

# Effects of Silanization Conditions on Flexural Properties of SiC Fiber-Reinforced Resin

Taka Norimasa<sup>1</sup>, Aoyagi Yujin<sup>1\*</sup>, Okawa Seigo<sup>2</sup> and Uoshima Katsumi<sup>1</sup>

<sup>1</sup>Division of Bio-prostodontics, Niigata University Graduate School of Medical and Dental Sciences, Niigata, Japan

<sup>2</sup>Division of Biomimetics, Niigata University Graduate School of Medical and Dental Sciences, Niigata, Japan

\*Corresponding author: Aoyagi Yujin, Division of Bio-prostodontics, Niigata University Graduate School of Medical and Dental Sciences, Niigata, Japan, Tel: +81252272900; E-mail: Aoyagi@dent.niigata-u.ac.jp

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## Abstract

**Objective:** The aim of this study was to evaluate the effects of silanization conditions on the mechanical properties of the SiC fiber-reinforced resin.

**Materials and Methods:** A mixture of urethane dimethacrylate and Triethylene Glycol Dimethacrylate (TEGDMA), with camphorquinone and 2-(N,N-dimethylamino)ethyl methacrylate as the visible-light initiator, was prepared as a matrix resin. The SiC fiber containing 10 mass% oxygen was silanized by two methods, using experimental silane coupling agents containing 0.5, 1.0, and 2.0 mass% 3-(Methacryloyloxy) Propyl Trimethoxy Silane ( $\gamma$ -MPTS). The silanization methods were the drying method, which enabled silanization at atmospheric conditions for two weeks, and the heating method, which enabled silanization at 100°C for 30 min. After silanization, SiC fibers were analyzed by Fourier Transform Infrared (FTIR) spectroscopy. Mechanical properties of experimental SiC fiber-reinforced resin were measured by the three-point bending test according to ISO 4049:2009, and the fracture surface of SiC fiber-reinforced resin was observed using an Electron Probe Micro Analyzer (EPMA).

**Results:** The FTIR absorbance peaks at 815  $\text{cm}^{-1}$  attributed to the Si-O-CH<sub>3</sub> groups of the  $\gamma$ -MPTS and 1087  $\text{cm}^{-1}$  attributed to the Si-O-Si siloxane bonding were observed on the SiC fiber silanized with 1.0 mass%  $\gamma$ -MPTS by the drying method. Moreover, EPMA observation showed that these SiC fibers were covered with the matrix resin. Thus, these SiC fibers could adhere chemically to the matrix resin. The flexural strength and modulus of the fiber-reinforced resin containing the SiC fiber silanized with 1.0 mass%  $\gamma$ -MPTS using the drying method were 238.7  $\pm$  41.1 MPa and 6.0  $\pm$  1.1 GPa, respectively. In contrast, those of the SiC fiber-reinforced resin containing the SiC fibers silanized by the heating method was not improved.

**Conclusion:** The reinforced resin containing the SiC fiber silanized with 1.0 mass%  $\gamma$ -MPTS by the drying method showed mechanical properties superior to those of the other SiC fiber-reinforced resin.

**Keywords:** SiC fiber; Fiber-reinforced resin; Silanization; Flexural properties

**Abbreviations:** TEGDMA: Triethylene Glycol Dimethacrylate;  $\gamma$ -MPTS: 3-(Methacryloyloxy) Propyl Trimethoxy Silane; PVA: Polyvinyl Alcohol; FTIR: Fourier Transform Infrared; EPMA: Electron Probe Micro Analyzer; OMPTS: Oligomer of Methacryloyloxy Propyl Trimethoxy Silane; PVA: Polyvinyl Alcohol

## Introduction

Dental alloys with high toughness and wear resistance have been applied in coronal restoration and prosthodontic treatment for missing teeth. However, the risks of metal allergy and unaesthetic color were problems. Recently, metal-free restorations have been proposed to solve these problems, and the clinical application of glass fiber-reinforced resin for dental treatment has increased. The glass fiber-reinforced resin has two merits: aesthetically pleasing color and providing long-term durability when the fiber is silanized [1]. Furthermore, the long filaments of glass fiber have been found to be safe for the human body [2]. However, the glass fiber has poor

mechanical properties, so the dental treatment applying glass fiber-reinforced resin has been limited to dental abutment construction with the glass fiber post and to fiber-reinforced resin dental bridge. However, root fracture could occur when the fiber post with an extremely large flexural modulus is used [3]. Thus, the flexural modulus of the fiber-reinforced resin needs to be adjusted. At present, fiber-reinforced composite resin bridges have only been applied as three-unit bridges; therefore, it is necessary to improve their mechanical properties for long-span bridges to resist the high occlusal force. Some studies reported that the mechanical properties of fiber-reinforced resin using ultra-high-molecular-weight polyethylene fiber and aramid fibers [4-7], but these fibers are not applied for dental treatment. Recently, a SiC fiber was developed as a new ceramic material and used for a SiC fiber-reinforced pure aluminium composite in the industry [8,9]. This fiber has superior mechanical properties and chemical stability than glass fibers. Subsequently, we attempted to fabricate a SiC fiber-reinforced resin for application in metal-free restoration.

Some SiC fibers contain oxygen and Si-O chemical bonding forms at the interface. Therefore, they could be silanized like glass fibers [10]. The silanized SiC fibers and the matrix resin can adhere chemically;

therefore, the mechanical properties of the SiC fiber-reinforced resin will be superior to those of a glass fiber-reinforced resin. Thus, the applications of fiber-reinforced resins in dental treatment are expected to increase.

However, it is not clear that the effective concentration of the silane coupling agent for the SiC fiber to prepare the SiC fiber-reinforced

resin. The aim of this study was to assess the effect of the silanization with  $\gamma$ -MPTS as the silane coupling agent on the mechanical properties of SiC fiber-reinforced resin.

Materials	Generic name	Product name	Manufacturer	Mass (g)
Matrix resin	Urethane	Art resin SH-500B	Negami Chemical Industrial	70
	dimethacrylate Triethylene glycol	3G	Shin-Nakamura Chemical	30
	dimethacrylate Camphorquinone	Camphorquinone	Aldrich Chemical	0.5
	Dimethylamino ethyl methacrylate	Dimethylamino ethyl methacrylate	Wako Pure Chemical Industries	1.0
Silane coupling agent	3-Methacryloxy propyl trimethoxysilane	KBM-503	Shin-Etsu Chemical	
	Acetic acid	Acetic acid (Guaranteed reagent)	Wako Pure Chemical Industries	
Reinforcement SiC fiber	( $\phi=10 \mu\text{m}$ , containing 10 mass% oxygen)	Nicalon HL-207	NGS Advanced Fibers	

Table 1: Materials used in this study.

## Material and Methods

The materials and reagents used for this study are shown in Table 1. All the materials and reagents were used as received without any further purification.

### Preparation of silane coupling agent

$\gamma$ -MPTS solutions with three concentrations-0.5, 1.0, and 2.0 mass% were prepared as a silane coupling agent using a liquid mixture (ethanol: distilled water=70:30 vol%). The solutions were stirred for approximately 2 min using a magnetic stirrer at atmospheric conditions. Then, the pH measurements were made using a pH meter (FP20, Mettler Toledo, Columbus, USA). The pH of the  $\gamma$ -MPTS solutions was adjusted to  $4.2 \pm 0.1$  by adding acetic acid. These solutions were used as the experimental silane coupling agents for silanizing the SiC fibers.

### Pretreatment of SiC fibers

The diameter of the SiC fiber was approximately  $10 \mu\text{m}$ . The SiC fibers as received were pre-bundled with Polyvinyl Alcohol (PVA). PVA was removed from the SiC fibers by means of pouring boiling water on the fibers and heating for 5 min at  $800^\circ\text{C}$  before the silanization, respectively.

### Silanization of the SiC fiber

In this study, two methods were used for silanizing the SiC fiber. One of them was the drying method: The SiC fibers after PVA removal were immersed in the silane coupling agent solutions with different concentrations for 1 h and then dried for 2 weeks at atmospheric conditions. The other method was the heating method in which the silanization duration is reduced by accelerating hydrolysis: each of the silane coupling agents (with different concentrations) was dropped on the SiC fibers using a syringe, followed by heating at  $100^\circ\text{C}$  in an electronic furnace for 30 min.

### Surface analysis of the silanized SiC fiber

The surface of the silanized SiC fiber was analyzed via FTIR spectroscopy (FT/IR 7300, JASCO, Tokyo, Japan) using the KBr pellet method.

### Preparation of matrix resin

The matrix resin (Mat) of all the experimental SiC fiber-reinforced resin was prepared as per the compositions reported by Aoyagi, et al. [11]. Urethane dimethacrylate and TEGDMA were mixed in the ratio listed in Table 1, and then, camphorquinone and 2-(N, N-dimethylamino)ethyl methacrylate were added for photopolymerization.

### Preparation of SiC fiber-reinforced resin specimen

Each  $2.00 \times 2.00 \times 25.0$  mm rectangular specimen was fabricated using a stainless mold according to ISO 4049: 2009 [12] for measuring the flexural strength and flexural modulus of the SiC fiber-reinforced resin.

First, a separating agent made by mixing ligroin and paraffin wax in a volume ratio of 1:1 was applied to the stainless mold. A plastic film (Celluloid strips, GC, Tokyo, Japan) was placed on a glass plate, and then, the mold was placed on it, with the aperture of the mold facing upward (Figure 1a). Three bundles of the silanized SiC fibers (approximately 1,500 fibers) were placed at the bottom of the mold after the SiC fibers were cut to a length of approximately 25 mm with forceps (Figure 1b). Subsequently, Mat was poured in the mold without voids, and then, the plastic film was placed on Mat. Finally, a glass plate was placed on the film. The molds, plastic films, and glass plates were integrated using a clip (Figure 1c). These were irradiated using a laboratory photopolymerizing unit (LABOCURE HL, GC, Tokyo, Japan) for 3 min from each side of the molds. After irradiation, the polymer was taken out from the mold and recontoured by dry polishing with #600 and #1200 silicon carbide waterproof abrasive paper. Then, the SiC fiber-reinforced resin was immersed in distilled

water at  $37 \pm 1^\circ\text{C}$  for  $24 \pm 1$  h. The resultant specimen was used for the three-point bending test.

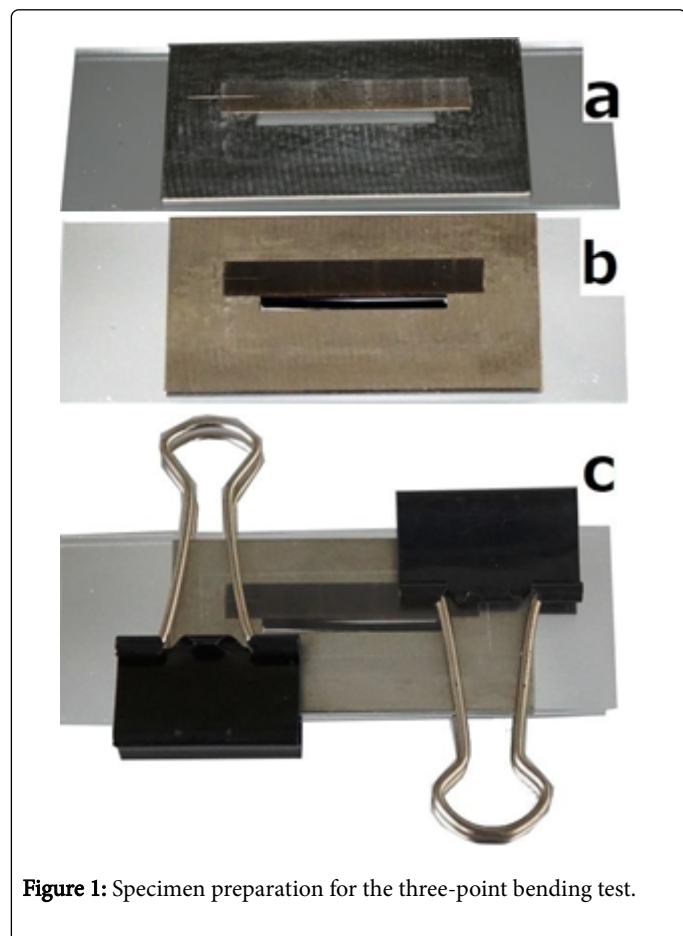


Figure 1: Specimen preparation for the three-point bending test.

Table 2 presents the specimens classified based on the concentration of the experimental silane coupling agent and the silanization method. The specimen containing SiC fibers that did not undergo silanization is classified as the control (Cont).

Type of silanization for the SiC fiber	The concentration of $\gamma$ -MPTS (mass%)	Abbreviation
Unsilanized	Unsilanized	Cont
Drying	0.5	0.5D
	1.0	1.0D
	2.0	2.0D
Heating	0.5	0.5H
	1.0	1.0H
	2.0	2.0H

Table 2: Classification of specimens used for the three-point bending test (n=7).

### Three-point bending test

Three-point bending tests were performed at a crosshead speed of 1.0 mm/min with a span length of 20 mm, according to ISO4049:2009,

using a universal testing machine (Autograph AG-1000E, Shimadzu, Kyoto, Japan). The width and thickness of the specimens were measured with a micrometer (MDQ-30M, Mitsutoyo, Kanagawa, Japan, with accuracy of at least 0.001 mm). The three-point flexural strength and flexural modulus were calculated using a software (SHIKIBU, Shimadzu, Kyoto, Japan) available with the universal testing machine.

### Fracture surface observation

After the three-point bending test, the specimens were fractured conveniently for the surface observation. The fracture surfaces of the specimens were sputter-coated with gold-palladium and examined by secondary electron imaging using a scanning electron microscope (EPMA-1610, Shimadzu, Kyoto, Japan).

### Statistical analysis

Statistical analysis was performed by Excel 2013 (Microsoft, Redmond, USA). The data were analyzed by one-way ANOVA followed by a Tukey's test ( $\alpha=0.05$ ).

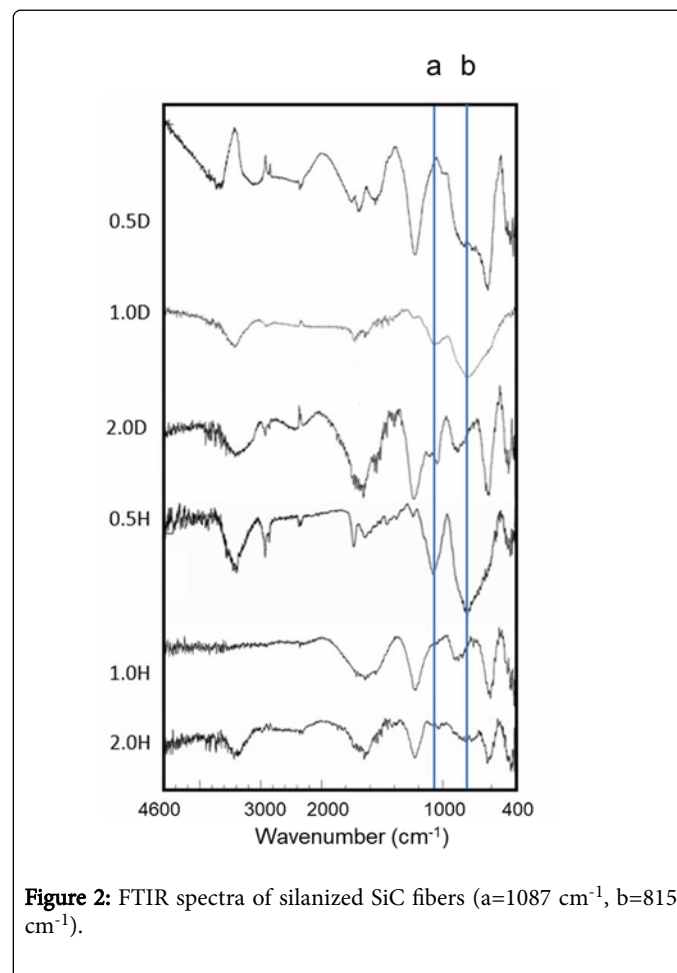


Figure 2: FTIR spectra of silanized SiC fibers (a=1087  $\text{cm}^{-1}$ , b=815  $\text{cm}^{-1}$ ).

### Result

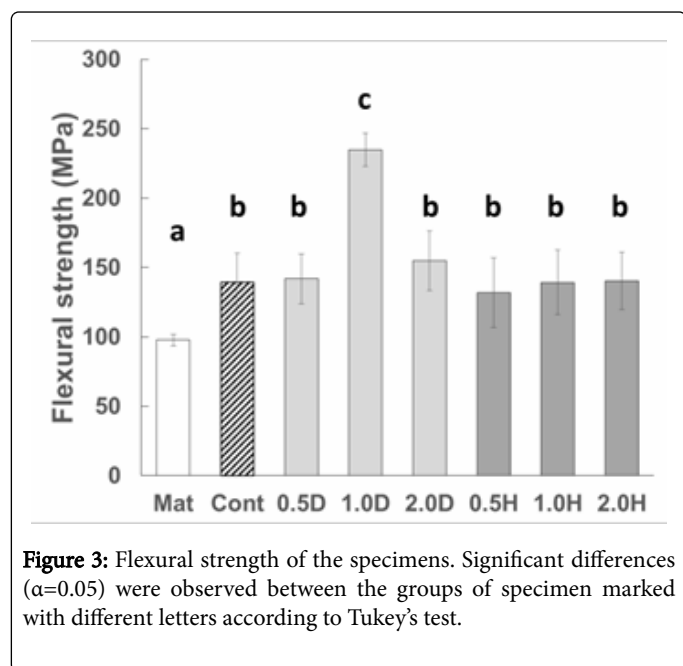
Figure 2 shows the FTIR spectra of the SiC fibers silanized with each concentration of the silane coupling agent. The absorbance peak at 815

and  $1087\text{ cm}^{-1}$  were observed for specimens 1.0D and 0.5H. These absorbance peaks were not found in the other specimens.

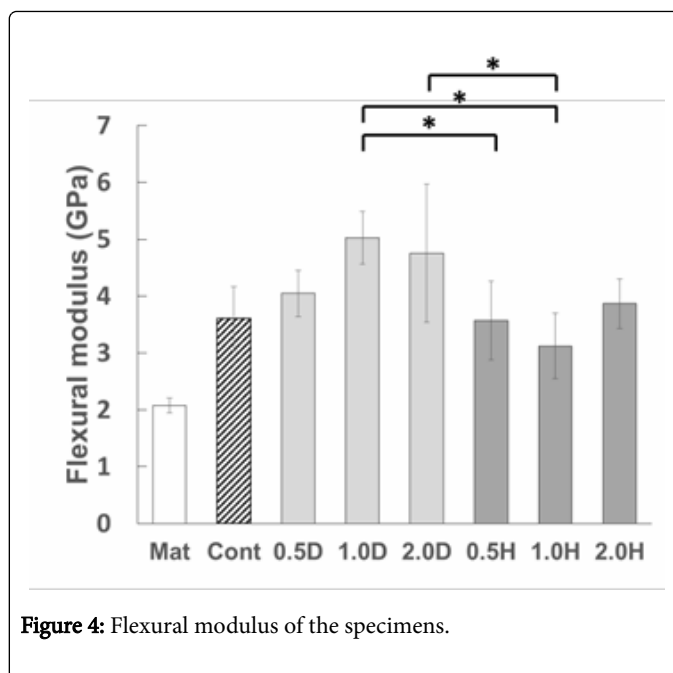
Figure 3 shows the flexural strength of the specimens. The flexural strength of all specimens was significantly higher than that of Mat without the SiC fiber. The flexural strength of specimen 1.0D was significantly higher than that of the other specimens and 1.5 times higher than that of specimen Cont.

Figure 4 shows the flexural modulus of the specimens. The flexural modulus of the specimens was significantly higher than that of Mat. Substantial differences were observed in the modulus of specimens between 1.0D and 0.5H, between 1.0D and 1.0H, and between 2.0D and 1.0H. The flexural modulus of specimen 1.0D was 1.4 times higher than that of specimen Cont.

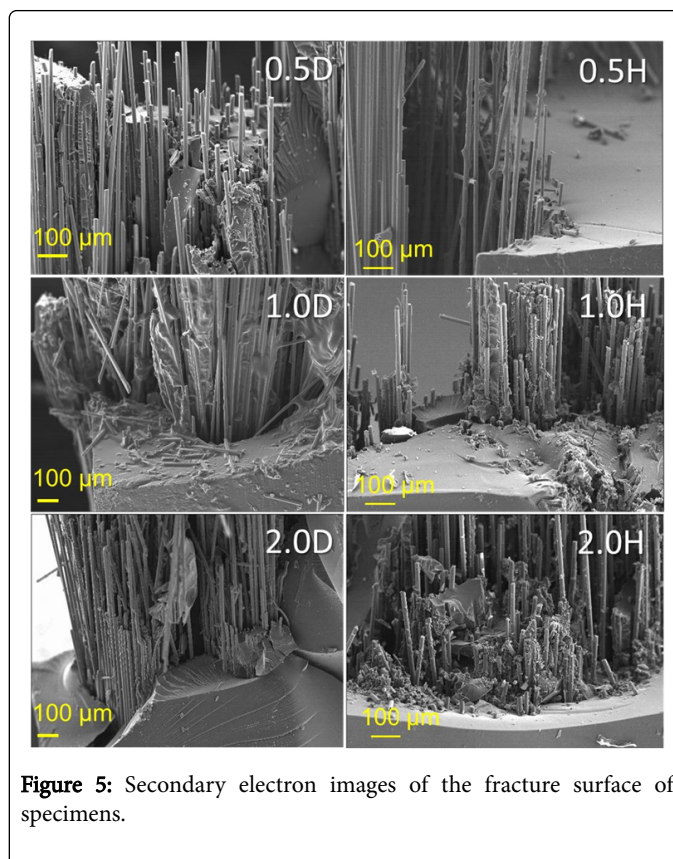
The secondary electron images of the fracture of the specimens after the three-point bending test are displayed in Figure 5. The adhered Mat on the SiC fiber surface was observed in specimens 1.0D and 0.5H. No adhered Mat on the SiC fiber was observed in the other specimens.



**Figure 3:** Flexural strength of the specimens. Significant differences ( $\alpha=0.05$ ) were observed between the groups of specimen marked with different letters according to Tukey's test.



**Figure 4:** Flexural modulus of the specimens.



**Figure 5:** Secondary electron images of the fracture surface of specimens.

## Discussion

According to the FTIR spectra, the absorbance peak at  $1087\text{ cm}^{-1}$  was due to the Si-O-Si siloxane bonding [13]. Moreover, the absorbance peak at  $815\text{ cm}^{-1}$  was attributed to the presence of Si-O-CH<sub>3</sub> groups of the  $\gamma$ -MPTS. Both absorbance peaks were observed for

specimens 1.0D and 0.5H. Therefore, a chemical bonding between the SiC fiber and the Mat could occur. On the other hand, the absorbance peak of the siloxane bonding was not found in specimens 0.5D, 2.0D, 1.0H, and 2.0H. Therefore, the effective silane coupling reaction between the SiC fiber and Mat would not occur. Therefore, the SiC fibers and Mat did not adhere chemically. In absence of this chemical adherence, the effect of the reinforcement provided by the fiber was not realized.

The flexural strength of specimen Cont was significantly higher than that of Mat. The mechanical properties of the SiC fiber and the bonding force between the SiC fiber and Mat could affect the flexural strength of Cont. The flexural strength of specimen 1.0D was the highest among the specimens in the case of the drying method. Based on the results of FTIR and the fracture surface observation, the SiC fiber and Mat adhered chemically in specimen 1.0D. On the other hand, the flexural strength of specimens except for specimen 1.0D was similar to that of specimen Cont. The flexural strength of specimen 0.5H was not improved due to the different silanization method, although the specimen was found to adhere chemically. Arksomnukit, et al. [14] reported that the flexural strength of a composite resin which contains the silica filler silanized at 50°C in 3h was higher than that of the composite resin whose filler silanized at 110°C in 3h. They suggested that the higher drying temperature for silanization caused the formation of a physisorbed layer via hydrogen bonding and van der Waals force on the silica surface, thus reducing the flexural strength of the composite resin. This physisorbed layer was formed on a part of the SiC fiber surface in specimen 0.5H. Therefore, the flexural strength of the specimen prepared with the heating method was lower than that of the specimen prepared with the drying method. Thus, the drying method was more efficient than the heating method for the silanization of the SiC fiber.

The flexural modulus of the specimen fabricated with the drying method tended to be larger than that of the specimen fabricated with the heating method. The silane coupling reaction in the drying method would be different from that in the heating method. A significant difference was not observed between the flexural modulus of specimen 1.0D and 2.0D, even though in specimen 2.0D, chemical bonding was not observed, as per FTIR results. Antonucci, et al. [15] reported that an Oligomer of Methacryloyloxy Propyl Trimethoxy Silane (OMPTS) was synthesized via the silane coupling reaction with the hydrolysis of MPTS and condensation reaction. The SiC fibers contained only 10 mass% oxygen, so the number of Si-O groups on the surface of the SiC fiber would be smaller than those on the surface of glass fibers. Thus, the amount of  $\gamma$ -MPTS would be in excess of the Si-O groups, and the surface of the SiC fiber would, therefore, be covered with OMPTS. This would affect the flexural modulus of specimen 2.0D. In particular, the flexural modulus of specimen 1.0D was the highest due to the integration of the SiC fibers and Mat.

Nagakura, et al. [16] reported that the flexural strength and flexural modulus of polypropylene containing 36.1 vol% glass fibers were  $170.5 \pm 7.4$  MPa and  $16.7 \pm 0.7$  GPa, respectively. Wang, et al. [17] reported that the flexural strength and flexural modulus of bisphenol A-glycidyl methacrylate/TEGDMA mixed resin containing 10 mass% SiO<sub>2</sub> nanofiber were approximately 130 MPa and 3.5 GPa, respectively. The flexural strength and the flexural modulus of specimen 1.0D containing 4 vol% (about 8.6 mass%) SiC fibers were  $235.0 \pm 11.8$  MPa and  $5.0 \pm 0.5$  GPa, respectively, in this study. Although the fiber content of the specimens was lower than that of the fiber-reinforced resin studied by Nagakura, et al. and Wang, et al., the flexural strength

of specimen 1.0D was higher than that of their specimens. This is because the tensile modulus of the SiC fiber was higher than that of the glass fiber [18,19]. Fortunately, the flexural modulus of the SiC fiber-reinforced resin could be improved by increasing the SiC fiber content. Therefore, the SiC fiber-reinforced resin would be applied to a long span dental bridge, and moreover, it would be useful to apply it to a metal-free treatment.

## Conclusion

Within the limitations of this study, chemical bonding occurred between the SiC fibers silanized with 1.0 mass%  $\gamma$ -MPTS by the drying method. The reinforced resin containing the SiC fibers silanized with 1.0 mass%  $\gamma$ -MPTS by the drying method had superior mechanical properties than the other SiC fiber-reinforced resin.

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