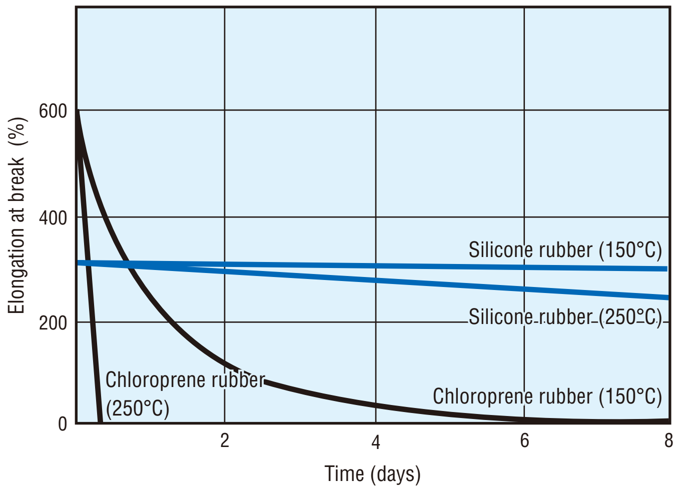
Low-temperature properties of various rubbers

<Test method> JIS K 6261, Section 5



Comparison of high-temperature operating life

Chloroprene rubber vs. silicone rubber



Chloroprene rubber deteriorates rapidly and discolors at temperatures between 150°–250°C, but there is little change in silicone rubber even at 250°C.

Weatherability

Silicone rubbers have exceptional weatherability. Ozone created by corona discharge rapidly deteriorates most organic rubbers, but has almost no effect on silicone rubber. In addition, silicone rubber can be exposed to wind, rain and UV rays for long periods with virtually no change in its physical properties.

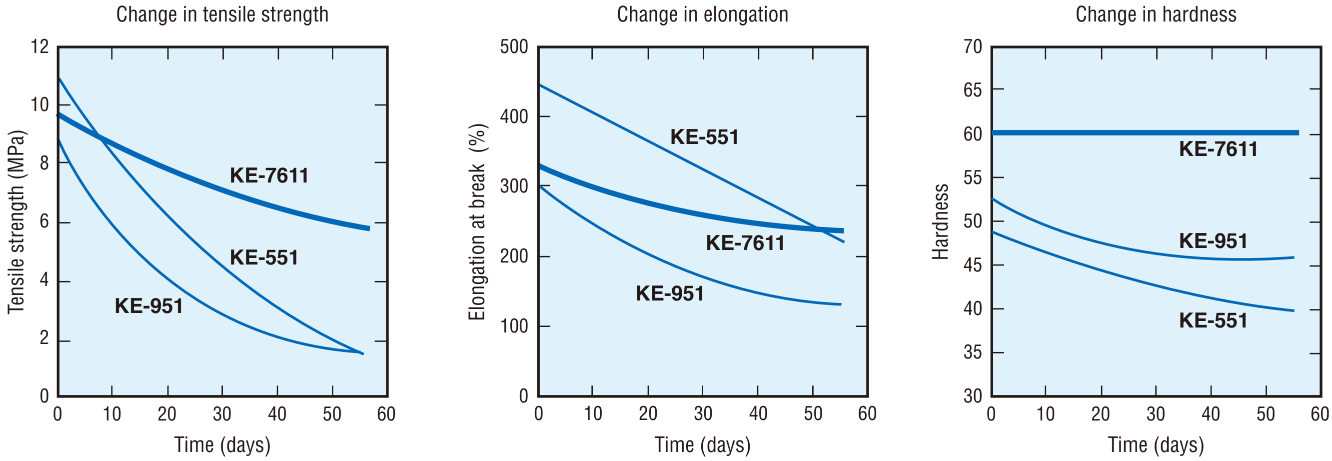
Results of long-term outdoor exposure testing of various rubbers

Rubber type / Deterioration conditions / Location	Time until surface cracks are first apparent (years)		Time of sunlight exposure until elongation is 1/2 that of the initial value (years)	
	Panama	Rock Island	Panama	Rock Island
Styrene butadiene	2 - 3.5	Over 10 years	4	10
Nitrile	0.5 - 1	—	7	10
Chloroprene	—	—	8.5	Over 10 years
Silicone (methyl vinyl)	Over 10 years	Over 10 years	Over 10 years	Over 10 years to decline to 75%
Silicone (methylphenyl)	—	—	Over 10 years	Over 10 years
Fluorosilicone	—	—	0.5	4
Ethylene propylene	—	—	10	Over 8.5 years to decline to 75%
Fluorine	10	10	Over 10 years to decline to 90%	

Moisture and steam resistance

Silicone rubber can be immersed in water (cold water, warm water, boiling water) for long periods with water absorption of about 1%, and with virtually no effect on mechanical strength or electrical properties. Typically, under ordinary pressure, contact with steam causes almost no deterioration of silicone rubbers. With pressurized steam, however, the effects increase as steam pressure increases. High pressure steam at temperatures over 150°C causes breakdown of the siloxane polymer and a decline in the properties of the rubber. This effect can be ameliorated by adjusting the silicone rubber formula, selecting a proper curing agent, and/or post-curing. There are numerous products available with improved resistance to steam and hot water.

Steam resistance of silicone rubber (flowing steam at 0.64 MPa)



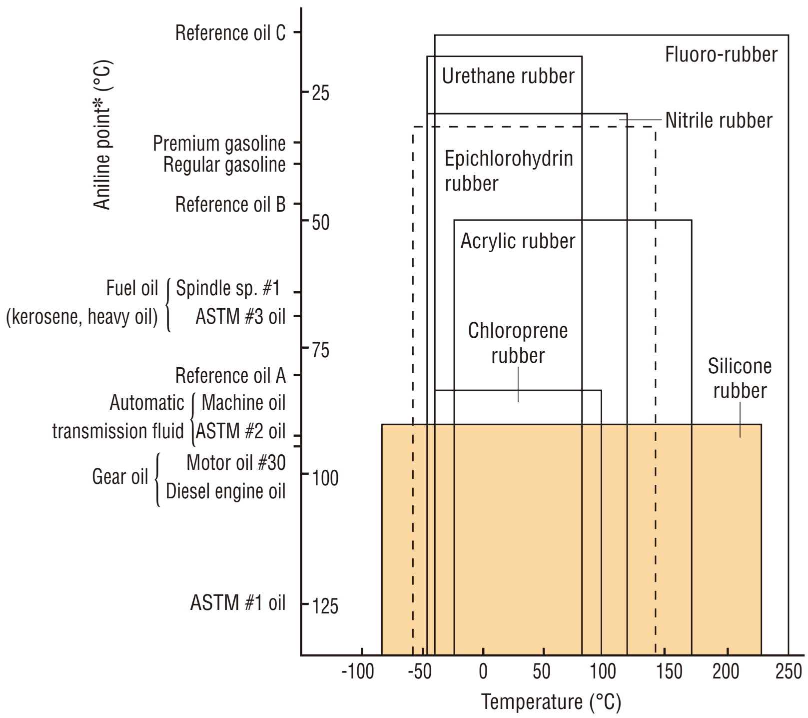
Resistance to oils, solvents, and other chemicals

Silicone rubber has outstanding resistance to oil at high temperatures. Among common organic rubbers, nitrile rubber and chloroprene rubber have somewhat higher oil resistance at temperatures below 100°C, but at higher temperatures silicone rubber is superior.

Silicone rubber also has excellent resistance to solvents and other chemicals. It is essentially unaffected by polar organic compounds (aniline, alcohol, etc.) or dilute acids or bases, with the increase in volume due to swelling in the range of only 10%–15%. Silicone rubber does swell in non-polar organic compounds like benzene, toluene and gasoline; but unlike most organic rubbers, it does not decompose or dissolve, and will return to its former state when the solvent is removed. Silicone rubber is, however, adversely affected by strong acids and bases, so it should not be used where it will come in contact with such chemicals.

Typically, the effects of solvents on silicone are evidenced by the swelling, softening and reduced strength of the rubber; the extent of these effects depends on the type of solvent involved.

Temperature range and various oils applicable to various rubbers

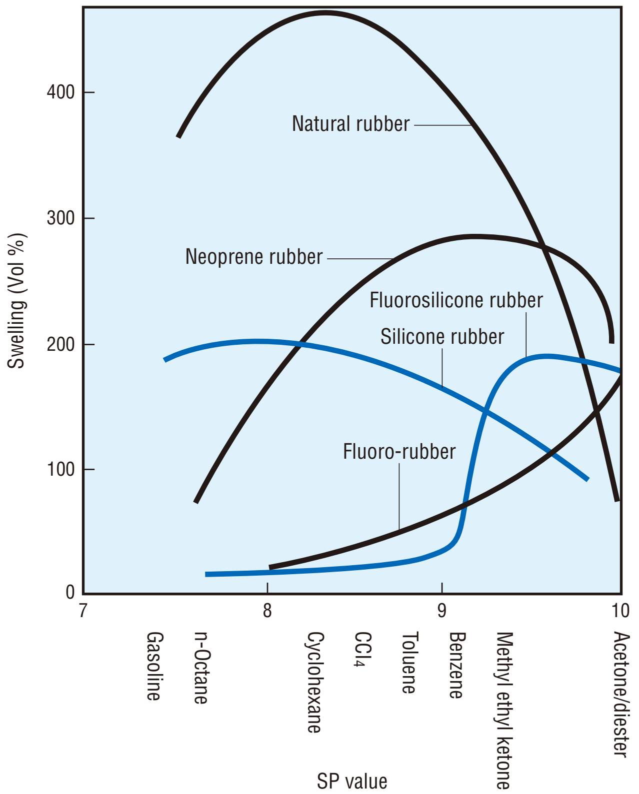


✻ Aniline point: the lowest temperature at which equal portions of an oil and aniline are completely miscible. The lower the aniline point, the greater the swelling effect of the oil.

Oil and chemical resistance of common methyl vinyl silicone rubber

		Type of oil/chemical	Immersion conditions	Change in properties				
			°C x h	Hardness points	Weight %	Volume %	Tensile strength %	Elongation %
Oil		ASTM #1 oil	150 x 168	-10		+10	-10	-10
Oil		ASTM #3 oil	150 x 168	-25		+40	-20	-20
Oil		GM Hydramatic Fluid	94 x 70	-35		+35	-40	-5
Oil		Ford Brake Fluid	150 x 72	-20		+15	-60	-40
Oil		Diesel Fuel	50 x 168	-30		+105	—	—
Oil		Gasoline	23 x 168	-20		+165	—	—
Oil		Skydrol 500A Fluid	70 x 168	-5		+10	-10	+5
Oil		Motor oil (SAE #30)	175 x 168	-8		-8	-70	-65
Chemical	Acid	Conc. Nitric acid	25 x 168		+10	+10	-80	30
Chemical	Acid	7% Nitric acid	25 x 168		< 1	< 1	-50	-30
Chemical	Acid	Conc. Sulfuric acid	25 x 168		Dissolves	Dissolves	Dissolves	Dissolves
Chemical	Acid	10% Sulfuric acid	25 x 168		< 1	< 1	0	0
Chemical	Acid	Acetic acid	25 x 168		+3	+4	-20	+10
Chemical	Acid	5% Acetic acid	25 x 168		+2	+2	-20	+10
Chemical	Acid	Conc. Hydrochloric acid	25 x 168		+3	+4	-40	-20
Chemical	Acid	10% Hydrochloric acid	25 x 168		+2	+2	-50	-50
Chemical	Alkali	10% Sodium hydroxide solution	25 x 168		-2	-1	-10	0
Chemical	Alkali	2% Sodium hydroxide solution	25 x 168		< 1	< 1	0	0
Chemical	Alkali	Conc. Ammonia water	25 x 168		+2	+1	-30	+10
Chemical	Alkali	10% Ammonia water	25 x 168		+2	+2	-20	0
Chemical	Other	Water	25 x 168		< 1	< 1	0	0
Chemical	Other	Water	100 x 70		< 1	< 1	-10	-10
Chemical	Other	Water	70 x 168		+1	< 1	-10	+10
Chemical	Other	3% Hydrogen peroxide solution	25 x 168		< 1	< 1	0	+20

Correlation between solubility parameter value (SP value) of a solvent and rubber swelling



The solvent resistance of fluorosilicone rubber is particularly high, although all silicone rubbers resist solvents better than other types of rubber.

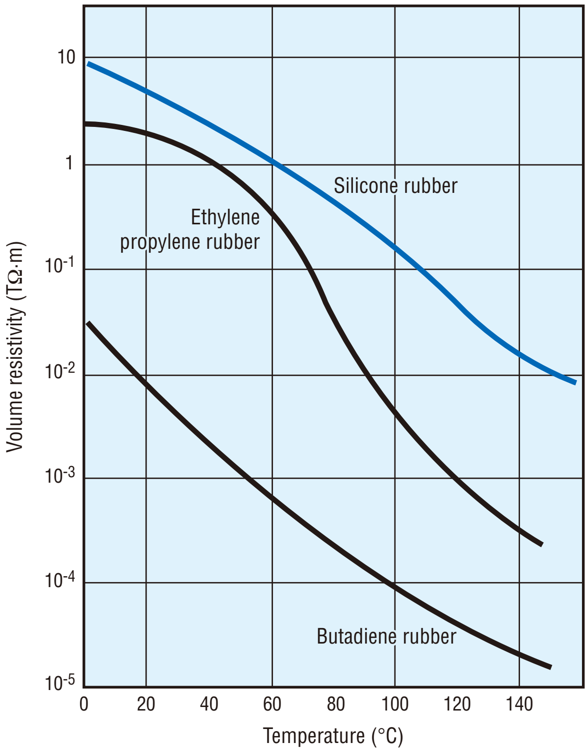
Change in volume of rubbers caused by various fluids (after 168-hour immersion)

Fluid type	Temperature °C	Nitrile			Chloroprene	Natural rubber	Styrene butadiene	Butyl	Silicone	Hypalon®
		28%	33%	38%						
Gasoline	50	15	10	6	55	250	140	240	260	85
ASTM #1 oil	50	-1	-1.5	-2	5	60	12	20	4	4
ASTM #3 oil	50	10	3	0.5	65	200	130	120	40	65
Diesel oil	50	20	12	5	70	250	150	250	150	120
Olive oil	50	-2	-2	-2	27	100	50	10	4	40
Lard	50	0.5	1	1.5	30	110	50	10	4	45
Formaldehyde	50	10	10	10	25	6	7	0.5	1	1.2
Ethanol	50	20	20	18	7	3	-5	2	15	5
Glycol	50	0.5	0.5	0.5	2	0.5	0.5	-0.2	1	0.5
Ethyl ether	50	50	30	20	95	170	135	90	270	85
Methyl ethyl ketone	50	250	250	250	150	85	80	15	150	150
Trichloroethylene	50	290	230	230	380	420	400	300	300	600
Carbon tetrachloride	50	110	75	55	330	420	400	275	300	350
Benzene	50	250	200	160	300	350	350	150	240	430
Aniline	50	360	380	420	125	15	30	10	7	70
Phenol	50	450	470	510	85	35	60	3	10	80
Cyclohexanol	50	50	40	25	40	55	35	7	25	20
Distilled water	100	10	11	12	12	10	2.5	5	2	4
Sea water	50	2	3	3	5	2	7	0.5	0.5	0.5

Electrical insulation

Silicone rubber has high insulation resistance of 1TΩ·m–100TΩ·m, and its insulating properties are stable over a wide range of temperatures and across a wide frequency spectrum. There is almost no decline in performance even when immersed in water, making silicone rubber an ideal insulating material. It has particularly good resistance to corona discharge and arcing at high voltages. Silicone rubber is thus used extensively as an insulator in high voltage applications.

Correlation between temperature and the volume resistivity of various rubbers



Arc resistance

Material	ASTM method sec
Fabric based phenol resin	4.5
Chlorosulphonated polyethylene	5.2
Butyl rubber	72
High butyl rubber	over 180
Chloroprene rubber	8.5
Epoxy resin	184
Polyester resin	134
Polytetrafluoroethylene (PTFE)	165-185
Silicone rubber	over 180

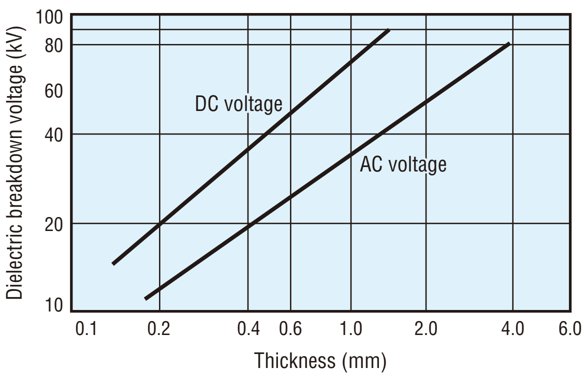
Tracking resistance

Material	DIN method	
	Rating	Erosion depth mm [ ] drip count
Butyl rubber	KA-3C	0.342
Ethylene propylene rubber	KA-3C	0.240
Chlorosulphonated polyethylene	KA-3C	0.224
Chloroprene rubber	KA-2	[18]
Polyethylene	KA-2	[46]
Cross-linked polyethylene	KA-3C	0.302
Polystyrene	KA-2	[15]
Silicone rubber	KA-3C	0.0064

✻ KA-3C Over 101 drops, less than 1 mm erosion
KA-2 Conduction path forms at 11-100 drops

Silicone rubber thickness and Dielectric breakdown voltage

(Temperature: 23°C. Based on JIS K 6249)



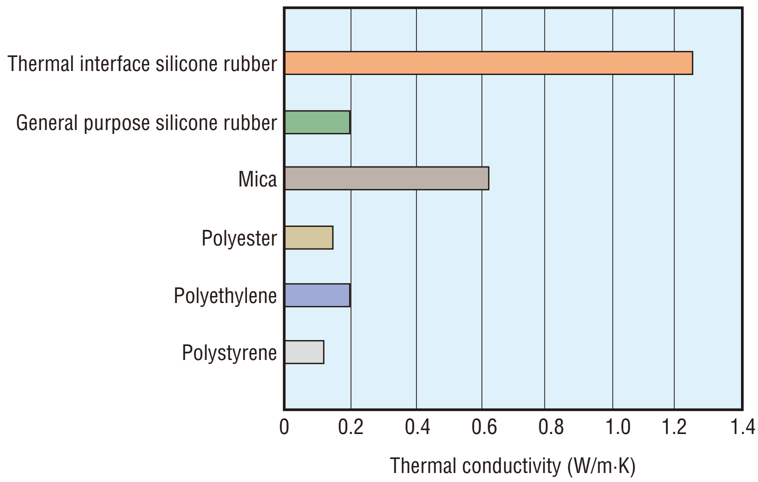
Corona resistance

Material	Operating life at 3kV h
Polyethylene	24.0
Polytetrafluoroethylene (PTFE)	33.5
Cellulose triacetate	36.5
Polyethylene terephthalate (PET)	50.0
Polyester varnish	22.0
Oil-modified phenol resin	55.0
Epoxy ester varnish	65.5
Asphalt varnish	81.0
Silicone rubber	over 35,600

Thermal conductivity

The thermal conductivity of silicone rubber is about 0.2 W/mΩ·K, a value higher than that of common organic rubbers. Some silicone rubbers contain a high proportion of special inorganic fillers to improve thermal conductivity (about 1.3 W/mΩ·K), and these are used to make products including thermal interface sheets and heating rollers.

Thermal conductivity of thermal interface silicone rubber



Flame retardancy

If silicone rubber is brought close to a flame, it will not ignite easily; but once ignited it will continue burning. It is possible to impart flame retardancy and/or self-extinguishing properties by adding a small amount of flame retardant. Some silicone rubber products have received UL94 V-0 certification according to the UL94 (USA) standards for flammability classification, shown at right. When they do burn, almost no black smoke or noxious gas is produced during combustion because these products contain none of the organic halogen compounds typically found in organic polymer rubbers. They are used in consumer electronics and business equipment; in closed spaces such as aircraft, subways, and building interiors. These silicone rubbers contribute to making all these environments safer.

✻ Please refer to "Standard for Safety: UL94" (Test for Flammability of Plastic Materials for Parts in Devices and Appliances) by Underwriters Laboratories Inc.® for UL94 Flammability Classification Standards.

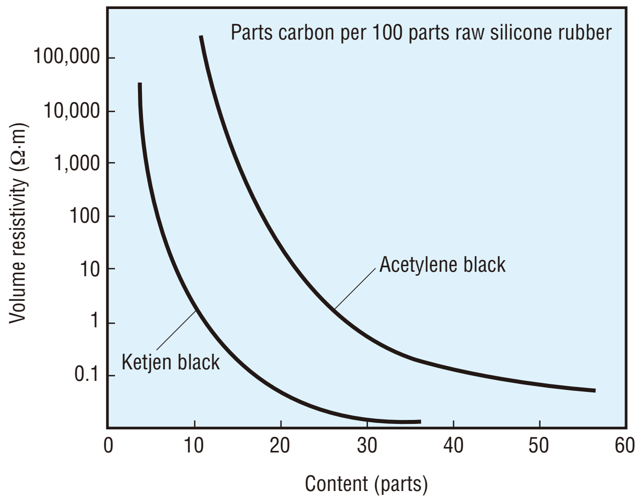
✻ Please refer to "Plastics Recognized Component Directory" by Underwriters Laboratories Inc.® for approved products. [File no. E48923]

Electrical conductivity

Conductive silicone rubbers contain electrically conductive materials such as carbon. A range of products are available, with resistance varying from 0.01Ω·m to 10Ω·m. Their other properties are basically the same as general purpose silicone rubbers. Conductive silicone rubbers are thus used extensively as a material for keyboard contact points, components used in heaters, an antistatic material, and high-voltage cable shielding.

✻ Typically, the volume resistivity of commercially available conductive silicone rubbers is between 0.01Ω·m and 10Ω·m. At values above 100Ω·m, resistance changes greatly with small amounts of carbon; attaining consistent resistance in the 10kΩ·m–100MΩ·m range is particularly difficult.

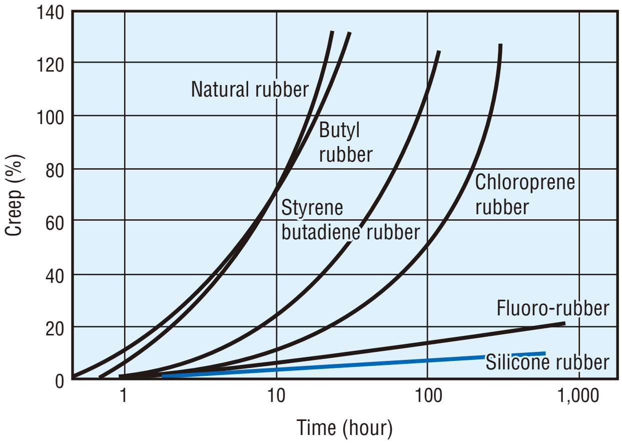
Volume resistivity and carbon black content



Compression set

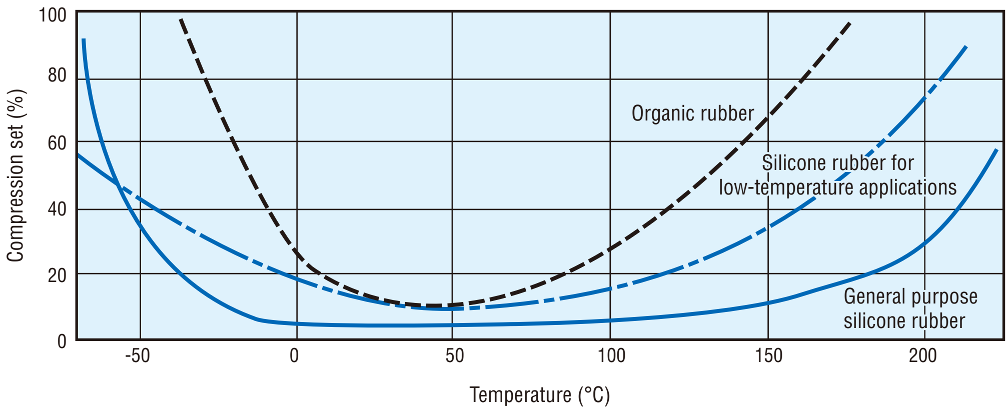
When using rubber materials for gaskets that will be under compression in heated conditions, the ability of these materials to recover from compression deformation is a crucial consideration. The compression set of silicone rubber is consistent over a wide temperature range, from -60° to +250°C. Although the compression set of typical organic rubbers is relatively low around room temperature, it increases significantly as temperatures rise. Silicone rubbers generally require post-curing. Post-curing and selection of a proper curing agent are particularly recommended when using silicone rubber to make molded items for which low compression set is desired.

Creep properties of rubbers* **(temp.: 100°C)**



✻ Creep is the deformation of a plastic material under constant load. Typically, creep increases as temperature rises. Rubbers that are firm and have greater thermal stability tend to exhibit lower creep values at higher temperatures.
Silicone rubber exhibits less creep than organic rubbers, and is more stable even than fluoro-rubber, which has good heat resistance.

Compression set at various temperatures
(test conditions: 22 hours at each temperature)



Flex fatigue resistance

Generally speaking, the strength of silicone rubber against dynamic stress is no greater than that of organic rubbers. But Shin-Etsu has overcome this shortcoming, developing silicone rubbers with flex fatigue resistance that is 8–20 times higher than conventional products. These special silicone rubbers are now used in OA equipment keyboards, transport vehicles, and other applications.

Flex fatigue resistance of silicone rubbers

Property / Brand name	KE-951	KE-9510	KE-9511	KE-5151
Elongation fatigue✻1 (x 10,000 times)	30-40	45-55	200-300	400-500
Keypad keystroke durability✻2 (x 10,000 times)	approx 250	approx 300	approx 1,100	approx 2,000

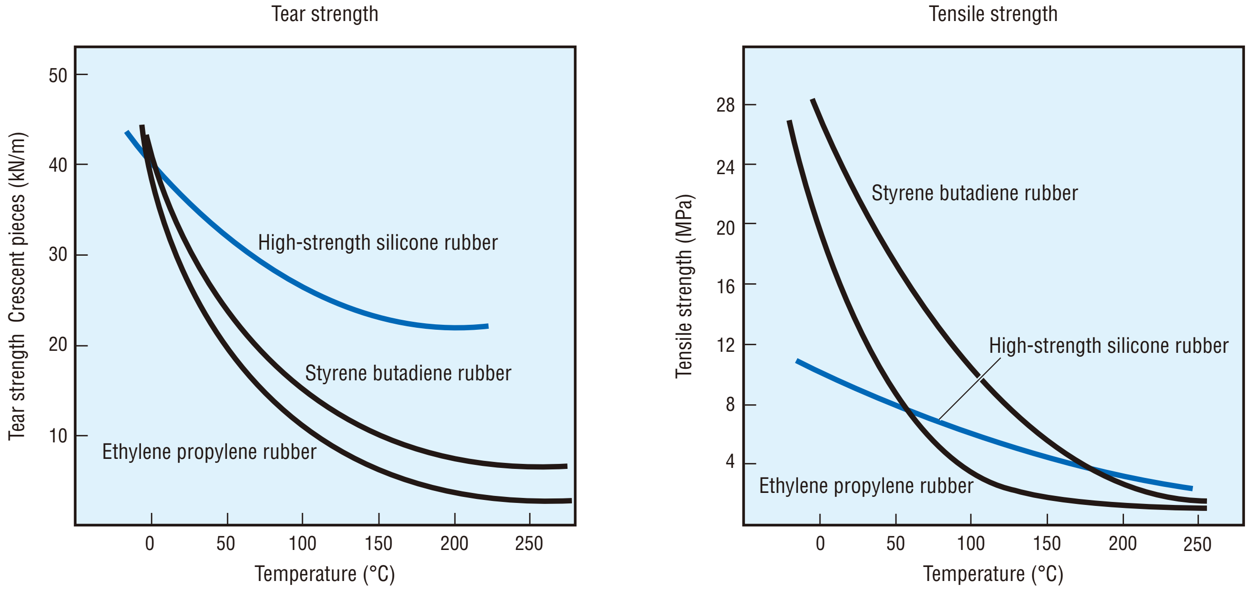
✻1 Tested using De Mattia flexing fatigue tester, 100% elongation, 5 cycles/sec.
✻2 Measured using a model keyboard. Expressed as the number of keystrokes until the rubber's recovery force is 50% its initial value.

Flex fatigue test

Tear strength and tensile strength

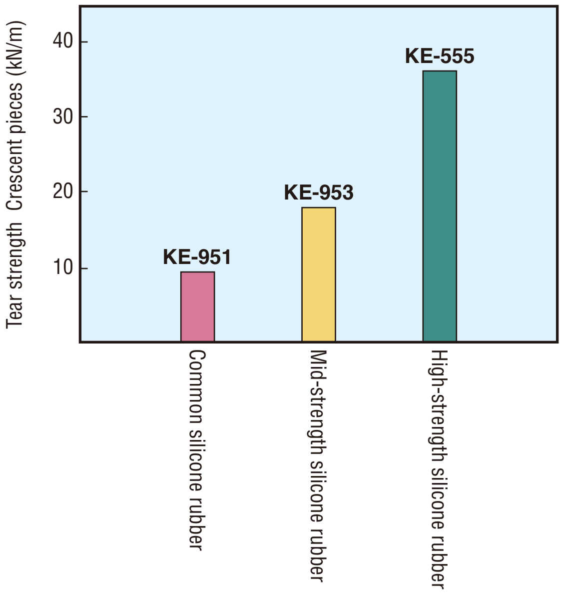
The tear strength of silicone rubber is generally around 9.8 kN/m. There are high-strength types available with tear strength between 29.4 kN/m and 49.0 kN/m, achieved through polymer modification and/or judicious selection of fillers and crosslinkers. These products are ideal for molding large items, reverse tapered forms, and complexly shaped items when high tear strength is required.

Temperature dependency of rubber strength



✻ The strength of silicone rubber at room temperature is inferior to that of organic rubber, but silicone rubber maintains strength better at high temperatures, such that the two eventually trade places on the graph.

Comparison of the tear strength of silicone rubbers (temp.: 23°C)



Tear strength test (crescent piece)

Gas permeability

Compared to organic rubber or plastic films, thin films of silicone rubber have better gas and vapor permeability, and they have selectivity. One application for silicone rubber being investigated is as a gas and water separation membrane in oxygen enrichment systems.

Comparison of gas permeability with natural rubber=100 for reference (25°C)

Material			H_2	O_2	N_2	CO_2	Air
Natural rubber	$\frac{P \times 10^8\ cc \cdot cm}{cm^2 \cdot sec \cdot atm}$		37.4	17.7	6.1	99.6	—
			100	100	100	100	100
Silicone rubber			1,070	2,200	3,300	1,600	2,700
Butyl rubber (isobutene 98, isoprene 2)			15	56	5	4	48
Polybutadiene (emulsified)			86	82	80	105	81
Nitrile	Acrylonitrile content	20%	51	35	31	48	33
		27%	32	17	13	24	15
		32%	24	10	7.5	14	8.5
Teflon®			46	44	43	19	—
Polyethylene d=0.926			15	11	9	8	—
Polypropylene			23	7	9	4	—
Polyvinyl chloride			6	2	2	1	—

Water vapor permeability of plastic films

Material	Water vapor permeability*
Silicone rubber	15.5-51.8
PVA	0.04-40.0
Ethylcellulose	21.5
Polyethylene	0.05-4.85
Polytetrafluoroethylene (PTFE)	2.94
Polycarbonate	1.0
Nylon	0.32-0.63

* Permeability $\frac{(cm^3\ gas)(cm\ thickness) \times 10^{-7}}{(sec)\ (cm^2)\ (cmHg\Delta p)}$

Transparency and coloring properties

Most organic rubbers are black due to their carbon content. In contrast, it is possible to make highly transparent silicone rubber because the fine silica it contains does not spoil the natural transparency of silicone. Shin-Etsu has developed high-transparency, high-strength silicone rubbers that are used for tubing and molded items in the food industry.

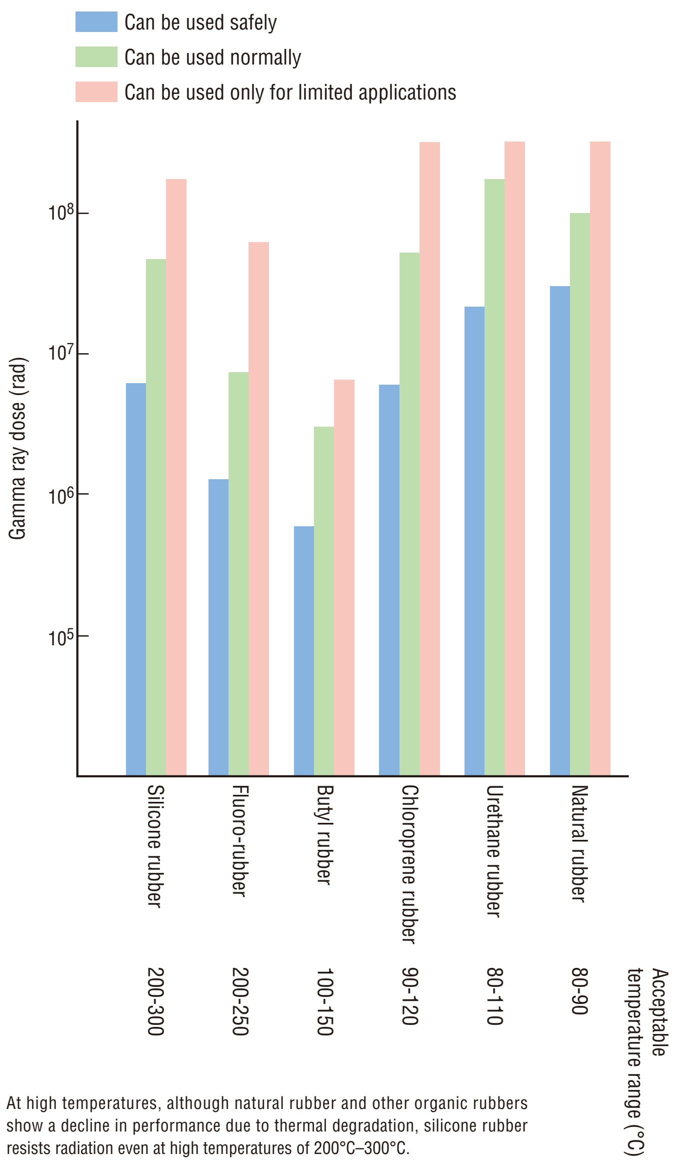
Its high transparency makes silicone rubber easy to color with pigments, so manufacturers can produce colorful molded items.

Radiation resistance

Common silicone rubber (dimethyl silicone rubber) really has no better radiation resistance than other organic rubbers. Methylphenyl silicone rubber, which features phenyl groups added to the polymer molecules, resists radiation and is used in the manufacturing of the cables and connectors used in nuclear power plants.

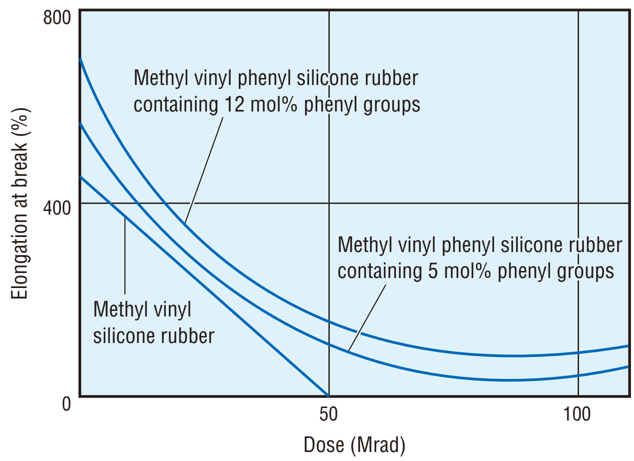
Silicone rubber with added phenyl groups has the same fine heat resistance, electrical insulating properties, flame retardancy and chemical resistance intrinsic to other silicone rubbers.

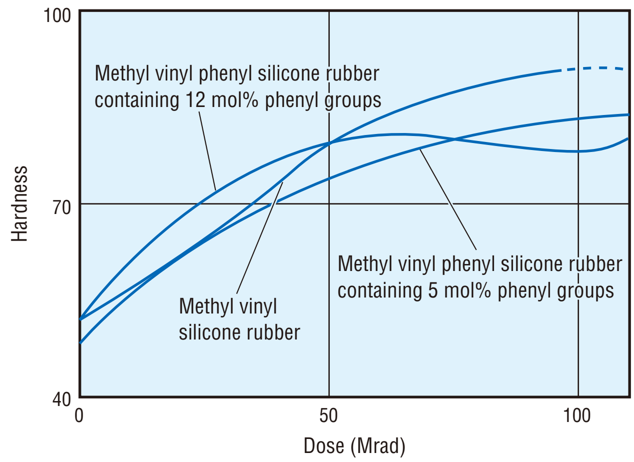
Radiation resistance of rubbers

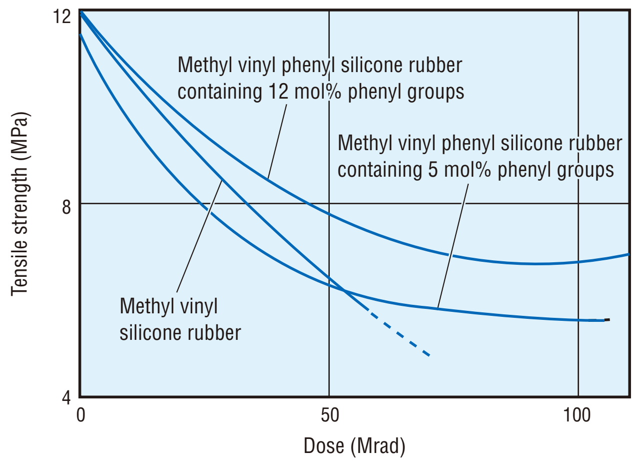


At high temperatures, although natural rubber and other organic rubbers show a decline in performance due to thermal degradation, silicone rubber resists radiation even at high temperatures of 200°C–300°C.

Radiation resistance of silicone rubber



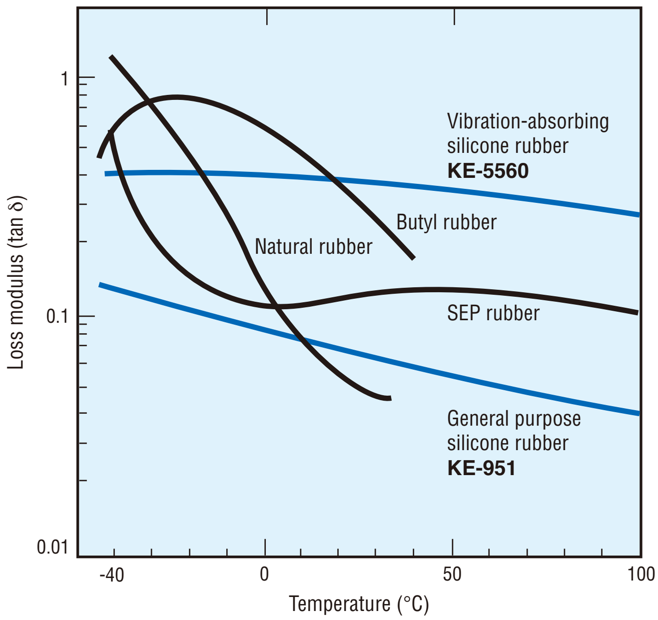




Vibration absorption

The loss modulus (tan δ)* of silicone rubber is generally low, making it ill-suited for use as a vibration insulator. Products with enhanced vibration absorption performance, however, absorb vibration consistently over a wide temperature range, from -50°C to +100°C.

Temperature dependence of vibration absorption of rubbers



* Loss modulus (tan δ) is expressed by the following equation:

$$\tan\delta = \frac{G_2}{G_1}$$ (G_1=storage modulus, G_2=loss modulus)

The larger the value of tan δ, the greater the ability of a particular material to absorb energy (vibration, etc.).

Releasability and Non-corrosivity

Silicone rubber is chemically inert with good release properties, so it does not corrode other materials. Silicone rubber is thus used for the fixing rollers, printing rollers and sheets of photocopiers, and for lost-wax casting.

Physiologically inert

Living tissues are affected by contact with silicone rubber to a lesser degree than by exposure to other organic polymers. Silicone rubber is physiologically inert, and is thus used for baby bottle nipples and stoppers in medical applications. In addition, it is pleasant to the touch with a high-grade feel, making it ideal for leisure items such as swimming caps and goggles.

The fine properties of silicone rubber

Perfect for an incredible array of applications.

Industry
• Application example
··· Required properties

Consumer electronics

• Defrosters	··· Heat resistance, cold resistance, electrical insulation
• Hot air brushes	··· Heat resistance, weatherability, good coloring properties
• Microwave oven window gaskets	··· Heat resistance
• Microwave oven drive belts	··· Low compression set

Office automation equipment

• Keypads of calculators, computer keyboards	··· Conductivity, electrical insulation, flex fatigue resistance
• EMI gaskets	··· Conductivity, flame retardancy, thermal conductivity
• Photocopier (PPC) rollers • FAX platen rollers • Printer platen rollers	··· Heat resistance, non-adhesiveness, low compression set

Automobiles

• Diaphragms, O-rings	··· Oil resistance, heat resistance, cold resistance, flex fatigue resistance
• Spark plug boots	··· Oil resistance, heat resistance
• Waterproof connectors	··· Heat resistance, oil resistance
• Hoses	··· Heat resistance, cold resistance, low compression set, steam resistance
• Turbo chargers • Intercooler hoses	··· Heat resistance, oil resistance, flex fatigue resistance

Electrical wiring

• Lead wires of motors and home electronic goods • Heater wires of rice cookers, etc. • Refrigerator defroster wires • Ignition wires	··· Electrical insulation, heat resistance, cold resistance, thermal conductivity, flame retardancy

Machinery

• Low frequency therapy devices	··· Conductivity
• Lost-wax casting	··· Heat resistance, non-adhesiveness
• Solar hoses	··· Chemical resistance, weatherability
• Hot stamping rollers	··· Heat resistance, low compression set
• Vibration insulation rubber	··· Vibration absorption

Food

• Gaskets for pressure cookers, electronic rice cookers and kettles	··· Steam resistance, chemical resistance, low compression set
• Milking machines	··· Transparency, high tear strength
• Nipples	··· Transparency, physiological inertness
• Food container gaskets	··· Low compression set

Leisure

• Swimming goggles • Snorkels • Mouthpieces • Goggle bands	··· Transparency, high tear strength, high tensile strength, physiological inertness

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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)

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