● Silsesquioxane derivatives UV-curable *SQ* Series

New Business Planning and Promotion Department, New Business Planning Group
Naomasa Furuta, Hiroshi Suzuki

1. Introduction

In recent years, silsesquioxane has attracted attention as a new silicon-based material [1]. Silsesquioxane is a siloxane compound whose main chain backbone consists of Si-O bonds. It is represented by the composition formula $(RSiO_{1.5})_n$. It is referred to as "sil-sesqui-oxane" because it is a siloxane with 1.5 (1.5 = sesqui) oxygen atoms in its unit composition formula. A well-known siloxane-based compound is polysiloxane, also known as silicone (unit composition formula: R_2SiO), a representative organosilicon polymer. Silica (unit composition formula: SiO_2), an inorganic compound, is another typical compound consisting of siloxane bonds. As can be seen by comparing these composition formulas, silsesquioxane can be regarded as an intermediate substance between silicone and silica.

Silsesquioxane can form many different types of backbone structures. **Figure 1** illustrates an example of a typical structure. Structurally, silsesquioxane can be regarded as a material (organic-inorganic hybrid material) that combines an organic unit and an inorganic unit (silsesquioxane backbone) at the molecular level.

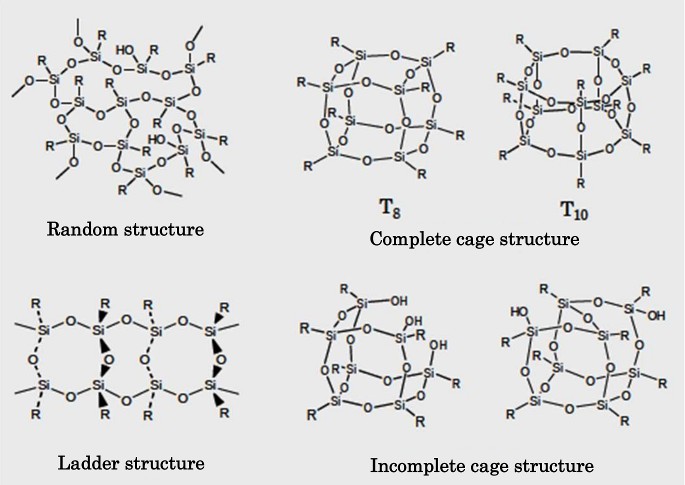


Figure 1: Example structures of silsesquioxane $(RSiO_{1.5})_n$

Silsesquioxane combines inorganic characteristics such as heat resistance and hardness with organic characteristics such as flexibility and solubility in organic solvents. Unlike insoluble silica, which is an entirely inorganic substance, silsesquioxane is homogeneously miscible with various general-purpose resins, offering the advantages of easy blending, preparation, processing, and molding. In addition, various organic functional groups can be introduced into the silsesquioxane backbone, enabling the design of materials that incorporate these functions [1)-8)].

Toagosei has developed the *SQ* Series—UV-curable silsesquioxane derivatives with photopolymerizable groups introduced into the silsesquioxane backbone (UV-curable SQ Series) [9)-11)]—and is expanding its applications as a specialty coating material in various fields, such as electronics. This paper introduces the UV-curable *SQ* Series.

2. UV-curable *SQ* Series

The UV-curable *SQ* Series (hereafter "*SQ* Series") is a new type of organic-inorganic hybrid material, which incorporates multiple photopolymerizable groups (organic unit) into a silsesquioxane backbone (inorganic unit) and combines them within the same molecule. The incorporated photopolymerizable groups are cationic polymerizable oxetanyl (OX) groups and radical polymerizable acryloyl (AC) groups.

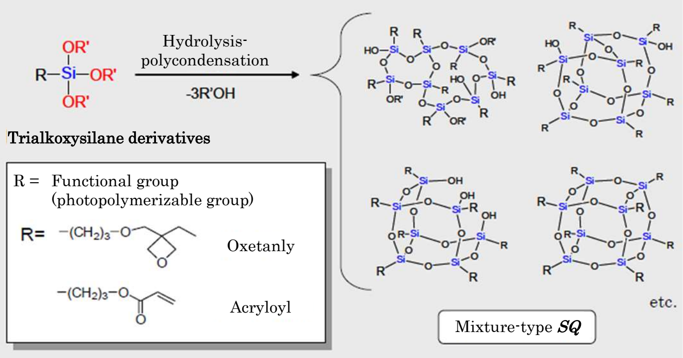


Figure 2: *SQ* Series production method

As shown in **Figure 2**, the *SQ* Series is synthesized through hydrolysis-polycondensation (formation of siloxane bonds) of the corresponding trialkoxysilane derivatives. The *SQ* Series that we have commercialized consists of a mixture of random and cage arrangements, in consideration of cost-effectiveness. It is a colorless, transparent, and viscous liquid in appearance (**Figure 3**). Refer to the reference for more information on the synthesis of the *SQ* Series [8)-10)].

Figure 3:
Appearance of the *SQ* Series

The characteristics of our representative *SQ* Series are shown in **Table 1** and the liquid properties are shown in **Table 2**. We currently offer the cationic polymerization type OX-*SQ* and the radical polymerization type AC-*SQ*. We also offer a unique product grade called OX-*SQ* SI-20, which incorporates polydimethylsiloxane (silicone) into part of the silsesquioxane backbone. The cured film obtained from OX-*SQ* SI-20 has excellent repellency to oil-based inks because the film surface exhibits the physical properties of silicone. In other words, it is useful as a contamination-resistant coating agent.

Table 1: Characteristics of the *SQ* Series

Grade	Curing method	Common characteristics	Individual characteristics
OX-*SQ* TX-100	Cationic polymerization	• Forms a hard film with excellent chemical and heat resistance • No inhibition of polymerization by oxygen in the air • Good curability even in thin films with a thickness of 10 µm or less • Low curing shrinkage (2-5%) • Good compatibility with aliphatic and alicyclic epoxies • UV curable, so it can be applied to non-heat-resistant substrates	• High heat resistance T_{d5}*1 = 400°C (in nitrogen) • High hardness Pencil hardness of 5H (steel plate*2)
OX-*SQ* SI-20			• Excellent contamination resistance • Excellent water repellency
OX-*SQ* ME-20			• High transparency and glossy surfaces can be obtained
AC-*SQ*	Radical polymerization	• Forms a high-hardness film with excellent chemical and heat resistance Pencil hardness of 6H (on a glass substrate) • High heat resistance. T_{d5}*1 = 390°C (in nitrogen) • Good compatibility with various acrylic monomers • UV curable, so it can be applied to non-heat-resistant substrates	

*1 T_{d5}:5% weight loss temperature
*2 Cold-rolled steel plate:SPCC-SD (JIS G 3141:2005), zinc phosphate-coated material

Table 2: Liquid properties of the *SQ* Series

Item	Unit	Measurement method	Conditions	OX-*SQ* TX-100	OX-*SQ* SI-20	OX-*SQ* ME-20	AC-*SQ*
Functional group	-	-	-	Oxetanyl group			Acryloyl group
Functional group equivalent	g/eq	Theoretical value	-	209	262	283	165
Inorganic content ($SiO_{1.5}$)	%	Theoretical value	-	25	32	34	32
Refractive index	-	JIS K 0062:1992	n_D^{20}	1.48	1.46	1.46	1.48
Specific gravity	-	JIS K 0061:2001 Pycnometer method	20/20 °C	1.15	1.09	1.12	1.23
Viscosity	mPa·s	JIS K 7117-2:1999	25°C	16,000 to 50,000	4,000 to 9,000	5,000 to 12,000	5,000 to 12,000
Solvent content	%	GC method	-	< 1%			
Hazen color scale (APHA)	-	JIS K 6901 :1999	-	≤ 100			
Good solvent	Determined by the appearance of the 10% and 50% solutions		25°C	IPA, THF, toluene, PGMEA, cellosolve acetate			
Poor solvent				Water			

3. Physical properties of UV-cured materials

Figure 4 shows a model of UV-curing for the *SQ* Series. When the photopolymerizable groups react and intermolecular cross-linking (curing) proceeds, it is assumed that an organic-inorganic nanohybrid structure is formed, in which the organic and inorganic regions are combined at the molecular level. Therefore, the resulting cured material exhibits characteristics, such as high hardness, transparency, high heat resistance, and high weather resistance.

Figure 5 shows the viscoelastic spectrum results of the UV-cured material, OX-*SQ* TX-100. As for viscoelastic properties, no clear transition of storage modulus (E') was observed in the range between -100 and 250°C. A high modulus of elasticity with a value close to 10^9Pa was maintained at temperatures of 200°C or higher. The tanδ was low across all temperature regions, and tanδ MAX was not observed. **Figure 6** shows the thermogravimetric analysis (TGA) results for the UV-cured material, OX-*SQ* TX-100. In the TGA evaluation of thermal resistance, 5% weight loss temperature by thermal decomposition (T_{d5}) was 330°C in air and 400°C in nitrogen.

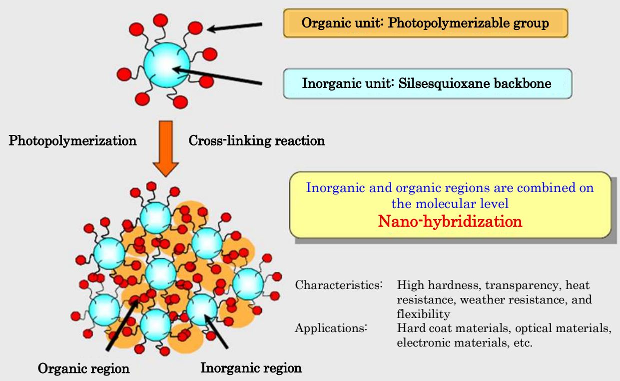
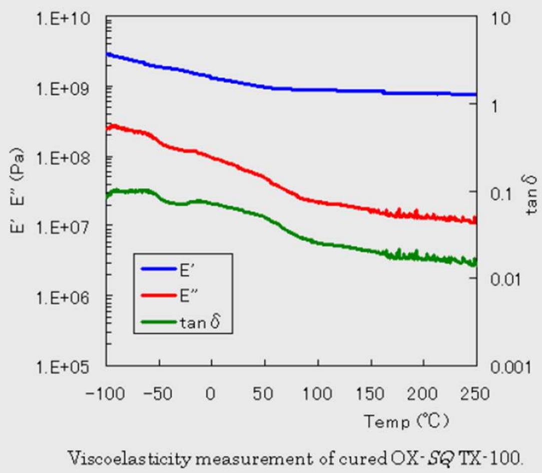


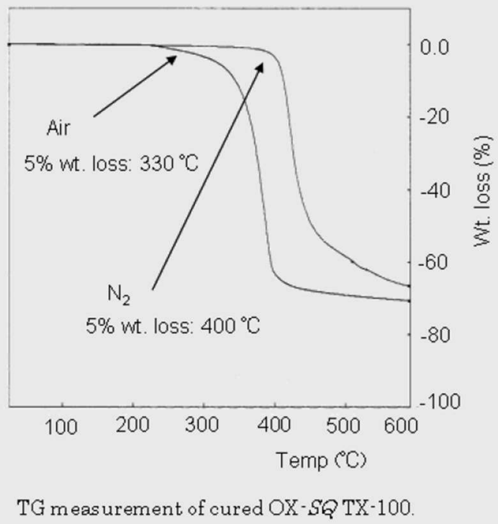
Figure 4: *SQ* Series UV-curing model



Storage modulus (E')

0℃	2×10⁹
150℃	1×10⁹
250℃	7×10⁸

Figure 5: Viscoelastic spectrum of OX-*SQ* TX-100



5% weight loss temperature (T_{d5})
400°C in nitrogen
330°C in air

Figure 6: Thermogravimetric analysis of OX-*SQ* TX-100

Table 3: Physical properties of the UV-cured materials of the *SQ* series*1

				OX-*SQ* TX-100	OX-*SQ* SI-20	AC-*SQ* TA-100
Composition of cured material	*SQ* Series			90	100	100
(Ratio by weight)	Epoxy monomer *2			10	1.5	-
	Photoinitiator			2*3, 4	1.5*3	3*5
Item	Unit	Measurement method	Conditions			
Specific gravity	-	JIS K 0061:2001	23/23ºC	1.18	1.14	1.34
Curing shrinkage	%	Specific gravity measurement *6	-	2.6	4.6	8.9
Storage modulus	Pa	DMA method	0ºC	2×10^9	1×10^9	1×10^9
			150ºC	1×10^9	4×10^8	1×10^9
			250ºC	7×10^8	-	-
Thermal expansion coefficient	ppm/ºC	TMA method	30 to 250°C	120	160	80
Refractive index	-	JIS K 7142:1996	n_D^{23}	1.49	1.47	1.51
Water absorption rate	%	JIS K 7209:2000 *7	Method A	0.24	0.16	1.09
			Method B	0.45	0.28	1.42
5% weight loss temperature	ºC	TG-DTA *8	In air	330	330	360
			In nitrogen	400	390	390

*1 Curing conditions: High pressure mercury lamp (60 W/cm), 30 cm lamp height, irradiation for ten minutes in air
*2 CELLOXIDE2021P (Daicel Corporation)
*3 BLUESIL PI 2074 (Elkem Silicones)
*4 WPI-113 (FUJIFILM Wako Pure Chemical Corporation) was used only for measuring the 5% weight loss temperature.
*5 Omnirad 1173 (IGM Resins)
*6 (Specific gravity of cured material - Specific gravity before curing)/Specific gravity before curing × 100
*7 Test piece dimensions: 100 mm × 100 mm × 2 mm, Method A: 23°C for 24 hours, Method B: Boiling for one hour
*8 Temperature increase rate: 20°C/min

This high thermal stability can be attributed to the strong network structure formed by the silsesquioxane units.

Table 3 lists the physical properties of the UV-cured materials of the *SQ* Series by grade.

4. Application to UV-curable coating materials

OX-*SQ* and AC-*SQ* are viscous liquids that are soluble in various solvents and resins. Therefore, they can easily be processed and formed into coating films and other shapes. They also have excellent compatibility with general-purpose UV-curable monomers, making it possible to formulate and prepare resins tailored to different purposes. The following describes the application of OX-*SQ* TX-100 and OX-*SQ* SI-20 to UV-curable coating materials.

Table 4 shows the results of thin-film photocuring tests on resins formulated and prepared using OX-*SQ* TX-100 and epoxy monomers. A typical bifunctional epoxy resin, Daicel Chemical Industry's Celloxide 2021P (chemical name: 3'-4'-Epoxycyclohexane (methyl 3'-4'-Epoxycyclohexyl-carboxylate), hereafter "CEL2021") was used as the epoxy monomer. The solvent resistance of the cured resin surface was evaluated using an acetone rubbing test (the number of rubs required to peel the film). As a result, CEL2021 (Exp. No.: SQ-0) alone exhibited no resistance to acetone immediately after UV curing. However, when OX-*SQ* TX-100 was blended, the acetone resistance was improved even immediately after curing. The resin (SQ-3) containing 40 parts of OX-*SQ* TX-100 is considered to have formed a stronger network and showed almost perfect resistance to acetone immediately after curing. The cured film containing only OX-*SQ* TX-100 exhibited a high surface hardness of 5H to 6H pencil hardness.

Table 4: UV-curing test on resin with OX-*SQ* TX-100 and CELLOXIDE 2021P a)

No.	CEL2021 b) (wt%)	OX-*SQ* (wt%)	Pencil Hardness c)	Acetone Resistance d) 10 min	1 h	2 h	6 h	24 h
SQ-0	100	-	2～3H	0	0	30	50	>200
SQ-1	90	10	3H	20	40	50	>200	>200
SQ-2	80	20	3～4H	20	60	>200	>200	>200
SQ-3	60	40	4H	>200	>200	>200	>200	>200
SQ-4	10	90	5～6H	>200	>200	>200	>200	>200

a) 1 wt% of UV9380C (GE Toshiba Silicone Corp.) was added to each composition and applied 5 μm thickness coating on glass plate with a bar coater. Then, it was cured with 80 W/cm of high pressure Hg lamp at 10 m/min conveyor speed.
b) Cycloaliphatic epoxy monomer, available from DAICEL CHEMICAL INDUSTRIES, LTD.
c) According to JIS K 5400.
d) The rubbing test was carried out at a given time after curing. Test results were shown as number of rubbing times by acetone wet cotton until breakthrough of the film occurs.

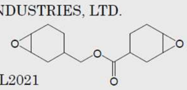

CEL2021

Table 5 shows the results of the UV curing tests and the examination of the cured film surface properties of OX-*SQ* SI-20 resin. OX-*SQ* SI-20 was miscible with CEL2021, resulting in a clear resin. The obtained cured films exhibited a pencil hardness of 3-4H. Next, a test was conducted to evaluate the resistance of the cured film surface to oil-based ink contamination. The cured film containing only CEL2021 and the cured film obtained from OX-*SQ* TX-100 (Exp. No.: Exp-2, 3, 6), which does not contain any silicone chain, did not repel oil-based ink at all. On the other hand, cured films (Exp-1, 4, and 5) obtained from OX-*SQ* SI-20 with silicone chains introduced showed excellent resistance to contamination, such as high repellency to oil-based inks. This indicates that the silicone properties have been properly imparted to the cured film surface. The performance of repellency to oil-based inks was well maintained even after a dry-wipe test involving 500-gram weight gauze applied 2,000 times, indicating that the product also has excellent abrasion resistance.

Table 5: Physical properties of the UV-cured resin film surfaces using OX-*SQ* SI-20 [a)]

Exp. No.	Exp1	Exp2	Exp3	Exp4	Exp5	Exp6
OX-SQ SI-20 [b)]	100	-	-	5	10	-
CEL2021	-	100	-	95	90	80
OX-SQ TX-100	-	-	100	-	-	20
Miscibility of resin	Clear	Clear	Clear	Clear	Clear	Clear
Pencil hardness [c)]	3～4H	2～3H	5～6H	2～3H	2～3H	3～4H
Pollution free [d)]	○	×	×	○	○	×
After wiping test [e)]	○	×	×	○	○	×
Contact angle (deg.)[f)]	99	52	70	95	96	55

a) 2 wt% of UV9380C was added and coated on glass substrate to 5 μ thickness with a bar coater and cured with 80 W/cm of high pressure Hg lamp at 10 m/min conveyor speed
b) Containing 20 wt% of silicone.
c) According to JIS K 5400.
d) Lines were drawn using oily Marker, ○: completely repellent; ×: no repellent.
e) Wiping with a dry gauze was effected 2,000 times under 500g load.
f) Measured toward water.

5. Examples of *SQ* Series applications

Examples include: additives for modifying various polymer materials; strengtheners; heat-resistant agents; cross-linking agents; protective films for various substrates; additives for modifying various coating materials; hard coating materials; other raw materials for coating materials; anti-contamination coating agents (OX-*SQ* SI-20); raw materials for composite materials made from various polymeric materials; low-dielectric-constant materials; insulating film materials; raw materials for LED encapsulants; materials for optical waveguides; semiconductor encapsulation materials; photoresist materials; hard mask materials; and optical and electronic materials.

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