

● Development of silsesquioxane derivatives to applications requiring heat resistance, and development of protective coating for spacecraft

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Key Word : Silsesquioxane, Siloxane compound, Heat resistance, Antifouling, Space, Atomic oxygen

1. Introduction

Silsesquioxane is a siloxane-based compound with the composition formula $(\text{RSiO}_{1.5})_n$, and it is regarded as an intermediate between silicone (R_2SiO) and silica (SiO_2). It therefore has both inorganic features, such as heat resistance and hardness, and organic features, such as flexibility and solubility in organic solvents.

We have been developing the *SQ* Series of silsesquioxane derivatives, which have radically polymerizable acryloyl (AC) and methacryloyl (MAC) groups, and cationically polymerizable oxetanyl (OX) groups as crosslinking groups¹⁻⁶. With the recent advances in electronic devices, heat resistance requirements for materials used in this field are becoming increasingly stringent. The *SQ* Series is used as a heat-resistant binder for inorganic fillers and as a material for imparting heat resistance to organic materials, and has received favorable evaluations. This article describes the development of the *SQ* Series for heat-resistant applications and introduces the latest topics on the protective coating agent for spacecraft developed jointly with the Japan Aerospace Exploration Agency (hereinafter “JAXA”).

2. Development for heat-resistant applications

2.1 Heat resistance of *SQ* Series “SI Grade”

The *SQ* Series with AC, MAC, and OX crosslinking groups includes the “SI-20 Grade,” in which silicone is introduced into part of the silsesquioxane skeleton^{7,8}. Its cured film is useful as an antifouling coating agent because it exhibits properties such as favorable repellence of oil-based ink due to the silicone properties being imparted to the film surface. In addition, the *SQ* Series has achieved particularly excellent results in heat resistance properties.

We first present its heat resistance and oil/water repellence (Table 1). We coated a steel plate with each SI-20 Grade to a film thickness of about 1 μm , and measured the contact angle of liquid (4 μL) dropped on the surface of the coating. The AC and MAC types (hereinafter “(M)AC type”) showed particularly high contact angles of more than 50°/approx. 100° for oleic acid/water, respectively, and maintained these contact angles even after heating at 200°C for 168 h (7 days). As shown above, SI-20 Grade antifouling coatings also have high heat resistance.

Table 1: Heat resistance and liquid repellence (contact angle against oleic acid/water (unit: °))

	After curing ^{*1}	200°C		
		After 24 h	After 48 h	After 168 h
AC- <i>SQ</i> SI-20 ^{*2}	52/100	55/101	54/101	52/99
MAC- <i>SQ</i> SI-20 ^{*2}	51/98	55/102	58/100	53/100
OX- <i>SQ</i> SI-20 ^{*3}	46/99	46/97	45/97	39/86

*1 High-pressure mercury, integrated light intensity 3 J/cm², air atmosphere

*2 *SQ* Omnirad 184 (IGM Resins) = 100/3

*3 *SQ* CELLOXIDE 2021P (Daicel Corporation)/ BLUESIL PI 2074 (Elkem Silicones) = 90/10/3

Next, we compared the resistance to cracking under heating (hereinafter “heat cracking resistance”) (Table 2). We coated a glass slide with *SQ* to a thickness of 10 to 20 μm , and compared the appearance of the coating film obtained by heating it at 200°C for 1 h. The SI Grade tended to be less susceptible to cracking, while cracks formed on the *SQ* products without silicone introduction (AC-*SQ* TA-100, MAC-*SQ* TM-100, and OX-*SQ* TX-100). This tendency was especially strong for the OX-*SQ* SI-20. It is assumed to have been caused by a decrease in the degree of crosslinking (increase in functional group equivalent) due to the introduction of silicone. Since the OX type has lower cure shrinkage than the (M)AC type and is thus expected to accumulate less internal stress, this likely accounts for its particularly excellent heat cracking resistance.

In addition, we compared the optical heat resistance. Fig. 1 shows the UV-visible light spectra of the ultraviolet (hereinafter “UV”) cured products of the SI-20 Grade. While neither the (M)AC nor OX types showed noticeable absorption in the visible light region of the spectra after UV curing (before the heat resistance test), the (M)AC type showed less absorption in the UV-visible light region and maintained higher transparency in the spectra after heating at 80°C for 1000 h.

As described above, the SI-20 Grade is an excellent material in terms of both heat cracking resistance and transparency after heating.

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The (M)AC type seems to be particularly suitable for applications requiring transparency. On the other hand, the OX type is particularly suitable for applications that require crack resistance. Since coloration is almost negligible when it is used in thin-film form, it shows promise for a variety of heat-resistant applications.

Table 2: Heat cracking resistance of each SQ Grade

		AC-SQ		MAC-SQ		OX-SQ	
		TA-100	SI-20	TM-100	SI-20	TX-100	SI-20
Functional group equivalent (theoretical value, g/eq)		169	207	179	224	209	262
Cure shrinkage *1 (%)		8.9 *2	8.0 *2	7.4 *2	7.7 *2	2.6 *3	4.6 *4
Heat cracking resistance *5,6	In atmosphere	×	○	△	○	△	◎
	In nitrogen	×	△	×	○	△	○

*1 Specific gravity method (calculated based on specific gravity before and after UV curing)

UV curing conditions: High-pressure mercury lamp (60 W/cm), 30 cm lamp height, irradiation for 10 minutes in air atmosphere

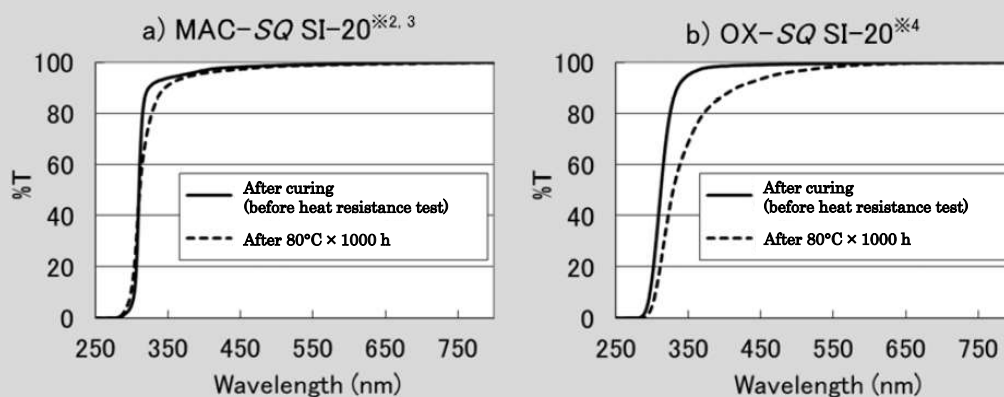
*2 SQ/Omnirad 1173 (IGM Resins) = 100/3

*3 SQ/CELLOXIDE 2021P/BLUESIL PI 2074 = 90/10/2

*4 SQ/CELLOXIDE 2021P/ BLUESIL PI 2074 = 100/1.5/1.5

*5 Heat-curing product (no initiator, heat curing of SQ alone)

*6 ◎: No crack formation, ○: Almost no cracks, △: Partial cracks, ×: Cracks on the entire surface



*1 UV-cured product (thickness: 1 mm)

Curing conditions: High-pressure mercury lamp (60 W/cm), 30 cm lamp height, irradiation for 10 minutes in air atmosphere

*2 SQ/Omnirad 1173= 100/3

*3 Omitted since the spectrum of AC-SQ SI-20 was nearly identical to that of the MAC type

*4 SQ/BLUESIL PI 2074 = 100/2

Figure 1: UV-visible light spectra *1

2.2 Improvement of heat resistance

Since the conventional *SQ* Series may not meet the heat resistance requirements of some applications, we developed a new improved grade by focusing on resistance to cracking and yellowing during heating and reviewing the molecular design of the *SQ* Series, including the degree of crosslinking.

We compared the resistance to cracking under repeated heating and cooling cycles (hereinafter “thermal impact resistance”) for the conventional AC-*SQ* SI-20 and AC-*SQ* Developed Product 1, which has improved heat resistance (Table 3).

Table 3: Thermal impact resistance*1,2

	Number of specimens with crack generation after thermal impact test *3		
	1st cycle	2nd cycle	3rd to 10th cycle
AC- <i>SQ</i> SI-20	1/3	3/3	-
AC- <i>SQ</i> Developed Product 1	0/3	0/3	0/3

*1 Coating film size: 1 cm × 1 cm × 0.1 mm

*2 Curing conditions: Omnirad 1173 3% addition, high-pressure mercury, integrated light intensity 3 J/cm², air atmosphere

*3 Thermal impact resistance: Number of specimens that cracked out of 3 specimens after repeating [260°C × 30 seconds ↔ room temperature] up to 10 times

We prepared three UV-cured products approximately 0.1 mm thick on a glass slide for each sample, then repeatedly placed them in an electric furnace at 260°C for 30 seconds before removing them to room-temperature conditions. As a result of evaluation based on the number of repetitions until appearance abnormalities such as cracks were observed in the

cured product, we did not observe any appearance abnormality in the AC-*SQ* Developed Product 1 even after 10 repetitions, while we observed appearance abnormalities in all three specimens by the second repetition with AC-*SQ* SI-20. This improvement of the *SQ* structure has enabled us to impart thermal impact resistance even in a temperature range high enough to accommodate lead-free soldering by the reflow method.

Next, we will explain the results of heat resistance tests in which the cured products of AC-*SQ* Developed Product 1, MAC-*SQ* Developed Product 1, and MAC-*SQ* Developed Product 2, which have improved resistance to yellowing under heat in addition to heat cracking resistance, were heated for a long period of time. We prepared a cured product with a thickness of approximately 1 mm and heated it in an electric furnace at 150°C to evaluate the changes in appearance of the cured product over time. While cracks appeared throughout the specimen in less than 100 h and the specimen turned yellow remarkably with AC-*SQ* SI-20, no cracks were observed after 1000 h and the specimens maintained the same shape as before heating with all three developed products. Table 4 shows the change in yellowness (Yellow Index: Y.I.) of the two MAC-*SQ* developed products over time. The cured product of MAC-*SQ* Developed Product 1 maintained a Y.I. of 3.3 after 1000 h, and that of MAC-*SQ* Developed Product 2 maintained a very small value of 1.8. As shown in Table 4, through careful molecular design, we can also adjust the viscosity to suit the application while maintaining the resistance to yellowing under heat, enabling applications such as optical materials used in LEDs.

The molecular design concept for improving heat resistance described above can also be applied when the *SQ* Series is used in formulation with other organic materials. As the proportion of *SQ* is increased to improve the heat resistance of the formulation, the cured product becomes harder and less deformable. If this is a problem, the various properties of the formulation can be improved by revising the molecular design of *SQ*.

Table 4: Resistance to yellowing under heat of MAC-*SQ* Developed Products*1,2

	Yellowness of cured product (Y.I.) *3					Liquid viscosity before curing (mPa·s)
	0 h	250 h	500 h	750 h	1000 h	
MAC- <i>SQ</i> Developed Product 1	1.4	3.0	2.9	2.7	3.3	160
MAC- <i>SQ</i> Developed Product 2	No data	1.9	1.8	1.7	1.8	1290

*1 Specimen size: 1 cm × 1.5 cm × 1 mm

*2 Curing conditions: 3% thermal initiator addition, 110°C × 1 h → 150°C × 1 h

*3 Resistance to yellowing under heat: Y.I. measured with a colorimeter after heating at 150°C for a specified period

3. Development of a protective material for spacecraft

3.1 Necessity and current status of atomic oxygen-resistant coatings

Although space is often thought of as a vacuum, Atomic Oxygen (hereinafter “AO”) is a major component of the atmosphere at altitudes of 200 to 600 km, including the 400 km altitude range where the International Space Station (hereinafter “ISS”) orbits⁹. It has become clear in recent years that when a spacecraft flies through this space, it collides with highly reactive AO at the spacecraft's speed of 7 to 8 km/s, resulting in oxidation and corrosion of metallic materials with poor oxidation resistance (such as silver) and significant erosion of organic materials through gasification¹⁰.

At the same time, spacecraft are exposed to harsh temperature environments ranging from low to high temperatures. To protect the electrical and electronic equipment of spacecraft from such severe temperature cycles, satellite surfaces are generally coated with multilayer insulation (hereinafter “MLI”), which is produced by laminating polyimide (hereinafter “PI”) film and other materials with excellent resistance to the space environments, including heat, radiation, and ultraviolet rays.

Because PI, like other common polymeric materials, is subject to erosion by AO¹¹, an AO-resistant coating is often adopted on its outermost surface. Inorganic coatings have been used as conventional AO-resistant coatings, and silicone-based coatings have been evaluated in trials. However, each has various shortcomings^{6,11}. For example, inorganic coatings of oxide films such as ITO and silica are hard and brittle, and many defects exist on the surface due to the manufacturing process or subsequent handling. When they are irradiated with AO, it has been found that AO penetrates into the defects and erodes the substrate PI film to a greater extent. On the other hand, issues with silicone-based coatings include a tendency to absorb sunlight (and store heat) due to discoloration caused by UV irradiation, as well as contamination caused by silicone-derived volatile components (outgas) recondensing on other surfaces in a vacuum.

3.2 Development of a PI film with AO-resistant coating using *SQ*

In collaboration with JAXA, we have developed an innovative AO-resistant coating agent that overcomes the aforementioned shortcomings by applying the *SQ* Series, which has intermediate properties between inorganic materials such as silica and silicone-based materials^{6-8,12-14}. We optimized the *SQ* to be suitable for this application, taking into consideration the coating process and ensuring curability. We then added a photoinitiator and a solvent (propylene glycol monomethyl ether acetate: PGMEA) to the *SQ* to prepare a coating material. Using Kaneka Corporation's APICAL AH (approx. 1 m wide, 25 μm thick, with Al vapor deposited on one side to reflect sunlight) as the PI film, we examined mass production using the roll-to-roll method (hereinafter “R2R”). We established the R2R industrialization process by applying the coating agent on the surface without Al vapor deposition so that the *SQ* thickness after curing would be 1 μm, and optimizing the conditions of each process of coating, drying, UV curing, and winding¹⁵ (Photo 1). We carried out general physical property evaluations, such as adhesion between the *SQ* coating film and the substrate PI (cross-cut method) and confirmation of damages on the *SQ* coating film after bending

(mandrel bending test), as well as various ground tests assuming a space environment, all of which delivered favorable results. We believe that this product can be safely handled not only in actual use in space, but also in assembly operations on the ground.

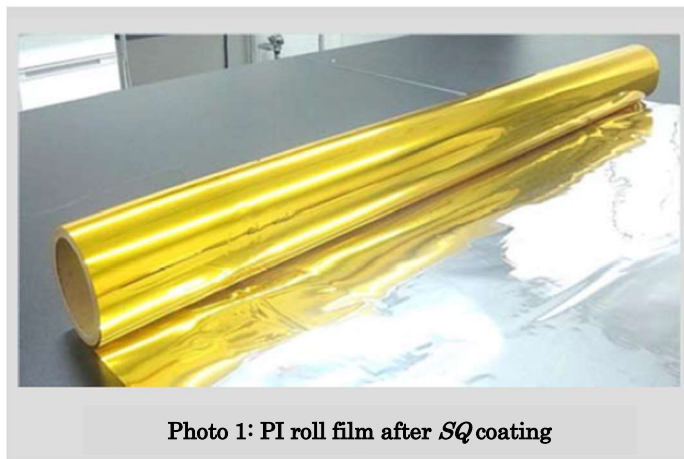


Photo 1: PI roll film after *SQ* coating

3.3 Mechanism of AO-resistance expression by *SQ* coating

As a result of X-ray photoelectron spectroscopy (XPS) analysis of the AO-irradiated *SQ* coating, Transmission Electron Microscope (TEM) and Scanning Transmission Electron Microscope (STEM) observations of the cross section of the coating, etc. by JAXA on the ground, it was confirmed that a silica (SiO₂) film with a thickness of approximately 20 nm was formed on its outermost surface (gray contrast layer in Fig. 2)¹⁶. It is assumed that this very thin silica film strongly suppresses the erosion of the film by AO. Furthermore, even when AO was irradiated onto defects, which occur very rarely after loading tests such as bending tests, no further erosion in the *SQ* coating film was observed. This is presumably because a new silica layer is formed by oxidation of the *SQ* layer that lies inside the defect even if a defect occurs in the outermost silica layer.

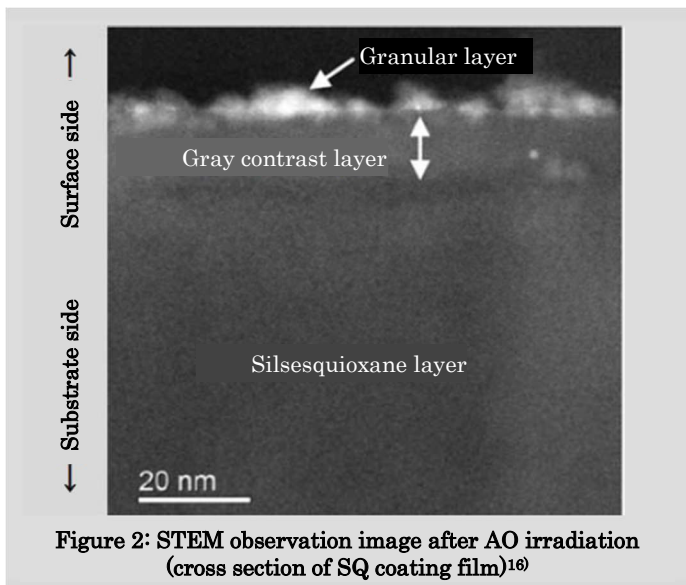


Figure 2: STEM observation image after AO irradiation (cross section of SQ coating film)¹⁶⁾

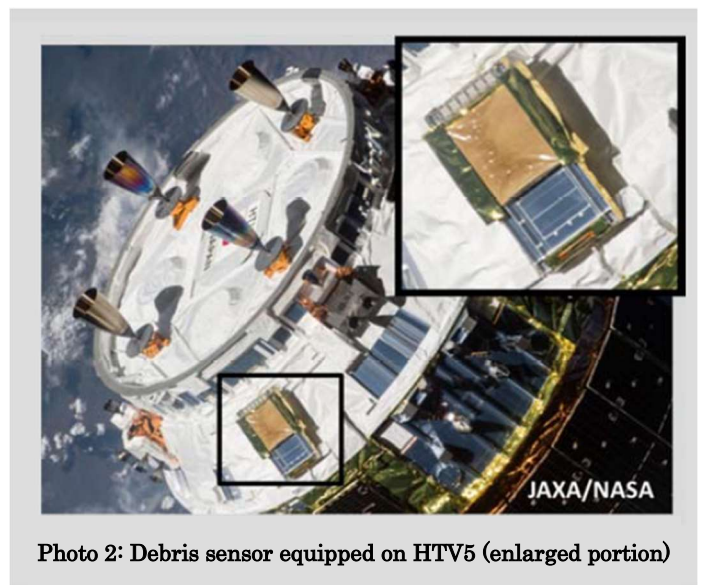


Photo 2: Debris sensor equipped on HTV5 (enlarged portion)

3.4 Example of application of AO-resistant coating in applications other than MLI

3.4.1 Spacecraft identification marks for space station transfer vehicles

While conventional oxide-based AO-resistant coatings such as ITO require sputtering or other methods of film formation, the *SQ* coating is an unprecedented “paintable protective film” that is expected to be applied to small-lot space equipment and even to repairs during spacecraft assembly.

Taking advantage of its characteristics as a paintable protective film, we have explored applying it to materials other than PI, and it has actually been used in space as a protective material for the spacecraft identification marks (national flag of Japan and the HTV and JAPAN logos) on H-II Transfer Vehicle “KOUNOTORI” (hereinafter “HTV”) No. 3 to No. 6^{6,7)}.

3.4.2 Debris sensor

The “KASPER” (Kounotori Advanced SPace Environment Research equipment) onboard the HTV5, which is being developed by JAXA and other organizations, incorporates two types of debris sensors. One of these sensors, KASPER-SDM (Space Debris Monitor; hereinafter “SDM”), has an *SQ* coating applied to its surface (Photo 2). The SDM was continuously operated from September 19, 2015, when the HTV5 was detached from the H-IIB launch vehicle, until September 30 of the same year, when it re-entered the atmosphere, and successfully detected debris of about 100 μm, as expected¹⁷⁾. In the meantime, *SQ* protected the SDM from erosion by AO and completed its mission as an AO-resistant coating.

3.4.3 High-precision planar marker for robot arms

SQ was adopted to protect the high-precision planar markers (samples for in-orbit demonstration experiments), which are expected to replace target markers for robotic arms, during space experiments. Since conventional target markers are three-dimensionally shaped with bar-type projections, there are issues such as installation being possible only at positions where contact with astronauts or robotic arms can be avoided. On the other hand, the high-precision planar marker is based on “ArrayMark,” which was invented by the National Institute of Advanced Industrial Science and Technology (hereinafter “AIST”). Despite being only 1 mm thick, this marker uses an array of tiny dots combined with lenses to change the position of the central black dot depending on the viewing angle, creating the illusion of depth. Currently, JAXA and AIST are jointly working on its practical application in space, and they carried out an exposure test from May 26, 2015 to June 10, 2016 by equipping these markers on Exposed Hybrid Attachment Mechanism (ExHAM) of the Japanese Experiment Module “Kibo” on the ISS to determine its practicality and durability in space. We confirmed that markers with *SQ*-coated covers would function sufficiently even after 6 months of exposure^{18,19)}. The markers are now back on earth and a detailed evaluation is underway. In addition to these, other uses of *SQ* in space are being examined, and further progress is expected.

4. Conclusion

This article described the development of the “*SQ* Series,” whose use is expanding along with the growing demand for heat resistance in various fields, into heat-resistant applications and space materials.

Although we were not able to fully convey it in this article, it is also possible to change the viscosity, molecular weight, refractive index, etc. by appropriately selecting the type of substituent in *SQ* and the synthesis conditions. When *SQ* is used in formulations, it is also possible to adjust the compatibility with the organic material with which it is combined. Taking advantage of these features, we will further develop the *SQ* Series as a high-functionality material mainly for heat-resistant applications.

5. Acknowledgements

The development of *SQ* as a protective coating agent for spacecraft was conducted in collaboration with the Research Unit I, Research and Development Directorate, Japan Aerospace Exploration Agency. We would like to express our deepest gratitude to the organization for their great cooperation.

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